

## Study of the reaction mechanisms and durability of innovative oxygen electrode materials for high temperature electrolysis

Lydia Yefsah

#### ► To cite this version:

Lydia Yefsah. Study of the reaction mechanisms and durability of innovative oxygen electrode materials for high temperature electrolysis. Chemical engineering. Université Grenoble Alpes [2020-..], 2023. English. NNT: 2023GRALI049. tel-04433509

## HAL Id: tel-04433509 https://theses.hal.science/tel-04433509

Submitted on 2 Feb 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

#### THÈSE

Pour obtenir le grade de

### DOCTEUR DE L'UNIVERSITÉ GRENOBLE ALPES

École doctorale : I-MEP2 - Ingénierie - Matériaux, Mécanique, Environnement, Energétique, Procédés, Production

Spécialité : 2MGE - Matériaux, Mécanique, Génie civil, Electrochimie

Unité de recherche : Laboratoire d'Electrochimie et de Physico-Chimie des Matériaux et des Interfaces.

Etude des mécanismes réactionnels et durabilité de matériaux innovants d'électrode à oxygène pour l'électrolyse haute température

# Study of the reaction mechanisms and durability of innovative oxygen electrode materials for high temperature electrolysis

Présentée par :

#### Lydia YEFSAH

Direction de thèse :

Elisabeth DJURADO PROFESSEURE DES UNIVERSITES, Université Grenoble Alpes Jérôme LAURENCIN Ingénieur HDR, Université Grenoble Alpes Directrice de thèse

Co-encadrant de thèse

#### Rapporteurs :

Paola COSTAMAGNA ASSOCIATE PROFESSOR, Università Degli Studi di Genova Pascal BRIOIS MAITRE DE CONFERENCES HDR, Université de Franche-Comté

#### Thèse soutenue publiquement le 29 juin 2023, devant le jury composé de :

Elisabeth DJURADO	Directrice de thèse
PROFESSEUR DES UNIVERSITES, Grenoble INP	
Paola COSTAMAGNA	Rapporteure
ASSOCIATE PROFESSOR, Università Degli Studi di Genova	
Pascal BRIOIS	Rapporteur
MAITRE DE CONFERENCES HDR, Université de Franche-Comté	
Isabelle GAUTIER-LUNEAU	Présidente
PROFESSEUR DES UNIVERSITES, Université Grenoble Alpes	
Jean-Marc BASSAT	Examinateur
DIRECTEUR DE RECHERCHE, CNRS délégation Aquitaine	

#### Invités :

Jérôme LAURENCIN DOCTEUR EN SCIENCES HDR, CEA LITEN



## Acknowledgments

This thesis work was carried out in tight collaboration between the « Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et Interfaces (LEPMI) » and the « Laboratoire Essais et Systèmes (LES) » of the French Alternative Energies and Atomic Energy Commission (CEA) in Grenoble. In this respect, I would like to thank all the people I have had the pleasure to met and who have contributed to the success of this research work.

Firstly, I would like to express my sincere thanks to my thesis director, Ms. Elisabeth Djurado. Your love of research made this work very rewarding and challenging. Your ability to pass on your knowledge allowed me to progress constantly throughout this work. I would also like to extend my deepest gratitude to my thesis co-director, Mr. Jérôme Laurencin. I am thankful for your expertise which led this work to an advanced stage. Your vast array of knowledge and your pedagogy have provided valuable skills and the tools I needed to achieve the best results. I am grateful to have had the chance to work with you both. Thank you for your encouragement and support along these years of thesis.

I would like to respectfully thank the jury members, Ms. Isabelle Gautier-Luneau, Ms. Paola Costamagna, Mr. Pascal Briois and Mr. Jean-Marc Bassat for the attention accorded to reviewing my manuscript and during the Ph.D. defense.

This Ph.D. work was supported by the French National Research Agency (ANR) as part of the ECOREVE research program. In this regard, I would like to thank the various partners of the project. I would like to thank the head of the project M. Jean-Marc Bassat (ICMCB). My thanks also go to Mr. Fabrice Mauvy (ICMCB), Ms. Karine Couturier (CEA-Liten), Mr. Johan Debayle (Armines-SPIN) and M. Giuseppe Sdanghi. Regarding this collaboration, I would like to thank Mr. Julien Vulliet (CEA-Le Ripault) as well as Ms. Emmanuelle Bichaud and Mr. Romain Billard from SRT-microcéramique for the supply of half-cells and for the contribution on some specific screen-printing deposition. Thank you for the high-quality exchanges held during the work meetings.

I would also like to express my warm thanks to the external collaborators who contributed in this work. I would like to express my appreciation to Mr. Christian Lenser and Mr. Norbert H. Menzler from the Forschungszentrum Jülich (FZJ) for supplied half-cells which I used to carry out several long-term tests. I would also thank Mr. Dario Ferreira Sanchez for the welcoming and time allocated for the synchrotron X-ray  $\mu$ -XRD and  $\mu$ -XRF in Swiss Light Source (SLS) at Paul Scherrer Institut (PSI), Switzerland. I am also thankful for the members of the Consortium des Moyens Technologiques Communs (CMTC) for the sample preparations and characterizations. In particular, I would thank Mr. Thierry Encinas for its reactivity and feedback on the XRD analysis. I am also extremely thankful to Mr. Frédéric Charlot for his professionalism and his deep involvement in SEM characterization.

I would like to thank all the laboratory teams of the LEPMI. Firstly, I would like to thank the head of the laboratory Ms. Fannie Alloin. I would like to express my thanks to the administrative staff for their commitment and professionalism. I would also like to thank Ms. Elisabeth Siebert and for the valuable exchanges we had about my work. I also thank Mr. Laurent Dessemond for setting up the test benches for electrochemical characterization. I was also able to benefit from the technical support provided by the M2E platform to carry out the screen printing deposition I did. In this respect, I would like to thank Mr. César Steil, head of

the plateform. I would also like to extend my warmest thanks to Mr. Franck Fournet Fayard on whom I have relied for help with any technical issues.

A large part of this work was carried out in the LES laboratory, within the STH2 service at CEA Grenoble. In this respect, I would like to thank Ms. Julie Mougin and Mr. Cyril Bourasseau, respectively heads of the department and the laboratory, for providing me the facilities I needed to carry out my work. I would like to express my gratitude to Ms. Karine Couturier for her deep involvement and her pedagogical support during my work. I would like to thank also Ms. Marie Petitjean and Mr. Bertrand Morel for their availability and assistance on the test benches. My thanks also go to Denis, Lionel, Pascal, Bastien, Jérémy, and Thibault who ensured the reliable operating of the test benches. Thanks to all of you, I quickly acquired an autonomy in the assembly and handling of the benches, which allowed me to make substantial advancement in my research work. I am also extremely grateful to Mr. Maxime Hubert for his wide-ranging skills from which I have benefitted. I would also like to thank all the members of the STH2 team for their warm welcome.

I also owe my gratitude to my colleagues Ms. Nur I. Khamidy, Ms. Ozden Celikbilek and Ms. Cintia Hartmann and Mr. Karthikeyan Saravanabavan with all of whom I have worked directly and who led to fruitful exchanges. I would also sincerely thank Giuseppe Sdanghi who I had meet during this project and who has now become a friend, your contribution has been extremely valuable. I am really grateful to have been able to rely on you. I would like to express a warm thanks to my colleagues: Amira, Léa, Elisa, Eduardo and Giuseppe Sassonne with whom I have forged strong friendships. I would also like to extend my thanks to the other doctoral and post-doctoral students met over the years: Manon, Quentin, Federico, Amandine, Hamza, François, Michael, Tristan, Davide, Angel, Zaman ... I couldn't name everyone, but I am pleased to have met you all.

I would like to thank all my friends on whom I can rely despite the distance. A special thank to my friend for many years now T.Y.

My warmest thanks go to my dear family. For my parents and my brothers, thank you for your endless love and support. I dedicate this thesis for you.

### Résumé de la thèse (en français)

Les cellules à oxydes solides (SOC) sont des convertisseurs électrochimiques à haute température (~ 750 °C - 800 °C) qui produisent de l'électricité (en mode pile à combustible) ou de l'hydrogène (en mode électrolyseur). L'enjeu aujourd'hui est d'abaisser la température de fonctionnement en utilisant de nouveaux matériaux d'électrodes afin d'améliorer la durée de vie des cellules tout en préservant de bonnes performances électrochimiques. Pour ce faire, les nickelates de terres rares  $Ln_2NiO_{4+\delta}$  (Ln = La, Pr) sont envisagés comme matériaux innovants d'électrodes à oxygène dans des cellules d'électrolyse (SOEC) pour leurs bonnes propriétés électrochimiques à température intermédiaire (650 °C - 750 °C). Les travaux antérieurs ont montré que les performances électrochimiques sont plus élevées pour Pr<sub>2</sub>NiO<sub>4+δ</sub> (PNO) que La<sub>2</sub>NiO<sub>4+δ</sub> (LNO) alors que la stabilité chimique du LNO est remarquable. Un compromis performances électrochimiques / stabilité est proposé pour le composé LaPrNiO<sub>4+ $\delta$ </sub> (LPNO). Dans le cadre d'une thèse précédente au LEPMI/CEA, des caractérisations structurales fines réalisées sur le matériau d'électrode à air LPNO vieilli en cellule complète d'électrolyse ont permis de détecter une décomposition majoritaire en  $Pr_6O_{11}$  (i.e.  $PrO_{1.833}$ ), phase reconnue pour ses propriétés électrocatalytiques remarquables. En revanche, la stabilité à long terme de ce nouveau matériau reste à ce jour à vérifier.

Ces résultats ont conduit à mener ce travail de thèse suivant deux études complémentaires. Dans une première partie, une approche expérimentale et de modélisation couplée a été menée sur LNO afin d'étudier les mécanismes de réaction de ce conducteur mixte qui serviraient ensuite comme préalable à une optimisation microstructurale. Il a été ainsi montré que des surtensions d'électrode pour ce matériau sont moins fortes en polarisation anodique (mode électrolyse) qu'en polarisation cathodique (mode pile à combustible). Ce résultat important a été analysé en identifiant les mécanismes réactionnels grâce au modèle.

La seconde partie de ces travaux de thèse est focalisée sur l'étude du  $PrO_{1.833}$ , qui présente de bonnes propriétés intrinsèques du transport de l'oxygène. Ainsi, des caractérisations électrochimiques (courbes i-V, spectres d'impédance électrochimique) de l'électrode  $PrO_{1.833}$ ont été réalisées dans des cellules complètes en fonctionnement d'électrolyse afin d'étudier les performances et la durabilité du matériau. Un matériau d'électrode constitué d'une couche active fonctionnelle à base de  $PrO_{1.833}$  nanostructuré recouverte d'un collecteur de courant, le manganite de lanthane dopé au strontium (LSM), s'est révélé être prometteur. Un taux de dégradation raisonnable de l'ordre de 5.8 % kh<sup>-1</sup> à 700 °C a été obtenu lors du test de durabilité de 1000 h d'une cellule fonctionnant en mode électrolyse sous -0.5 A cm<sup>-2</sup>. Afin d'identifier l'origine de ces pertes électrochimiques, une étude de différentes cellules a été menée en fonction de la température, du courant et du temps. Des caractérisations post-mortem de la composition chimique, des analyses microstructurales par MEB-EDX et structurales par  $\mu$ -diffraction et  $\mu$ -fluorescence des rayons X au synchrotron à PSI ont permis de mettre en évidence une évolution physicochimique du matériau d'électrode sans interdiffusion notable des éléments chimiques. Après 1000 h à 700 °C apparaît une transition majoritaire vers la phase PrO<sub>1.714</sub> induite par la température de fonctionnement. Cependant, en mode électrolyse, se distingue une phase supplémentaire plus réduite PrO<sub>1.5<x<1.7</sub> à l'interface avec la couche barrière de cérine gadoliniée (GDC). Cette phase qui aurait impacté les performances de la cellule serait pluôt observée à plus haute température (e.g. vieillissement thermique à 800 °C, 700 h). Ces résultats ont permis pour la première fois une meilleure compréhension de la durabilité de PrO<sub>1.833</sub>, un matériau d'électrode à air innovant pour cellules d'électrolyse à oxydes solides.

## **Abstract (English)**

Solid oxide cells (SOC) are high-temperature (~750°C - 800°C) electrochemical converters that produce electricity (in fuel cell mode) or hydrogen (in electrolyzer mode). The challenge today is to lower the operating temperature by using new electrode materials in order to improve their lifetime while maintaining good electrochemical performance. To do this, rare earth nickelates  $Ln_2NiO_{4+\delta}$  (Ln = La, Pr) are considered innovative materials for oxygen electrodes as an air electrode for electrolysis cells (SOEC) for their good electrochemical properties at intermediate temperatures (650 °C - 750 °C). Previous work has shown that the electrochemical performance is higher for Pr<sub>2</sub>NiO<sub>4+ $\delta$ </sub> (LPNO) than La<sub>2</sub>NiO<sub>4+ $\delta$ </sub> (LNO) while the chemical stability of LNO is remarkable. An electrochemical performance/stability compromise is proposed for the compound LaPrNiO<sub>4+ $\delta$ </sub> (LPNO). As part of a previous thesis at LEPMI/CEA, fine structural characterizations carried out on the LPNO air electrode material aged in a complete electrolysis cell have detected a major decomposition into Pr<sub>6</sub>O<sub>11</sub> (i.e. PrO<sub>1.833</sub>), an interesting phase for its remarkable electrocatalytic properties. However, the long-term stability of this new material remains to be verified.

These results led to carrying out this thesis work following two complementary studies. In the first part, an experimental approach and coupled modeling was carried out on LNO in order to study the reaction mechanisms of this mixed conductor which would then serve as a prerequisite for microstructural optimization. It has thus been shown that electrode overpotentials for this material are less strong in anodic polarization (electrolysis mode) than in cathodic polarization (fuel cell mode). This important result was analyzed by identifying the reaction mechanisms thanks to the model.

The second part of this thesis work is focused on the study of  $PrO_{1.833}$ , which presents interesting intrinsic properties of oxygen transport. Thus, we undertook electrochemical characterizations (polarization curves, electrochemical impedance spectra) of the  $PrO_{1.833}$  electrode in complete cells in electrolysis operation in order to study the performance and durability of the material. An electrode material consisting of a functional active layer based on nanostructured  $PrO_{1.833}$  covered with a current collector, strontium-doped lanthanum manganite (LSM), has shown to be promising. A reasonable degradation rate of around 5.8% kh<sup>-1</sup> at 700 °C was obtained during the 1000 h durability test of a cell operating in electrolysis mode at 0.5 A cm<sup>-2</sup>. In order to identify the origin of these electrochemical losses, a study of different cells was carried out as a function of temperature, current, and time. Post-

mortem characterizations of the chemical composition, microstructural analyzes by SEM-EDX, and structural analyzes by synchrotron  $\mu$ -X-ray diffraction and  $\mu$ -X-ray fluorescence at the Paul Scherrer Institute (PSI) have made it possible to highlight a physicochemical evolution of the electrode material without significant interdiffusion of the chemical elements. After 1000 h at 700°C, a major phase transition into PrO<sub>1.714</sub> occurred, correlated with operating temperature. However, in electrolysis mode, an additional, reduced PrO<sub>1.5<x<1.7</sub> phase appears at the interface with the gadolinia-doped ceria (GDC) barrier layer. This phase which would have impacted the cell's performance should be rather observed at higher temperatures (e.g. thermal aging at 800°C, 700 h). These results allowed for the first time a better understanding of the durability of PrO<sub>1.833</sub>, an innovative air electrode material for solid oxide electrolysis cells.

# Content

Rés	umé c	le la thèse (en français)	5
Abs	stract	(English)	7
Lis	t of fig	gures	13
Lis	t of ta	bles	19
Noi	nencla	ature	21
Gei	ıeral i	ntroduction	29
1.	Obje	ectives of the thesis	32
2.	Stru	cture of the manuscript	
3.	Refe	rences	34
Cha	apter	I: Literature review on solid oxide cells (SOCs)	
1.	Gen	eral principles concerning the SOCs	
	1.1	Operating principle	
	1.2	Single-cell configuration	41
2.	SOC	's materials	42
	2.1	Electrolyte	43
	2.2	Fuel/Hydrogen electrode	45
	2.3	Air/Oxygen electrode	46
3.	Degi	adation under operation	54
	3.1	Electrolyte degradation	54
	3.2	Hydrogen/Fuel electrode degradation	55
	3.3	Oxygen/Air electrode degradation	56
4.	Con	clusion and methodology of this thesis work	60
5.	Refe	rences	62
Cha	apter	II: Materials and methods	75
1.	Fabı	rication techniques	75
	1.1	Electrostatic spray deposition	75
	1.2	Screen-printing (SP)	80
	1.3	Influence of the microstructure and the architecture on the electrode	
		performances	
	1.4	Physical vapor deposition sputtering process (PVD)	84
2.	Cell	preparation	85
	2.1	$La_2NiO_{4+\delta}$ (LNO)	

	2.2	$PrO_{1.833}$ (i.e. $Pr_6O_{11}$ )	
3.	Cha	racterization techniques	
	3.1	SEM observations	
	3.2	Laboratory X-ray diffraction at room temperature	90
	3.3	Synchrotron-based X-ray: µ-XRD and µ-XRF characterization	90
4.	Elec	trochemical measurements and characterization	93
	4.1	Electrochemical impedance spectroscopy (EIS)	93
	4.2	Symmetrical cell measurements for LNO	95
5.	Long	g-term test on complete cell	96
	5.1	Description of the test bench	96
	5.2	Testing protocol	97
	5.3	Polarization curves (i-V)	
	5.4	Degradation rate	
6.	Con	clusion	
7.	Refe	rences	
Ch	apter	III: Reaction mechanisms of La2NiO4+8 oxygen electrode for SOCs	
<u>Par</u>	<u>† I:</u> Re	eaction mechanisms of $La_2NiO_{4+\delta}$ oxygen electrodes operated in electrolys	sis and
fue	l cell n	node	
1.	Intro	oduction	
2.	Mat	erials and methods	
	2.1	Description of the electrochemical cell	
	2.2	Experimental setup and testing conditions	116
	2.3	Microstructural characterization by FIB-SEM reconstruction	117
3.	Mod	el description	118
	3.1	Reaction mechanisms and kinetic rates	
	3.2	Thermodynamic description	121
	3.3	Transport phenomena and conservation equations	
4.	Exp	erimental results and model validation	
	4.1	Experimental results	
	4.2	Calibration and validation of the electrochemical model	
5.	Disc	ussion	
	5.1	Effect of polarization and temperature on the reaction mechanism	
	5.2	Effect of the oxygen partial pressure on the reaction mechanism	
	5.3	Effect of the contact resistance on the electrode response	137

6.	Conc	lusion	140
7.	Supp	lementary Information	142
8.	Refe	ences	145
<u>Part</u>	<u>t II:</u> R	eaction mechanisms of of mixed ionic and electronic conductors used as oxyg	en
elect	trodes	in Solid Oxide Cell: focus on $La_{1-x}Sr_xCo_{y-1}Fe_yO_{3-\delta}$ and $La_2NiO_{4+\delta}$	151
1.	Intro	duction	152
2. Se	cientif	ic Approach	153
	2.1	Experiments	153
	2.2	Model Description	153
3.	Expe	rimental Results	155
4. M	lodelli	ng, Results and Discussion	157
	4.1	Model calibration and validation	157
	4.2	Effect of polarization, temperature and $pO_2$ on the reaction pathways	158
5.	Conc	lusion	162
6.	Refe	ences	163
Gen	eral c	onclusion of the chapter III	165
Cha perf	pter I forma	V - PrO <sub>1.833</sub> as a promising oxygen electrode for SOEC: electrochemical nce and durability	171
Elec Elec	troche trolys	mical performance and stability of PrO <sub>1.833</sub> as an oxygen electrode for Solid C is Cells	)xide 173
1. Ir	ntrodu	ction	174
<b>2.</b> E	xperii	nental	177
	2.1	Cell preparation	177
	2.2	Electrochemical characterization of cell 3	179
	2.3	Structural and microstructural characterizations	181
3. R	esults	and Discussion	182
	3.1	Performances and durability study of cell 3	182
	3.2	Post-mortem microstructural characterization	186
	3.3	Post-mortem structural and elemental characterizations	188
4.	Conc	lusion	197
5.	Refe	·ences	200
Sup	portin	g information	207
Gen	eral c	onclusion of the chapter IV	209
General conclusion			215
Appendix I - Development of the elementary kinetic model for the LNO electrode223			

Appendix II - Complementary results on Pr <sub>6</sub> O <sub>11</sub> electrode	233
Appendix III - Scientific production	

# List of figures

### **General introduction**

Figure 1: Evolution of energy consumption in the world with projection for the year 2040.	29
Figure 2: Comparison of different energy storage systems.	30

## Chapter I: Literature review on solid oxide cells (SOCs)

Figure 1: Solid oxide cell operating principle (a) SOEC mode (b) SOFC mode [1]39
Figure 2: Energy demand for the steam electrolysis [3]41
Figure 3: Single-cell configurations (a) Electrolyte-supported cell (b) Electrode-supported cell (c) Metal-supported cell [10]42
Figure 4: Variations in ionic conductivity at 1000°C for $(ZrO_2)_{1-x}(Me_2O_3)_x$ (Me = metal) with different Me content [18]
Figure 5: Evolution of the ionic conductivity as a function of the temperature for electrolyte materials [19]
Figure 6: Schematic representation of the reaction at the TPBs (a) single-phase electronic conductor (b) composite electrode (c) MIEC conductor (reproduced from [33])47
Figure 7: Crystal structure of (a) simple perovskite (b) double perovskite (c) Ruddlesden-Popper (RP) phase [57]
Figure 8: Differential thermal analysis on sample of Pr <sub>6</sub> O <sub>11</sub> (i.e. PrO <sub>1.833</sub> ) [73]52
Figure 9: Growth of the porosities in the YSZ electrolyte (a) Schematic representation of the evolution along the cell (b) TEM image of the porosity along the grain boundaries in the electrolyte close to the electrode interface [93]
Figure 10: Delamination of LSM electrode after aging (a) SEM image at the electrode/electrolyte interface of the delamination of LSM after aging at 800 °C under - $0.5 \text{ A cm}^{-2}$ (b) SEM image of the inner surface of the LSM electrode in contact with the electrode after aging (c) Schematic representation of the delamination mechanism proposed by Chen et al. [106]
Figure 11: SEM and EDX images of the electrode/electrolyte interface for an LSCF/GDC/YSZ/Ni-YSZ cell (a) pristine cell, (b) cell aged in SOFC mode (c) cell aged in SOEC mode. The Sr is highlighted in red. The blue arrow represents the Co particles [45]
Figure 12: XRD-maps of the local distribution of the phases detected in (a) Pristine cell (LPNO electrode deposited on GDC electrolyte) (b) Thermally aged cell (700 °C, 1000 h) and (c) Aged cell in electrolysis mode (700 °C, 960 h at $i = -0.3 \text{ A cm}^{-2}$ ). The color brightness indicates the increase in local intensity of the corresponding compound [112]

## Chapter II: Materials and methods

Figure 1: Different microstructures that can be obtained by ESD, a) dense b) columnar and c) coral [7] and d) coral-type microstructure with plate-like grains [8]
Figure 2: Scheme of electrostatic spray deposition (ESD) [9] and image of the jet-mode cone77
Figure 3: ESD deposition stages with the sequential ESD stages: 1 – aerosol formation; 2 – droplet transport; 3 – droplet impact; 4 – spreading and drying; 5 – decomposition and reaction (adapted from [2])

Figure 4: Schematic representation of the microstructures developed by ESD [10]. (a) Spreading of a liquid droplet leading to the formation of a dense to reticulated coating (b) Growth of solid particles by preferential attraction leading to "Coral" type microstructure
Figure 5: Schematic representation of the screen printing process [12]80
Figure 6: Schematic representation of the working mechanism of a triple roll mill [14]81
Figure 7: Arrhenius plot of various LNO electrodes architectures [19]
Figure 8: Arrhenius plot of double layer LSCF electrode with various thicknesses of (a) CCL and (b) AFL [20]
Figure 9: Schematic representation of the physical vapor deposition sputtering process
Figure 10: SEM image of the LNO electrode on 8YSZ electrolyte with GDC barrier layer
Figure 11: Schematic representation of the studied complete cell (Ni- YSZ/YSZ/GDC/PrO <sub>1.833</sub> /LSM)
Figure 12: SEM micrograph of double layer oxygen electrode (PrO <sub>1.833</sub> -ESD topped by LSM-SP) deposited in Ni-YSZ/YSZ/GDC half-cell provided by Forschungszentrum Jülich GmbH Institute (FZJ).
Figure 13: Schematic representation of the PFIB sample preparation (a) Pt deposition (b) FIB milling (c) Extracted lamella from the cell mounted on the Al pin
Figure 14: Schematic representation of μ-XRF and μ-XRD characterization at μ-XAS beamline, SLS, PSI, Switzerland [22]
Figure 15: Representation of the impedance spectra: a) Nyquist plot – b) Bode plot94
Figure 16: Schematic representation of the 3-electrodes setup with a symmetrical cell configuration [35]
Figure 17: Schematic representation of the experimental test bench for complete cell measurement96
Figure 18: Typical i-V curve for SOC indicating the performances losses
Figure 20: Evolution of voltage versus time for a typical cell101

## Chapter III: Reaction mechanisms of $La_2NiO_{4+\delta}$ oxygen electrode for SOCs

<u>**Part I:**</u> Reaction mechanisms of  $La_2NiO_{4+\delta}$  oxygen electrodes operated in electrolysis and fuel cell mode

Figure 1: Three electrode setup with a symmetrical cell configuration	.5
Figure 2: 3D rendering volume for a cube of $10 \times 10 \times 10 \ \mu m^3$ extracted from the whole LN reconstruction	0 . 8
Figure 3: Schematic description of the reaction pathway considered in the model (in electrolysis mode	;). .9
Figure 4: a) Experimental (marks) and simulated (solid lines) polarization curves obtained at 650, 700 and 750 °C under air for LNO electrodes. b) Experimental LNO electrode polarization resistance plotter a function of the electrode overpotential for the three investigated temperatures	0, ed ?6
Figure 5: Europimental (marks) and simulated (solid lines) FIS diagrams for the LNO electrodes	<b>a</b> t

Figure 8: a) Ratio of the surface to the bulk path under air for the LNO electrode at 650°C, 700 °C and 750 °C plotted as a function of the electrode overpotential. b) Kinetics rates for the oxygen excorporation/incorporation reaction and the oxidation/reduction reaction at the TPBIs as a function of the electrode overpotential at 700 °C b) Oxygen over stoichiometry in the electrode thickness at different polarization, under air and 700 °C.

Figure 10: EIS diagrams for the LNO electrodes at OCP under air obtained by fitting the frequency distribution. Nyquist plots for: (a) 650 °C, (b) 700 °C and (c) 750 °C. Bode plot for: (d) 650 °C, (e) 700 °C and (f) 750 °C.

#### Supplementary

<u>**Part II**</u>: Reaction mechanisms of of mixed ionic and electronic conductors used as oxygen electrodes in Solid Oxide Cell: focus on  $La_{1-x}Sr_xCo_{y-1}Fe_yO_{3-\delta}$  and  $La_2NiO_{4+\delta}$ 

Figure 1: Schematic description of the reaction pathway considered in the elementary model (in	
electrolysis mode) represented for the LNO electrode.	.154
Figure 2: Experimental (marks) and simulated (solid lines) polarization curves obtained at 650, 7 and 750 °C under air for a) LSCF[9] and b) LNO electrodes	700, .155

# Chapter IV: PrO<sub>1.833</sub> as a promising oxygen electrode for SOEC: electrochemical performance and durability

Figure 1: Schematic representation of the experimental test bench for complete cell measurements.180

 Supplementary

Figure S1: Elementary distribution map by $\mu$ -XRF in the thickness of the lamella of cell 3	after aging
at 700 °C for 1000 h under current (- 0.5 A cm <sup>2</sup> )	207
Figure S2: EDX maps of cell 3 after aging at 700 °C for 1000 h under current (-0.5 A cm <sup>-2</sup> ).	208

## List of tables

### Chapter I: Literature review on solid oxide cells (SOCs)

### Chapter III: Reaction mechanisms of $La_2NiO_{4+\delta}$ oxygen electrode for SOCs

<u>**Part I:**</u> Reaction mechanisms of  $La_2NiO_{4+\delta}$  oxygen electrodes operated in electrolysis and fuel cell mode

Table 1: Microstructural parameters of the LNO electrode reconstructed via FIB-SEM1	18
Table 2: Reactions and expressions of the kinetics rates    1	21
Table 3: Equations for the thermodynamic equilibrium constants    1	22
Table 4: Equations of charge and mass conservations associated with the current and fluxes taken in account in the physically-based model       1	ito 24
Table 5: Boundary conditions for the simulations    1	24
Table 6: Input parameters used to fit the experimental data ( $pO_2 = 0.21$ atm)1	32
Supplementary	
Table S1: Input parameters used to fit the experimental frequency distribution data ( $pO_2 = 0$ . atm)	21

# Chapter IV: PrO<sub>1.833</sub> as a promising oxygen electrode for SOEC: electrochemical performance and durability

Table 1: Non-exhaustive list of homologous series of the praseodymium oxides       17	7
Table 2: Summary of the samples reporting the praseodymium phases detected by the synchrotron p         X-ray diffraction.         17	ı- '9
Table 3: Summary of the praseodymium oxide phases with crystallographic data from $Pr_2O_3$ to $PrO_3$ versus temperature and $pO_2$ . $Pr(OH)_3$ is also given since it has been observed experimentally. Transition temperatures are given for micron grain sizes.	) <sub>2</sub> n 7

## Nomenclature

## Abbreviations

ALS	Adler-Lane-Steele model
AFL	Active functional layer
BSE	Back-scattered electrons
CCL	Current collector layer
CE	Counter Electrode
CGO	Ceria doped gadolinium oxide $Ce_{1-y}Gd_yO_{2-y/2}$ . (also called GDC)
DL	Double-layer electrode, which consists of an AFL layer of deposited by ESD and then topped by a CCL deposited by SP
EDX	Energy-dispersive X-ray spectroscopy
EHT	Electron high tension
EIS	Electrochemical impedance spectroscopy
ESD	Electrostatic spray deposition
FIB	Focused-ion beam
G	Gerischer
GDC	$Ce_{1-y}Gd_yO_{2-y/2}.$
LNO	$La_2NiO_{4+\delta}$
LPNO	LaPrNiO <sub>4+<math>\delta</math></sub> , a Ruddlesden-Popper phase (A <sub><i>n</i>+1</sub> B <sub><i>n</i></sub> X <sub>3<i>n</i>+1</sub> )
LSCF	Lanthanum strontium cobalt ferrite $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$
LSM	Lanthanum Strontium Manganite, $La_{1-x}Sr_xMnO_{3-\delta}$
MIEC	Mixed ionic and electronic conductor
OCP	Open circuit potential
OCV	Open circuit voltage

OER	Oxygen evolution reaction	
ORR	Oxygen reduction reaction	
PVB	Polyvinyl butyral, (C <sub>8</sub> H <sub>14</sub> O <sub>2</sub> ) <sub>n</sub>	
PVD	Physical vapor deposition	
PNO	$Pr_2NiO_{4+\delta}$	
RE	Reference electrode	
ROI	Region of interest	
RP	Ruddlesden-Popper phase	
SC	Steam conversion	
SE	Secondary electrons	
SEM	Scanning electron microscope	
SOC	Solid oxide cell	
SOEC	Solid oxide electrolysis cell	
SOFC	Solid oxide fuel cell	
SP	Screen printing	
TEC	Thermal expansion coefficient	
TPB	Triple-phase boundary	
WE	Working electrode	
XRD	X-ray diffraction	
XRF	X-ray fluorescence	
YSZ	Yttria-stabilized zirconia	

# Roman symbols

a,b,c	Lattice parameter	Å
	-	

$C_{dl}^{surface}$	Surface double layer capacitance	$(F m^{-2})$
c <sub>0''</sub>	Concentration of interstitial oxygen in LNO	$(\text{mol } \text{m}^{-3})$
<i>C<sub>0''</sub></i> <sup>eq</sup>	Concentration of interstitial oxygen in LNO at equilibrium	$(\text{mol } \text{m}^{-3})$
C <sub>0i</sub> '' <sup>max,eq</sup>	Maximum concentration of interstitial oxygen in LNO	$(\text{mol } \text{m}^{-3})$
d	ESD needle-substrate distance	(mm)
D <sub>chem</sub>	Bulk oxygen chemical diffusion coefficient in LNO	$(m^2 s^{-1})$
$D_{O}^{eff}$	Oxygen adsorbate diffusion coefficient in LNO	$(m^2 s^{-1})$
$D_{k,O_2}$	Knudsen diffusion coefficient	$(m^2 s^{-1})$
$D_{O_2,N_2}$	Molecular diffusion coefficient	$(m^2 s^{-1})$
$D_{O_{s_{LNO}}}$	Diffusion coefficient of the oxygen ad-ions	$(m^2 s^{-1})$
D <sub>OSLNO</sub>	Diffusion coefficient of the oxygen ad-atoms	$(m^2 s^{-1})$
$D_{O_{2s_{LNO}}}$	Diffusion coefficient of the oxygen ad- molecules	$(m^2 s^{-1})$
e-	Electrons in LNO	(-)
Ε	(i) Voltage or potential (also called U)	(V)
	(ii) Local electrode potential	(V)
F	Faraday's constant	$(C mol^{-1})$
i	Current density	$(A \text{ cm}^{-2})$
ī <sub>io/e</sub> ,	Ionic current density in CGO/Electronic current density in LNO	(A m <sup>-2</sup> )
$K_e^i$	Thermodynamic equilibrium constant	(-)
<i>k</i> <sub>+</sub>	Forward reaction kinetic constants for R1	$(mol m^{-2} s^{-1})$
$k_{ox}^{LNO/gas}$	Forward reaction kinetic constants for R2	$(s^{-1})$
$k_{ox}^{TPB}$	Forward reaction kinetic constants for R3	$(m s^{-1})$
k <sub>deion</sub>	Forward reaction kinetic constants for R4	$(s^{-1})$
k <sub>ass</sub>	Forward reaction kinetic constants for R5	$(mol m^{-2} s^{-1})$
k <sub>des</sub>	Forward reaction kinetic constants for R6	$(s^{-1})$

l	Electrode thickness	(µm)
l <sub>CGO</sub>	Electrolyte thickness	(µm)
M <sub>i</sub>	Molar mass for the i species	$(g mol^{-1})$
п	(i) Number of consecutive perovskite layers	(-)
	(ii) Reaction order	(-)
$\vec{N}_i$	Molar flux of the i-th species	$(\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1})$
$O_i^{\prime\prime}(LNO)$	Interstitial oxygen in the LNO lattice	(-)
$O_0^X(CGO)$	Oxygen atom in the CGO lattice	(-)
$O^{-}_{s,LNO}$	Oxygen ad-ion on the LNO surface	(-)
$O_{s_{LNO}}$	Oxygen ad-atom on the LNO surface	(-)
$O_{2s_{LNO}}$	Oxygen ad-molecule on the LNO surface	(-)
O <sub>2,gas</sub>	Gaseous oxygen molecule	(-)
$p_{O_2}$	Oxygen partial pressure	(atm)
$P_t$	Total pressure	(atm)
Q	Flow rate (ESD)	mL $h^{-1}$
$\bar{r}_{pores}$	Mean pore radius	(m)
R	Boltzmann gas constant	$(J \text{ mol}^{-1} \text{ K}^{-1})$
R <sub>pol</sub>	Polarization resistance	$\Omega \text{ cm}^2$
$S_p^{CGO/LNO}$	Specific surface area between CGO and LNO	(-)
$S_p^{LNO/gas}$	Specific surface area between LNO and gas phase	(m <sup>-1</sup> )
Т	Temperature	(K)
t	(i) time	(s)
	(ii) ESD deposition time	(h)
U	Voltage or potential	(V)
V <sub>i</sub>	Fuller's volume for the i species	(-)
$V_i^X(LNO)$	Interstitial vacancy in the LNO lattice	(-)
$V_0^{\bullet\bullet}(CGO)$	Oxygen vacancy in the CGO lattice	(-)
$y_{(i)}$	Molar fraction of species i species	(-)

# Greek symbols

$\alpha_{Ri}^{ox/red}$	Charge transfer coefficient for oxidation or reduction for the reaction Ri	(-)
α, β, γ	Unit cell angular parameters	(°)
γ	Solution surface tension	$(N m^{-1})$
δ	Oxygen stoichiometry	(-)
Г	Surface density of available sites on LNO	$(\text{mol } \text{m}^{-2})$
$\varepsilon_0$	Vacuum permittivity	$(F m^{-1})$
$\mathcal{E}_X$	Phase volume fraction for the phase X	(-)
η	Overpotential	(V)
$\theta_{O_{S_{LNO}}}$	Coverage of oxygen atoms on LNO surface	(-)
$\theta_{s_{LNO}}$	Free sites on the LNO surface	(-)
$\theta^{eq}_{{}^{O_{S_{LNO}}}}$	Coverage rate of oxygen atoms on LNO at equilibrium	()
$ heta^{eq}_{s_{LSCF}}$	Free site on LNO at equilibrium	(-)
$ u_{(i)}$	Kinetic rate of chemical/electrochemical reaction (i) in the electrode <sup>(*)</sup> or at the electrolyte interface <sup>(**)</sup>	<sup>(*)</sup> (mol m <sup>-3</sup> s <sup>-1</sup> ) or <sup>(**)</sup> (mol m <sup>-2</sup> s <sup>-1</sup> )
$ ilde{\mu}_i$	Electrochemical potential	$(J mol^{-1})$
$\xi_{TPBls}$	Density of triple phase boundary lengths	$(m^{-1})$
ρ	Solution density	$(g \text{ cm}^{-3})$
$\sigma_i$	Ionic conductivity	$(S m^{-1})$
$\sigma_e$ -	Electronic conductivity	$(S m^{-1})$
$\sigma_{io,CGO}$	Ionic conductivity of CGO	$(S m^{-1})$
$\sigma_i^{eff}$	Effective conductivity for the i species	(S m <sup>-1</sup> )
$\varphi_i$	Potential of the i species	(V)
arphi	Phase angle	(°)
$ au_X$	Tortuosity factor for the phase X	(-)
ω	Angular frequency	$(rad s^{-1})$

# General introduction

## **General introduction**

The global demand for energy is in constant growth and this trend seems to persist considering the population rise and the evolution of the contemporary lifestyle. The U.S. Energy information administration [1] has predicted a 28% increase in global energy demand by the year 2040 (Figure 1). To date, 80% of the world's primary energy needs are met by fossil fuels. Aside from the upcoming scarcity of primary sources, the exploitation of fossil fuels has a serious environmental impact due to the emission of greenhouse gases (GHG). According to the intergovernmental panel on climate change [2], GHG emission due to human activities, with a major release of  $CO_2$  and  $CH_4$  in the atmosphere, is responsible for the climate change which already have a direct impact on our ecosystem (droughts, water unavailability, low crop yields, ice melting and seal rising, wildfires, flooding, loss of biodiversity, ...). To cope with these environmental concerns, a change in lifestyle and consumption habits are requested. Besides, our societies need to reduce their dependency on fossil fuels. To partly deal with this issue, rising the share of renewable energies in final energy production is required.



Figure 1: Evolution of energy consumption in the world with projection for the year 2040 (source: U.S. Energy information administration [1]).

A wide range of mature renewable energies (hydroelectric, wind, solar, marine, geothermal ...) is already available to suit the diversity of the earth's climate and environment. For example, Iceland runs on nearly 100% renewable electricity provided by geothermal energy and hydraulic dams by harnessing its spectacular panorama of volcanoes and glaciers [3]. However, this natural landscape remains an exception, and Iceland is a small country (5 times smaller than France, with only 103125 km<sup>2</sup>) with only 372520 inhabitants with comparison to 67.75 million of French inhabitants. Generally, the use of renewable energies remains nowadays limited due to their intermittency (e.g. the availability of sunlight for solar panels or the availability of wind for wind energy). For this reason, a system for storing this intermittent electricity is necessary to ensure a supply of electricity on demand to the consumer.



Figure 2: Comparison of different energy storage systems [4].

Many solutions for electricity storage are available [4], which are differentiated by storage capacity, charging time, cost ... (Figure 2). Among these technologies, dihydrogen H<sub>2</sub>, usually referred to as 'hydrogen', appears to be a good energy vector for storage and transport. Indeed, dihydrogen has a very high mass density of energy (120 MJ kg<sup>-1</sup>). Thus, when needed, the chemical energy stored in the hydrogen can be converted into electrical energy through a fuel cell to generate "clean" electricity at high efficiency, with a reaction that only produces water. As one illustration of this operating model, the Myrte platform (*Mission hydrogène renouvelable pour l'intégration au réseau électrique*) installed in Corsica (France) allows to

store of photovoltaic energy produced during low consumption hours thanks to the operation of steam electrolyzers, and releases it via a fuel cell when the panels are off. Moreover, hydrogen can be stored in various state (solid, liquid, gas), offering a multitude of possible applications (fuel for rockets, motor propulsion for vehicle, glass manufacturing for flat screens ... ). Besides, the use of hydrogen as a reactant is not unusual since it is widely used in the chemical (e.g. ammonia production), petrochemical (refining of petroleum products), and steel industries [5,6]. However, to date, 95% of this hydrogen is produced by steam reforming, partial oxidation of hydrocabons, and gasifications of coal based on fossil fuels. All these processes present the drawback of substantial greenhouse gas emissions. For example, vaporeforming generates 11 kg of  $CO_2$  per kg of hydrogen [5]. To remain within the target of low environmental impact, hydrogen must be produced from low-pollution sources. Therefore, the steam electrolysis studied in this thesis appears as a valuable technology for the production of "clean" hydrogen and a more sustainable one.

The electrolysis of water consists in dissociating the H<sub>2</sub>O molecule through the effect of an electric current to produce dihydrogen and oxygen. There are several types of electrolyzers that can be grouped into two main categories [7]. The low temperature electrolyzers such as "Alkaline electrolysis (40 - 90 °C)" and "Proton Exchange Membrane (PEM) electrolysis (20 -100 °C)" and the high temperature steam electrolysis (HTSE) (T = 800 °C). The core of this thesis work is focused on the HTSE technology through the solid oxide electrolysis cells (SOEC). This HTSE technology, that will be described in details in the chapter 1, offers many advantages. One of them is that part of the energy demand required for the H<sub>2</sub>O molecule splitting is provided by heat. Therefore, the amount of electrical energy to produce hydrogen is decreased with increasing the temperature. In this view, it is worth noting that the heat supply can be less expensive than electricity. Indeed, heat recovery from industrial systems such as nuclear plants [8] or geothermic sources can be used for steam electrolysis [9]. The other advantage of HTSE technology is that it can operate in a reversible mode as solid oxide cells (SOC), i.e. either in electrolysis mode (SOEC) to produce hydrogen or in fuel cell mode (SOFC for solid oxide fuel cell) to produce electricity. As previously discussed, this reversibility confers a particular interest in the storage of renewable energies (e.g. Myrte). For other purposes, the HTSE technology is interesting because it can be used to convert the CO<sub>2</sub> emissions of the hydrocarbon factories into alternative natural gas through the co-electrolysis reaction of water vapor and carbon dioxide [10].

The main challenge for the large-scale deployment of HTSE is to provide a functional technology over long periods of time at competitive cost. Indeed, due to the high operating temperatures, this technology suffers from severe degradation mainly related to materials instabilities (reactivity, microstructure evolution, mechanical constraints...) [11,12]. To limit the degradation, increase the lifetime, and reduce the cost, this technology can be operated at an intermediate temperature (T $\leq$  700 °C). However, lowering the operating temperature down to 700 °C leads to many challenges. One of them is to develop oxygen electrodes with sufficiently high electrocatalytic activity for the electrochemical reaction. Intensive research has thus been dedicated to exploring alternative oxygen electrode materials in order to achieve superior and stable electrochemical performance. These electrodes are usually made of mixed ionic and electronic conductors (MIEC) with interesting intrinsic properties such as high oxygen exchange coefficient and high chemical diffusivity. To improve the electrochemical performances, it is also of great importance to design the oxygen electrode microstructure and architecture.

#### 1. Objectives of the thesis

In this context, it is proposed in this thesis to study several oxygen electrode materials in terms of electrochemical performances and chemical stability for SOEC application.

The first part of this work focuses on the first member of the layered Ruddelsden-Popper  $(Ln_{n+1}Ni_nO_{3n+1})$  series,  $La_2NiO_{4+*}$  (LNO) that exhibits an oxygen over-stoichiometry. This material has recently attracted significant attention as a promising alternative solution to conventional oxygen deficient perovskites for IT-SOCs application [13-15]. Indeed, it has been shown that LNO exhibits high electrocatalytic properties combined with a good stability in operation [13-16]. However, despite its interest, the underlying reaction mechanisms for this oxygen-deficient material are still not precisely understood. Moreover, no electrochemical model has been proposed for this family of materials. In this work, LNO has been studied in symmetric cell configuration as a function of temperature (650 – 750 °C), oxygen partial pressure (0.15-1 atm), and polarization ( $\pm 100 \text{ mA cm}^2$ ). This experimental approach has been coupled with modeling work in order to better understand the LNO underlying mechanisms.

The second part concerns the study of an innovative oxygen electrode material,  $PrO_{1.833}$  (i.e.  $Pr_6O_{11}$ ) characterized by remarkable catalytic properties [17]. Indeed, several studies detected the presence of this secondary phase on the La<sub>2-x</sub>Pr<sub>x</sub>NiO<sub>4+δ</sub> (x = 1, 1.5, 2) electrode [16,18]. Specifically, a study supported by advanced structural characterization reported that  $Pr_6O_{11}$  was a major decomposition product of the LPNO (x = 1) air electrode aged in electrolysis mode (700 °C, 900 h in 90/10 H<sub>2</sub>O/H<sub>2</sub>, at 200 mA cm<sup>-2</sup>) [19]. The objective here is to reach high electrochemical performances with limited degradation at an intermediate temperature (700 °C) for SOEC operation through the elaboration of controlled microstructures and architectures with PrO<sub>1.833</sub> as an oxygen electrode. For this purpose, a durability study of PrO<sub>1.833</sub> is carried out by long-term-test (up to 1000 h) in complete SOEC configuration to investigate the evolution of the electrochemical performances. This work has been combined with ante and post-mortem characterizations with scanning electron microscopy (SEM) and synchrotron  $\mu$ -XRD and  $\mu$ -XRF (realized at Swiss Light Source, PSI, Switzerland) in order to analyze the impact of the cell operating conditions on the microstructural and chemical evolution of the material.

#### 2. Structure of the manuscript

The first chapter consists in a literature review of the solid oxide cells. A state-of-the-art of the performances and the main causes of material degradation developed for SOCs is presented. Particular attention is given to classical oxygen electrode materials such as the pure electronic conductor LSM ( $La_{1-x}Sr_xMnO_{3-\delta}$ ) and the mixed ionic and electronic conductor LSCF ( $La_xSr_{1-x}Co_vFe_{1-v}O_{3-\delta}$ ) as well as materials developed in this work (*i.e.* LNO, PrO<sub>1.833</sub>).

The second chapter starts with the technical description of the manufacturing techniques employed in the thesis combining electrostatic spray deposition (ESD) and screen-printing (SP). In a second step, a description of the characterization techniques used is given (scanning electron microscopy, laboratory X-ray-diffraction (XRD), synchrotron  $\mu$ -X-ray-diffraction and  $\mu$ -fluorescence). Finally, the experimental setup for the electrochemical characterizations of each of the studied cells (LNO and PrO<sub>1.833</sub>) is described.

The third chapter is devoted to the study of reaction mechanisms governing the electrochemical behavior of  $La_2NiO_{4+\delta}$  (LNO). The chapter is divided into two parts. The first part describes the development and the validation of a micro-scale model. This model which

considers two reaction pathways (i.e. bulk and surface paths) allow to describe the main reaction mechanisms controlling the LNO under both SOEC and SOFC modes A set of experiments performed on a symmetrical cell using a three-electrode setup has been specifically conducted to validate this model. In the second part of the chapter, a comparison is carried out between the reaction mechanisms of the over-stoichiometric La<sub>2</sub>NiO<sub>4+ $\delta$ </sub> (LNO) to the classical oxygen under-stoichiometric La<sub>1-x</sub>Sr<sub>x</sub>Co<sub>y-1</sub>Fe<sub>y</sub>O<sub>3- $\delta$ </sub> (LSCF). The details of the LNO model extended to elementary reactions used in this second part will be provided in appendix.

The fourth chapter is dedicated to the electrochemical, microstructural and structural characterization of a nanostructured  $PrO_{1.833}$  as oxygen electrode for SOEC application. This chapter deals with a durability study of a complete SOEC based on an oxygen electrode,  $PrO_{1.833}$ , topped by a current collecting layer (CCL) made in strontium-doped lanthanum manganite (LSM). The long-term test is performed at 700 °C for 1000 h in SOEC mode (at – 0.5 A/cm<sup>2</sup>). Characterizations of the pristine and tested cells have been carried out using SEM,  $\mu$ -XRD and  $\mu$ -fluorescence to detect and understand the microstructural and structural evolutions of the oxygen electrode at a micrometer scale. This study has been complemented with a comparison conducted with thermally aged samples (700 °C for 1000 h and 800 °C for 700 h) in order to better understand the evolution of the praseodymium phases.

Some conclusions are given in the last part and some perspectives are proposed to reinforce the current results.

#### 3. References

- [1] U.S. Energy Information Administration, International Energy Outlook 2017. https://www.eia.gov/.
- [2] H.-O. Pörtner, D.C. Roberts, M.M.B. Tignor, E.S. Poloczanska, K. Mintenbeck, A. Alegría, M. Craig, S. Langsdorf, S. Löschke, V. Möller, A. Okem, B. Rama, eds., Climate Change 2022: Impacts, Adaptation and Vulnerability. Contribution of Working Group II to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, 2022.
- [3] National energy authority of Iceland (NEA) https://nea.is/.

- [4] A. Valera-Medina, H. Xiao, M. Owen-Jones, W.I.F. David, P.J. Bowen, Ammonia for power, Progress in Energy and Combustion Science. 69 (2018) 63–102. https://doi.org/10.1016/j.pecs.2018.07.001.
- [5] CEA, Dossier les énergies renouvelables, l'hydrogène: Modes de production du dihydrogène, (2014).
- [6] A. Nechache, S. Hody, Alternative and innovative solid oxide electrolysis cell materials: A short review, Renewable and Sustainable Energy Reviews. 149 (2021) 111322. https://doi.org/10.1016/j.rser.2021.111322.
- J.D. Holladay, J. Hu, D.L. King, Y. Wang, An overview of hydrogen production technologies, Catalysis Today. 139 (2009) 244–260. https://doi.org/10.1016/j.cattod.2008.08.039.
- [8] R. Elder, R. Allen, Nuclear heat for hydrogen production: Coupling a very high/high temperature reactor to a hydrogen production plant, Progress in Nuclear Energy. 51 (2009) 500–525. https://doi.org/10.1016/j.pnucene.2008.11.001.
- [9] C. Mansilla, J. Sigurvinsson, A. Bontemps, A. Maréchal, F. Werkoff, Heat management for hydrogen production by high temperature steam electrolysis, Energy. 32 (2007) 423– 430. https://doi.org/10.1016/j.energy.2006.07.033.
- [10] J. Aicart, Modélisation et validation expérimentale d'un co-électrolyseur de la vapeur d'eau et du dioxyde de carbone à haute température, These de doctorat, Grenoble, 2014. https://www.theses.fr/2014GRENI095
- K. Chen, S.P. Jiang, Review—Materials Degradation of Solid Oxide Electrolysis Cells, J. Electrochem. Soc. 163 (2016) F3070. https://doi.org/10.1149/2.0101611jes.
- [12] Y. Wang, W. Li, L. Ma, W. Li, X. Liu, Degradation of solid oxide electrolysis cells: phenomena, mechanisms, and emerging mitigation strategies—A review, J Mater Sci Technol. 55 (2020) 35–55. https://doi.org/10.1016/j.jmst.2019.07.026.
- [13] V. Vibhu, A. Rougier, C. Nicollet, A. Flura, J.-C. Grenier, J.-M. Bassat, Solid State Ionics, 278 (2015) 32–37. https://doi.org/10.1016/j.ssi.2015.05.005.
- [14] S. Takahashi, S. Nishimoto, M. Matsuda, M. Miyake, Electrode Properties of the Ruddlesden–Popper Series, La<sub>n+1</sub>Ni<sub>n</sub>O<sub>3n+1</sub> (n=1, 2, and 3), as Intermediate-Temperature Solid Oxide Fuel Cells, Journal of the American Ceramic Society, 93 (2010) 2329– 2333. https://doi.org/10.1111/j.1551-2916.2010.03743.x
- [15] G. Amow, I. J. Davidson, S. J. Skinner, A comparative study of the Ruddlesden-Popper series, La<sub>n+1</sub>Ni<sub>n</sub>O<sub>3n+1</sub> (n = 1, 2 and 3), for solid-oxide fuel-cell cathode applications, Solid State Ionics, 177 (2006) 1205–1210. https://doi.org/10.1016/j.ssi.2006.05.005
- [16] V. Vibhu, J.-M. Bassat, A. Flura, C. Nicollet, J.-C. Grenier, A. Rougier, Influence of La/Pr ratio on the ageing properties of La<sub>2-x</sub>Pr<sub>x</sub>NiO<sub>4+ δ</sub> as cathodes in IT-SOFCs, ECS Transactions. 68 (2015) 825. doi 10.1149/06801.0825ecst.
- [17] C. Nicollet, A. Flura, V. Vibhu, A. Rougier, J.-M. Bassat, J.-C. Grenier, An innovative efficient oxygen electrode for SOFC: Pr<sub>6</sub>O<sub>11</sub> infiltrated into Gd-doped ceria backbone, International Journal of Hydrogen Energy. 41 (2016) 15538–15544. https://doi.org/10.1016/j.ijhydene.2016.04.024
- [18] A. Montenegro-Hernández, J. Vega-Castillo, L. Mogni, A. Caneiro, Thermal stability of  $Ln_2NiO_{4+\delta}$  (Ln: La, Pr, Nd) and their chemical compatibility with YSZ and CGO solid electrolytes, International Journal of Hydrogen Energy. 36 (2011) 15704–15714. doi.org/10.1016/j.ijhydene.2011.08.105.
- [19] N.I. Khamidy, J. Laurencin, D. Ferreira Sanchez, F. Monaco, F. Charlot, E. Djurado, Durability of nanostructured LaPrNiO<sub>4+δ</sub> electrode for solid oxide cells: Electrochemical, microstructural, and structural investigation, Journal of Power Sources. 450 (2020) 227724. https://doi.org/10.1016/j.jpowsour.2020.227724.

# Chapter I Literature review on solid oxide cells (SOCs)

## **Chapter I: Literature review on solid oxide cells (SOCs)**

This chapter I is an overview of the state of the art of solid oxide cells (SOCs). An introduction to the general operating principle as well as the types of architectures of SOCs is presented. The second part of this review is focused on the various materials used in solid oxide cells, with particular attention to the oxygen electrode components. A subsection is dedicated to each of the materials selected for this study, namely:  $Ln_2NiO_{4+\delta}$  (Ln = La, Pr) and PrO<sub>1.833</sub>. Subsequently, the main causes of degradation observed on SOCs during operation are presented in order to better understand the limitations observed of this technology. Finally, a brief overview of the objectives of this thesis is presented based on this literature study.

## 1. General principles concerning the SOCs

## 1.1 Operating principle

SOCs are high-temperature electrochemical energy-conversion devices that produce efficiently clean electricity (solid oxide fuel cell, SOFC mode) or hydrogen (solid oxide electrolysis cell, SOEC mode). A single cell is composed of an assembly of two porous electrodes separated by a dense electrolyte. The operating principle of the SOCs is shown in Figure 1.



Figure 1: Solid oxide cell operating principle (a) SOEC mode (b) SOFC mode [1].

Considering the example of an electrolysis operation, the reactions occur as follows. Steam is introduced in the hydrogen electrode. Then, under current, the water molecule is reduced and

splits into one oxygen ion and one dihydrogen gaseous molecule according to the following reaction

$$H_2 0 + 2e^- \to H_2 + 0^{2-}$$
 Eq. 1

This oxygen ion diffuses through the electrolyte which is an ionic conductor. Thereafter, the oxygen ion is oxidized and produces dioxygen molecule in the oxygen electrode and electrons as follows

$$O^{2-} \to \frac{1}{2}O_2 + 2e^-$$
 Eq. 2

The complete cell reaction is  $H_2O \rightarrow \frac{1}{2}O_2 + H_2$  Eq. 3

In the case of fuel cell operation, the opposite reactions occur. In these conditions, the device will convert the chemical energy contained in fuel (that is hydrogen or hydrocarbons) into electricity and heat.

These technologies operate at high temperatures between 700 °C and 800 °C to ensure the ionic conductivity of the solid electrolyte which is thermally activated. The high temperature presents a significant interest in terms of thermodynamic and kinetic aspects which provides an economic advantage. For sake of clarity, the main explanations will be provided for electrolysis operation which is the major concern of this work. From a thermodynamic aspect, in SOEC mode, the enthalpy energy required for the water dissociation reaction can be expressed as follows:

$$\Delta H(T) = \Delta G(T) + T \times \Delta S(T) \qquad \text{Eq. 4}$$

where  $\Delta G$  per mole of reaction (I-3) (Gibbs free energy change) is the electrical energy and T $\Delta S$  the thermal energy with  $\Delta S$ , the variation of the entropy. As shown in Figure 2, when increasing the temperature, the amount of provided heat increases while the amount of requested electrical energy decreases. Therefore, the high-temperature operation allows reducing production costs since the electrical supply is reduced. Moreover, the efficiency of high-temperature electrolyzers is higher than that of low temperature. The efficiency is about 3 kWh Nm<sup>-3</sup> at high temperature against 4 kWh Nm<sup>-3</sup> for alkaline electrolysis or PEMFC [2]. Finally, high-temperature electrolysis does not require the use of an expensive catalyst.

The thermo-neutral cell voltage of the electrolyzer is defined as follows

$$U_{TN} = \frac{\Delta H}{nF}$$
 Eq. 5

where n is the number of electrons involved in the reaction and F is the Faraday constant.

At this value, the heat consumed by the endothermic reaction of steam electrolysis is compensated by the Joule effect produced in the cell. Hence, the efficiency of the cell can reach 100 % if the heat supply is free. For an operation below this potential, the system requires an external heat supply to balance the thermal sink due to the reaction thus reducing the cell efficiency.

High-temperature electrolysis is therefore of considerable interest. The challenge now is to develop technologies that are sustainable and robust over the long term.



Figure 2: Energy demand for the steam electrolysis [3].

#### 1.2 Single-cell configuration

Various configurations of single cells have been developed over the years. The first studies on SOECs were conducted by Doenitz and Erdle [4] in the 1980s using electrolyte-supported tubular cells. The design of the cell consists of two electrodes separated by an electrolyte, in a cylinder shape. However, despite the mechanical robustness of this cell architecture, their use has been largely neglected due to the low performance achieved. Indeed, it appears that this cell geometry limits gas transport and generates high ohmic losses in the interconnectors. Some authors keep working on the improvement of this specific model of the cell through innovative designs [5–7].

Nowadays, the most developed SOCs are based on the planar configuration which can be classified by the nature of the mechanical support layer (Figure 3). The electrolyte-supported cells require very high operating temperatures (> 850°C) to limit the ohmic losses in the electrolyte. This cell configuration is not widely developed as these operating conditions lead to reactivities and chemical degradation of the components. However, a few studies initiated with more conductive materials have shown promising results at lower temperatures [8,9]. The electrode supported cell design is widely favored as it allows reducing of the ohmic drop in the thin electrolyte offering the possibility to work at much lower temperatures (700°C<T<850°C). The best results in terms of performance and durability have been observed with this type of configuration. Recently, cells based on metal-support have also been developed. The active ceramics materials (anode/electrolyte/cathode) are deposited on a thick metallic substrate which ensures the cell mechanical strength. This cell configuration has the advantage of being more resistant to thermal cycling. Moreover, it would allow reducing production costs thanks to the reduction of the thickness of the ceramic layers that are the most expensive.

A stack is built from a set of these single cells linked together by interconnectors for electrical contact and fluid supply for a life-scale operation.



Figure 3: Single-cell configurations (a) Electrolyte-supported cell (b) Electrode-supported cell (c) Metal-supported cell [10].

## 2. SOCs materials

The development of a stable and efficient system must respect several criteria in the choice of materials. In general, it is required that all materials have a low chemical reactivity between them, good compatibility on the thermal expansion coefficient (TEC), and good mechanical resistance [11]. On the other hand, the cost of the materials as well as the long-term availability of the raw material also remains a selection criterion.

The choice of materials plays a fundamental role in the performance but also in stability of the system over time. A more detailed overview will be presented in this section. Particular attention will be paid to the oxygen electrode which is the core of the thesis work.

## 2.1 Electrolyte

The electrolyte is a dense membrane separating the anode from the cathode. The main role of an electrolyte is to ensure the migration of  $O^{2-}$  ions between the two electrodes, to prevent fuel-oxygen mixing, and to be a good insulator for electrons. Therefore, the electrolyte must exhibit excellent ionic conductivity and a fully negligible electronic conductivity at the SOCs operating temperatures. Moreover, it has to be stable in a large domain of the oxygen partial pressure  $(10^{-22} < pO_2 \text{ (atm)} < 0.2)$ . It has also to be dense and thick enough to ensure gas impermeability. A compromise between gas tightness and resistance to current flow must be found in the thickness of the electrolyte.

Generally, the electrolyte materials that satisfy these criteria are made of fluorite-type ceramic oxides (e.g. ZrO<sub>2</sub>, CeO<sub>2</sub> ...) substituted with rare-earth cations (Sc, Y, Sm ...) [12]. Among the most developed materials, Yttria Stabilized Zirconia (YSZ) is used, with yttria (yttrium oxide) substitution rates ranging from 3 to 12 mol. %. The substitution of the  $Zr^{4+}$  ion by the trivalent  $Y^{3+}$  cation leads to the formation of oxygen vacancies that is at the origin of the conductivity of the O<sup>2-</sup> ions. The reaction is expressed using the Vink-Kröger notation as follows

$$Y_2 O_3 \stackrel{ZrO_2}{\Longleftrightarrow} 2 Y'_{Zr} + V_o^{"} + 3 O_0^x \qquad \text{Eq. 6}$$

For YSZ, the highest ionic conductivity is achieved with a dopant value of 8 - 10 mol. % of  $Y_2O_3$  [13] crystallizing in the cubic structure. On the other hand, micronic zirconia doped with 3 mol. % of  $Y_2O_3$ , the tetragonal one, exhibits lower ionic conductivity but higher mechanical strength. For comparison, the ionic conductivity of the zirconia stabilized at 8 mol. % of Yttria  $((ZrO_2)_{0.92}(Y_2O_3)_{0.08} - 8YSZ)$  is about 0.05 S cm<sup>-1</sup> at 800 °C while that of the 3 mol. % of Yttria (3Y-TZP, tetragonal zirconia polycrystalline) is 0.03 S cm<sup>-1</sup> [14,15]. A too-high dopant concentration leads to a phenomenon of association between punctual defects, reducing their mobility and consequently diminishing the ionic conductivity [16]. As can be seen in Figure 4,

the nature of the dopant must also be considered. Indeed, it has been shown that when the dopant ionic radius has a close size mismatch to the ionic radius of the host, a larger ionic conductivity has been observed [17]. On the other hand, a larger mismatch leads to stresses lattice which can destabilize the crystalline structure leading to a phase transition.



Figure 4: Variations in ionic conductivity at 1000°C for  $(ZrO_2)_{1-x}(Me_2O_3)_x$  (Me = metal) with different Me content [18].

Other substitution elements are also investigated. In particular, much higher ionic conductivity has been measured with the use of scandia (Sc<sub>2</sub>O<sub>3</sub>) [19]. However, the cost of this electrolyte and its poor stability [20] limit its application. However, due to the low conductivity of YSZ at intermediate temperatures (i.e. 0.0005 - 0.01 S cm<sup>-1</sup> at T<700°C:[19,21]) and its reactivity with the oxygen electrode materials, alternative electrolyte materials are being investigated. Among the candidates, ceria substituted with gadolinia (Gd<sub>2</sub>O<sub>3</sub>), samaria (Sm<sub>2</sub>O<sub>3</sub>) or yttria (Y<sub>2</sub>O<sub>3</sub>) with molar percentage of 10-30 %, in a fluorite structure type, is considered. For example, ceria doped with 10 mol. % of gadolinia exhibits an ionic conductivity of 0.0544 S cm<sup>-1</sup> at 700 °C [22]. Moreover, a substituting level of 10 mol. % (CGO10: Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub>) shows a larger ionic conduction than 20 mol. % doping (CGO20: Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>1.9</sub>) [22], even though both CGO10 and CGO20 are considered for the application.

However, at high temperatures under reducing atmosphere, the cerium oxygen state Ce<sup>4+</sup>

tends to be reduced into  $Ce^{3+}$ , resulting in n-type electronic conductivity in the electrolyte and inducing a short circuit in the cell [23]. As illustrated in Figure 5, many other materials are available with higher conductivities than YSZ. Some of them could be materials belonging to the Bi<sub>2</sub>O<sub>3</sub> group, the LAMOX family (e.g. La<sub>2</sub>Mo<sub>2</sub>O<sub>9</sub>), or even other perovskites such as La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>MgO<sub>2-δ</sub> (LSGM). However, most of these materials exhibit a high thermal expansion coefficient (TEC) compared to the electrode materials, and many reactivities are observed due to the sintering temperatures required for their manufacturing [24–27]. To date, the 8YSZ is the most commonly used as electrolyte material for electrode supported cells



Figure 5: Evolution of the ionic conductivity as a function of the temperature for electrolyte materials [19].

## 2.2 Fuel/Hydrogen electrode

The SOC hydrogen electrode should provide high electro-catalytic activity for the fuel oxidation/reduction reactions. The percolation of the gas, ionic and electronic phases at the so-called Triple Phase Boundaries (TPBs) ensures the effective operation of the electrode. This electrode has also to be permeable to gas and should show no chemical reaction with typical electrolyte materials such as 8YSZ, and CGO. Nickel (Ni) based cermet is the most developed hydrogen electrode for SOCs. The typical electrode is a porous Ni-8YSZ composite where Ni ensures the electronic conductivity, YSZ the ionic conductivity and the pores serve the gas transport. The performance of the cell depends also on the microstructural parameters of the

electrodes. Indeed, a fine microstructure allows increasing in the active region meanwhile an increase of the porosity would facilitate the gas transport. In the case of hydrogen-supported electrodes, the hydrogen electrode is the mechanical support of the cell. It should present an appropriate thermal expansion coefficient (TEC) with the common electrolytes. Therefore, the electrode is composed of an active functional layer (AFL) and a thicker current collecting layer (CCL). The 8YSZ will generally be favored because of the high ionic conductivity, especially in the thin functional layer where reactions occur. However, as a collecting layer made of Ni\_3Y-TZP is sometimes use to enhance the cell mechanical strength. However, Ni/YSZ-based fuel electrode has some drawbacks; for example, sulphur poisoning and carbon deposition are observed when using natural gas as fuel due to the cracking of methane. Nickel metal is not only chosen because of its cost effectiveness but also because it can be easily produced by cosintering NiO and YSZ, followed by in-situ reduction of the nickel oxide. Other metals that may be used are copper, cobalt and noble metals. Copper could also be considered as a replacement for nickel [28,29] but it exhibits a higher propensity for carbon deposition and sulphur poisoning at lower temperature. Other materials are currently being investigated as potential replacements for the Ni/YSZ combination. Developments regarding fuel materials have been extensively addressed in details in a review article [30].

## 2.3 Air/Oxygen electrode

The oxygen oxidation/reduction reactions (OER/ORR) take place in the SOC air electrode. The main requirements for an oxygen electrode are

- High electronic conductivity (in general > 100 S cm<sup>-1</sup>) [31] at the operating temperature. In the case of the use of a mixed conductor, a high enough ionic conductivity will be also required (even if it will be at least four orders of magnitude lower that the electronic one).
- High catalytic activity with respect to the associated (OER/ORR) half-reactions.
- Sufficient porosity to allow gas transport.
- Thermal expansion coefficient to be comparable to that of the other materials (electrolyte and interconnects).
- Chemical and mechanical stability in air.
- Sufficient durability when operating at high temperatures and temperature cycling [32].
- Low cost.

Many materials have been studied as oxygen electrodes for solid oxide cells. There are three categories of oxygen electrodes made of pure electronic conductor, mixed ionic and electronic conductors (MIEC), and composite materials based on a pure electronic phase (i.e. LSM) and a pure ionic one (i.e. 8YSZ, CGO). For pure electronic conductor materials, the reaction zone is limited to the electrode/electrolyte/gas interface where the TPBs area are located (Figure 6a). The microstructure plays an important role in improving the performance because an optimized microstructure will maximize the number of TPB sites leading to increase the active regions for OER/ORR. In particular, the porosity has to be sufficient through the oxygen electrode to bring oxygen molecules in contact with the electrolyte. The development of composite materials has allowed increasing in the number of TPBs sites and thus extending the reaction in the depth of the porous electrode (Figure 6b) [33]. A third type oxygen electrodes uses MIEC-type oxides (Figure 6c). Thanks to the use of mixed ionic and electronic conductors, the reactions are no more limited to TPB lines but can occur onto the whole surface of the electrode particles as shown in Figure 6c. As a consequence, a significant improvement in the cell performance is expected at a lower operating temperature.



Figure 6: Schematic representation of the reaction at the TPBs (a) single-phase electronic conductor (b) composite electrode (c) MIEC conductor (reproduced from [33]).

Perovskite type (i.e. cubic type (ABO<sub>3</sub>), layered perovskites (AA'B<sub>2</sub>O<sub>6</sub>) or Ruddlesden-Popper phases (A<sub>n+1</sub>B<sub>n</sub>O<sub>3n+1</sub>, (n = 1, 2 and 3)) are classically used as air electrodes (Figure 7). The strontium-doped lanthanum manganite, (La,Sr)MnO<sub>3</sub> (LSM), with the ABO<sub>3</sub> structure, is an example of a commonly used material that shows good stability under oxidizing atmospheres [34,35]. The LSM is characterized by a high (p-type) electronic conductivity  $\sigma_{el}$  =108 S cm<sup>-1</sup> at 800 °C and a TEC compatible with that of the classical YSZ electrolyte (Table 1). Since LSM is a pure electronic conductor material, it is usually associated with YSZ to form a composite electode in order to increase the density of TPB lengths and thus increase the cell performance. However, LSM suffers from some degradation phenomena at the electrode/electrolyte interface due to high operating temperatures. In electrolysis mode, it has been shown that this electrode is subjected to a delamination due to the local production of oxygen at the TPBs. Moreover, a substantial reactivity has also been reported for this electrode in contact 8YSZ. Particularly, the formation of resistive phases such as lanthanum zirconate (La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>) leads to a drastic decrease in cell performances [36,37]. A short review of the degradation of the materials will be developed in more detail in the next section.

The LSM-YSZ composite is nowadays replaced in standard cells by MIEC materials. Among them are  $La_{0.8}Sr_{0.2}FeO_{3-\delta}$  (LSF) [38],  $La_{0.8}Sr_{0.2}CoO_{3-\delta}$  (LSCo) [38], and Sr<sub>2</sub>Fe<sub>1.5</sub>Mo<sub>0.5</sub>O<sub>6-8</sub> (SFM) [39]. For example, LSCo exhibits higher electronic and ionic conductivity than LSM at a lower temperature. Particularly, it appears that the oxygen transport and exchange properties increase with the amount of Co [40]. However, the increase in cobalt (Co) leads to a significant increase in TEC [41] which results in mechanical stress at the interface with the electrolyte. The substitution of a part of the cobalt (Co) by iron (Fe) to form La<sub>1-x</sub>Sr<sub>x</sub>Co<sub>1-y</sub>Fe<sub>y</sub>O<sub>3-δ</sub> can help to reduce these mechanical stresses. To date, LSCF is the other commonly used perovskite material for SOCs because of its superior mixed ionic and electronic conduction compared to LSM. The study of the impact of the material composition to find a compromise between good electrical conductivity and its thermo-mechanical stability has been widely investigated [41–43]. For instance, it appears that the electrical conductivity increases with Co content [42,43]. Meanwhile, the TEC coefficient was found to decrease when increasing the Co content for La<sub>0.3</sub>Sr<sub>0.7</sub>Co<sub>1-v</sub>Fe<sub>v</sub>O<sub>3-δ</sub> composition [42] while it tends to decrease only for y > 0.4 with  $La_{0.8}Sr_{0.2}Co_{1-y}Fe_yO_{3-\delta}$  composition [43]. However, the studies revealed that LSCF electrode suffers from demixing [44–46], reactivity with the electrolyte [47,48], and microstructural modification [47] Especially, it has been shown that the operating condition influences the electrode performances as well as their stability. Indeed, The et al. [46] show that the Sr diffusion which starts during the sintering process increases during electrolysis operation.

In the same way, Laurencin et al. [45] show a higher degradation rate when operating under electrolysis conditions. These issues will be detailed in the following section; however, it can be stated that selecting a material for a fuel cell application may not be relevant for electrolysis.

A-site deficient  $(La_{0.7}Sr_{0.3})_{0.95}(Co_{0.2}Fe_{0.8})O_{3-\delta}$  (LSCF) perovskite film has been reported to be a potential high-performance cathode for SOFC with microstructural details at the nanometer length scale. This electrode exhibits polarization resistance (measured at open circuit voltage using a symmetrical cell) as low as 0.037  $\Omega$  cm<sup>2</sup> and peak power density of 1.4 W cm<sup>-2</sup> in a Ni/YSZ supported cell at 650 °C. X-ray diffraction and electron microscopy analyses revealed a closely related two-phase perovskite structure for LSCF and a well-dispersed, nanoscale Bsite precipitate (CoFeOx) decorating the LSCF surfaces. Such large improvements in the electrode performance were attributed to the altered LSCF perovskite structure due to nonstoichiometry and to the very high active surface area of the film [49].

Another disadvantage of these materials is that they easily form insulating phases such as  $La_2Zr_2O_7$  and  $SrZrO_3$  at the interface with the YSZ electrolyte, which further degrades the performance of the cell.

	Material	TEC (10 <sup>-6</sup> K <sup>-1</sup> )	Reference
		30-1000 °C	
Electrolyte	8YSZ	10.5 – 11	[25]- [50]
	$Ce_{0.9}Gd_{0.1}O_{2-\delta}$	13.1	[50]
	$Ce_{0.8}Gd_{0.2}O_{2-\delta}$	12.5 - 12.7	[51] - [50]
	$La_{0.9}Sr_{0.1}Ga_{0.8}MgO_{2-\delta}(LSGM)$	11.6	[52]
02	$La_{0.6}Sr_{0.4}CoO_{3-\delta}(LSCo)$	20.5	[41]
electrode	$La_{0.6}Sr_{0.4}MnO_{3-\delta}(LSM)$	12.3	[51]
	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	15.3	[43]
	$Pr_2NiO_{4+\delta}$ (LNO)	13.2 - 13.4	[53] - [54]
	$La_2NiO_{4+\delta}$ (LNO)	13.0	[54]
	Nd <sub>2</sub> NiO <sub>4+δ</sub> (NNO)	12.4	[54]

Table 1: Thermal expansion coefficient (TEC) of a selection of electrolyte and oxygen electrode materials

Among the available materials, the nickelates belonging to Ruddlesden-Popper (RP) series have recently attracted much attention as promising oxygen electrode materials for the next generation of SOECs [55,56].



Figure 7: Crystal structure of (a) simple perovskite (b) double perovskite (c) Ruddlesden-Popper (RP) phase (adapted from [57]).

#### Ruddlesden-Popper (RP) series $(A_{n+1}B_nO_{3n+1}, n = 1, 2, and 3)$

The Ruddlesden-Popper (RP) phases have a general formula of  $A_{n+1}B_nO_{3n+1}$ , where A is a rare-earth, B is a transition metal and with  $n = 1, 2, 3, \infty$  [58]. The layered crystal structure of the RP phases, (AO)(ABO<sub>3</sub>)<sub>n</sub>, is shown in Figure 7c (for n=1). It consists of (ABO<sub>3</sub>)<sub>n</sub> perovskite block inter-grown between AO rock-salt layers along the c-axis direction. This structure exhibits interstitial oxygens within the AO layers with maintaining stability. The ability of the oxygen excess to move within the structure is driving the ionic conductivity of these materials [59]. In addition, this over-stoichiometry behavior can induce partial oxidation of the B cation. This mixed valence of the material can explain the material electronic conductivity. The mixed ionic and electronic conduction coupled with the ability to accommodate oxygen excess make them suitable candidates as electrode material for electrolysis operation.

Among the different components, the first-order (n = 1) rare-earth nickelates  $Ln_2NiO_{4+\delta}(Ln)$ = La, Pr, Nd) has been widely studied over the last few years [60-64]. These materials exhibit a sufficient electronic conductivity at the SOCS operating temperature (40-100 S cm<sup>-1</sup> at 700 °C [65]). Besides, they offer excellent oxygen transport and oxygen exchange properties. Indeed, Boehm et al. [65] have measured the value of the oxygen diffusion (D\*) and surface exchange (k\*) coefficients of these nickelates over a wide range of temperatures. It has been shown that the D\* and k\* coefficients of the  $Ln_2NiO_{4+\delta}$  (Ln = La, Pr) are higher than those of the typical LSCF electrode [65]. The highest value has been reached for the Pr-rich  $Pr_2NiO_{4+\delta}$ compound with  $D^* = 9 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  and  $k^* = 1 \times 10^{-6} \text{ cm s}^{-1}$  at 700 °C. Moreover, it has been reported that the electrical conductivity of these materials appears to be higher for the Pr-based component in a wide range of temperatures [65]. Besides, the conductivity properties can be improved by adding Pr content in  $Ln_2NiO_{4+\delta}$ . For example, for the composition LaPrNiO<sub>4+ $\delta$ </sub> and  $La_{0.5}Pr_{1.5}NiO_{4+\delta}$ , the electronic conductivity reaches a value close to the one of  $Pr_2NiO_{4+\delta}(\sigma_{el} =$ 110 S cm<sup>-1</sup> at 600 °C) [60]. The investigations on La<sub>2-x</sub>Pr<sub>x</sub>NiO<sub>4+ $\delta$ </sub> showed that materials made from praseodymium-rich solid solution offered better electrochemical performance. For example, the polarization resistance ( $R_{pol}$ ) at 600 °C and OCV for  $Pr_2NiO_{4+\delta}$  is 0.83  $\Omega$  cm<sup>2</sup> compared to  $3.33 \Omega$  cm<sup>2</sup> for La<sub>2</sub>NiO<sub>4+ $\delta$ </sub>[66]. Moreover, it was reported that, when the electrode was architecturally designed, a further decrease of R<sub>pol</sub> was measured, respectively from 0.42 to 0.08  $\Omega$  cm<sup>2</sup> for respectively La<sub>2</sub>NiO<sub>4+ $\delta$ </sub> and Pr<sub>2</sub>NiO<sub>4+ $\delta$ </sub>. However, it is observed in the literature that the LNO phase exhibits higher chemical stability than the PNO one [67,68]. Therefore, the use of this material as oxygen electrode for long-term operation in electrolysis mode seems promising. Indeed, under electrolysis current (i.e.  $i = -0.15 \text{ A cm}^{-2}$ , H<sub>2</sub>O/H<sub>2</sub> (80/10)), Kim, et al. [63] have reported lower degradation for the cell with LNO electrode than that with LSCF for about 160 h operation at 650 °C. At higher temperature, Mauvy et al. [69] also reported a rather low degradation rate of the cell based on LNO of 1.5 % kh<sup>-1</sup> at 800 °C after 500 h of operation in electrolysis mode (i.e.  $i = -0.5 \text{ A cm}^{-2}$ , H<sub>2</sub>O/H<sub>2</sub> (90/10) with a total gas flow of 24 Nml min<sup>-1</sup> cm<sup>-2</sup>). Despite these first studies, it is still require to improve the performances and to better understand the effects of operating conditions such as current or temperature on stability. On the other hand, the use of the praseodymium-rich phases remains limited due to the phase transformation. This point is discussed in more details in section 3.3. Nonetheless, one should note that  $La_{1-x}Pr_xNiO_{4+\delta}$  undergoes a decomposition under operation conditions to form higher-order Ruddlesden-Popper phases (n = 2 and 3). It appears that these secondary phases exhibit good electrochemical properties and electrical conductivity. For instance, Takahashi et al. [55] reported an electronic conductivity of 170 S cm<sup>-1</sup> for La<sub>4</sub>Ni<sub>3</sub>O<sub>10-δ</sub> compared

to 70 S cm<sup>-1</sup> for the first order phase  $La_2NiO_{4+\delta}$  (LNO). In addition to these high-order phases, it has been reported a substantial phase transformation into  $Pr_6O_{11}$  (i.e.  $PrO_{1.833}$ ) phase, which exhibits interesting electrocatalytic properties at low temperatures.

#### Praseodymium oxide, PrO<sub>1.833</sub> (i.e. Pr<sub>6</sub>O<sub>11</sub>)

The compound  $PrO_{1.833}$  belongs to the family of the praseodymium oxides between  $Pr_2O_3$ and  $PrO_2$ , and represented a well-defined series of phases with a large number of stoichiometries with the general formula  $Pr_nO_{2n-2}$  (n = 4, 5, 6, 7, 9, 10, 11, 12,  $\infty$ ) [49-50].  $PrO_2$ has a fluorite structure while  $Pr_2O_3$  has either a hexagonal phase (h- $Pr_2O_3$ ) or cubic phase (c- $Pr_2O_3$ ). The intermediate phases  $PrO_x$  (1.5 < x < 2) are oxygen deficient structures of the fluorite structure (i.e.  $PrO_{2-\delta}$ ). The transition between the various phases is widely controlled by the temperature as well as the oxygen partial pressure [70–73].



Figure 8: Differential thermal analysis on sample of Pr<sub>6</sub>O<sub>11</sub> (i.e. PrO<sub>1.833</sub>) [73].

For IT-SOCs application, the  $PrO_{1.833}$  (i.e.  $Pr_6O_{11}$ ) is nowadays attracting attention as an oxygen electrode thanks to its good transport properties and high electrocatalytic activity at low temperatures. Indeed, high oxygen diffusion (D\*) and oxygen exchange coefficients (k\*), respectively equal to  $3.4 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup> and  $5.4 \times 10^{-7}$  cm s<sup>-1</sup>, have been reported at 600°C [74].

Moreover, it has been shown that  $PrO_{1.833}$  exhibits a mixed ionic and electronic conductivity thanks to the presence of oxygen vacancies in its fluorite structure and the the two valence states +3/+4 of the praseodymium ion. However, it should be pointed out that its electrical conduction properties are rather low (i.e.  $\sigma < 4$  S cm<sup>-1</sup>) [74–77]. For instance, Thangadurai et al. [75] reported a low electrical conductivity ranging from 0.677 S cm<sup>-1</sup> to 1.4 S cm<sup>-1</sup> for temperatures between 400 to 850 °C for the PrO<sub>x</sub> system. Nevertheless, this relatively poor conductivity seems not to be limiting when used in the thin functional layer [78,79] or as catalysts infiltrated in electrode materials backbones [74,80-82]. For instance, Sharma et al. [78,83] reported a rather low polarization resistance of 0.02  $\Omega$  cm<sup>2</sup> at 600°C for a nano-structured Pr<sub>6</sub>O<sub>11</sub> in agreement with a value of 0.028  $\Omega$  cm<sup>2</sup> at 600°C reported by Nicollet et al. [74] by infiltrating PrO<sub>1.833</sub> into GDC backbone. Several other studies have also revealed a strong decrease in the polarization resistance by a factor of 3 to 10 for different composite electrodes when infiltrated by PrO<sub>1.833</sub> [80,81,84–86]. Moreover, high electrochemical performances have been measured on complete cells with PrO<sub>1.833</sub> electrodes. Dogdibegovic et al. [82] performed a series of measurements on metal-supported solid oxide cells using different oxygen electrode materials such as perovskite, nickelates, or praseodymium oxide. The highest power density peak (1.56 W cm<sup>-2</sup> at 700°C) has been achieved for the cell using an infiltrated electrode withn  $PrO_x$ catalyst. However, most of the results have been obtained for fuel cell operation (SOFC) [53, 59, 62, 65] but very few as oxygen electrodes for high-temperature electrolyzers (SOEC) [86,87]. Among them, a study conducted by Wang al. [87] revealed a very high efficiency (-1.5 A cm<sup>-2</sup> at 1.4 V) for a  $PrO_{1.833}$  electrode under electrolysis mode. Moreover,  $PrO_{1.833}$  can crystalize at low temperatures (around 450 °C) which will prevent possible reactivities due to high annealing temperatures. Some studies have mentioned a reactivity between CGO and PrO1.833 leading to the formation of Ce1-xPrxO2-6, (CPO) [80] phase or between 8YSZ and PrO<sub>1.833</sub> at 900 °C that produces Pr<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> [79]. Sharma et al. [78] reported good stability of the PrO<sub>1.833</sub> electrode deposited by electrostatic spray deposition (ESD) on GDC electrolyte at a lower temperature (~ 800°C). However, at 900°C, partial decomposition of PrO<sub>1.833</sub> led to the formation of Pr<sub>2</sub>O<sub>3</sub> and an unknown phase [78]. Besides, from the T/pO<sub>2</sub> dependency, it has been shown that the formation of these various PrO<sub>x</sub> phases can be also dependent on other parameters such as the electrode grain size or the experimental conditions. For instance, Sönstrom et al. [88] reported the phases transitions of nanostructured praseodymium oxide films with grain size of around 20 to 70 nm. The phases transitions are observed at lower temperatures than the above-mentioned articles. From HT-XRD analysis, the authors reported a complete transition from PrO<sub>1.833</sub> (i.e. Pr<sub>6</sub>O<sub>11</sub>) to PrO<sub>1.714</sub> (i.e. Pr<sub>7</sub>O<sub>12</sub>) at 430 °C. The Pr<sub>7</sub>O<sub>12</sub>

starts to decompose into unspecified  $PrO_x$  phases at 500 °C before to start another decomposition into  $Pr_2O_3$  at 650°C. Moreover, the manufacturing method, precursors, or heating and cooling rate could influence the phase transition [89–91]. Therefore, the stability of the  $PrO_{1.833}$  phase has to be investigated in more detail for SOCs application.

### 3. Degradation under operation

The stability of the SOCs under operation is a fundamental requirement for their commercialization. Therefore, the understanding of the origin of the performance degradation mechanisms remains a major issue. The most common observed degradation phenomena for SOCs are listed below:

- Microstructural evolution (agglomeration, pores/grain size evolution ...).
- Inter-diffusion and/or formation of isolating secondary phases between the cell components.
- Contamination and poisoning with impurities.
- Corrosion/oxidation of the metal interconnectors components of the stack.
- Mechanical deterioration (delamination, cracks ...).

These degradations result from the materials themselves as well as from the operating conditions (such as current, and temperature...). A brief review of the main observed mechanisms under SOEC mode at the cell level will be presented in this section.

#### 3.1 Electrolyte degradation

In the specific operation in the electrolysis mode, degradations related to the formation of porosities at grain boundaries and insulating phases near the interface to the oxygen electrode have been observed [47,92,93]. Knibbe et al. [93] showed the formation of holes/pores along the grain boundaries of the YSZ electrode in the region close to the LSM-YSZ electrode after operating under electrolysis mode at a high current density of 1-2 A cm<sup>-2</sup> (Figure 9). This phenomenon has been ascribed to the strong oxygen partial pressure gradient in the electrolyte during SOEC operation. In particular, an increase in series resistance has been observed at high current density due to an increase in oxygen accumulation at the interface. The nucleation and the growth of the porosities result in cracks that lead to the mechanical fragility of the electrolyte. The formation of porosities at the grain boundaries of the electrolyte has also been reported by Tietz et al. [47]. In this case, this behavior is followed by the formation of an

insulating phase such as SrZrO<sub>3</sub> at the YSZ/GDC interface.



Figure 9: Growth of the porosities in the YSZ electrolyte (a) Schematic representation of the evolution along the cell (b) TEM image of the porosity along the grain boundaries in the electrolyte close to the electrode interface [93].

On the other hand, the modification of the crystalline structure is among the other reason for the decrease in the electrolyte performance. Indeed, a modification of the crystalline structure of the YSZ from the cubic phase to the tetragonal or monoclinic phases has been observed [94,95]. Since the cubic zirconia doped with 8 mol. % yttrium oxide (8YSZ) has been shown to have the highest ionic conductivity, this phase change has led to a decrease in the ionic conductivity of the electrolyte.

## 3.2 Hydrogen/Fuel electrode degradation

For the Ni-YSZ hydrogen electrode, the main degradation is the nickel agglomeration and migration. The nickel agglomeration is related to an increase in the mean Ni particle size in the electrode. This coarsening of Ni grains induces degradation of the percolation path of the nickel phase and thus, leads to a decrease in cell performances. Coarsening of the Ni grains has been widely observed in both SOFC and SOEC modes [96–101]. However, polarization does not seem to play a major role in this phenomenon. For example, simulations performed by Hubert et al. [99] have shown that the degradation rate associated with Ni agglomeration was found to be similar in both operation modes (30 % in SOFC and 25 % in SOEC at 850 °C for 2000 h). Moreover, it has been demonstrated that temperature is the dominant factor behind the increase in grain size. In general terms, this degradation process is driven by an energy minimization by decreasing the surface to volume ratio of Ni particles. The Ni mass transport can be done via

surface diffusion or in the gas phase transport with Ni(OH)<sub>2</sub> volatile species. In the last case, the high amount of steam can favor the rate of the Ni particle growth. Conversely to Ni agglomeration, the Ni migration seems to be highly affected by the operating mode. Indeed, more severe Ni migration degradation has been observed in SOEC mode. This phenomenon is characterized by Ni redistribution in the volume of the electrode. In electrolysis mode, the Ni migrates from the electrode/electrolyte interface to the bulk of the electrode and leads to a significant Ni depletion at the interface. Therefore, these phenomena result in a decrease in the cell performance due to a contact loss and a decrease of the three-phase boundary (TPBs) at the electrode/electrolyte interface. From the operating conditions, both steam partial pressures [101] and polarization [102,103] would accelerate the degradation. However, to date, the underlying mechanism of Ni migration is still not fully understood.

On a larger scale, in a stack, additional degradation due to the presence of impurities can lead to decrease the cell performance. Silicon pollution from the glass sealant (Si(OH)<sub>4</sub>) is among the most encountered [101]. The corrosion of the glass seal induces the formation of the glassy phase SiO<sub>2</sub> which gathers near the Ni-YSZ/YSZ interface [ref]. The presence of these impurities at the reaction sites induces a loss in the cell performance.

## 3.3 Oxygen/Air electrode degradation

The main degradation issues of the oxygen electrode are delamination, physicochemical phenomena (reactivity, interdiffusion, and cation segregation), and microstructural modification. In the following we consider the different possible degradations first in pure electronic conductor such as LSM, then the ones of MIEC perovskite materials, understoichiometric in oxygen, and finally the ones of MIEC nickelate materials, over-stoichiometric in oxygen.

Delamination is a phenomenon that leads to the detachment of a part of the electrode at the interface with the electrolyte. In some cases, this degradation results from a high difference in the TEC coefficients between the different materials which induces mechanical stresses [85, 86]. However, in most cases, this phenomenon is triggered by an evolution of the material during operation. As described above, the formation of holes/pores appears on the YSZ during operation. These porosities accumulate and progress along the grain boundaries, resulting in cracks that expand towards the electrode [93,104,105]. Another mechanism has been proposed by Chen et al. [106] to explain the delamination observed in LSM-YSZ composite electrodes

during SOEC operation at -  $0.5 \text{ A cm}^{-2}$  at 800 °C. According to them, during operation in the electrolysis mode, an excess of O<sup>2-</sup> ions accumulates at the electrode/electrolyte interface (Figure 10) and incorporates into the LSM matrix. This phenomenon leads to local tensile strains at the electrode which decomposes into LSM nanoparticles and thus results in the detachment of the electrode.



Figure 10: Delamination of LSM electrode after aging (a) SEM image at the electrode/electrolyte interface of the delamination of LSM after aging at 800 °C under - 0.5 A cm<sup>-2</sup> (b) SEM image of the inner surface of the LSM electrode in contact with the electrode after aging (c) Schematic representation of the delamination mechanism proposed by Chen et al. [106].

For LSCF or LSC electrodes, the physicochemical phenomena that lead to degradation are quite numerous. The diffusion phenomena of the different elements of the oxygen electrode (La, Sr, Co...) towards the electrolyte can be at the origin of the formation of secondary phases such as La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>,  $\beta$ -Sc<sub>2</sub>Zr<sub>7</sub>O<sub>17</sub> [37]. The formation of these phases at the electrode/electrolyte interface induces an increase in the ohmic resistance of the cell because of their insulating properties. To prevent reactivity between the YSZ and the oxygen electrode, a dense barrier layer, usually ceria-based (such as GDC), is added between the electrode and the electrolyte. Despite this, SrZrO<sub>3</sub> appeared to form at the barrier layer/YSZ interface (Figure 11). The formation of this phase is believed to take place either during the sintering process [107] or during operation. Moreover, in addition to the insulating phases such as SrZrO<sub>3</sub> at the electrolyte interface the Sr migration and segregation lead to the formation of a SrO film at the surface of the electrode particles. The SrO phase can passivate the surface by blocking the oxygen exchange with the gas phase [45,108,109]. It has been observed a higher LSCF decomposition for the cell tested under electrolysis current compared to the fuel cell mode [45].

This behavior is still not precisely understood and could be related to the depletion of the oxygen vacancies in LSCF in anodic polarization.



Figure 11: SEM and EDX images of the electrode/electrolyte interface for an LSCF/GDC/YSZ/Ni-YSZ cell (a) pristine cell, (b) cell aged in SOFC mode (c) cell aged in SOEC mode. The Sr is highlighted in red. The blue arrow represents the Co particles [45].

Microstructural modification can also lead to a decrease of the performance of the cell. For instance, Tietz et al. [47] observed an increase in the grain size of the LSCF electrode after aging in electrolysis mode at 778°C. This local increase in the size leads to a decrease in the catalytic activity of the electrode and thus a decrease in the cell performance. However, it should be pointed out that this size evolution is a minor degradation and is not detrimental to the cell contrary to a delamination.

Finally, at the stack level, impurities can also contaminate the cell and lead to a degradation of the performance. Generally, this contamination comes from the chromium-based interconnectors [110,111]. It has been reported the presence of the insulating phase  $Cr_2O_3$  at the surface of the electrode or even a reactivity with the Sr (SrCrO<sub>4</sub>) for the Sr-rich based electrode.

#### For rare-earth nickelates $Ln_2NiO_{4+\delta}$ (Ln = La, Pr)

Regarding lanthanum nickelates  $La_{2-x}Pr_xNiO_{4+\delta}$  (O  $\leq x \leq 2$ ), it has been shown that compounds rich in Pr are more prone to decomposition at intermediate temperature (700 °C) [60,67]. For instance, Montenegro-Hernández, et al. [67] studied the stability of  $Ln_2NiO_{4+\delta}$  (La, Pr) powders at 700 °C and 900 °C. It has been shown that La<sub>2</sub>NiO<sub>4+ $\delta$ </sub> (LNO) remains chemically stable while the  $Pr_2NiO_{4+\delta}$  (PNO) decomposes into  $Pr_6O_{11}$  and  $Pr_4Ni_3O_{10+\delta}$  after annealing for only 24 h at 700 °C. The same observations have been reported by Vibhu et al. [68] for La<sub>2</sub>.  $_{x}Pr_{x}NiO_{4+\delta}$  (x = 0, 0.5, 1, 1.5, 2) powders after aging during 1 month at 700°C. According to the authors, the compounds with the stoichiometry x = 0 and x = 0.5 are stable while the Pr-rich phases (x  $\geq$  1) decomposed into (La,Pr)NiO<sub>3- $\delta$ </sub>, (La,Pr)<sub>4</sub>Ni<sub>3</sub>O<sub>10+ $\delta$ </sub>, and Pr<sub>6</sub>O<sub>11</sub>. Furthermore, by advanced structural characterizations, Khamidy et al. [112] investigated the impact of temperature and polarization on this decomposition for the stoichiometry LaPrNiO<sub>4+ $\delta$ </sub> (LPNO, x =1). In this study, the authors compared the evolution of LPNO after thermal aging (700  $^{\circ}$ C, 1000 h) and after a long-term test in fuel and electrolysis modes (at 700 °C, 960 h and  $\pm$  300 mA cm<sup>-2</sup>) with the pristine cell. First, this work have revealed the presence of minor decomposition phases such as (La,Pr)<sub>3</sub>Ni<sub>2</sub>O<sub>7-δ</sub> and Pr<sub>6</sub>O<sub>11</sub> (i.e. PrO<sub>1.833</sub>) in the pristine cell (Figure 12a). Then, an acceleration of the decomposition has been reported when the anodic polarization was applied leading to the appearance of another decomposition product  $(La,Pr)_4Ni_3O_{10-\delta}$  and a high increase of the quantity of  $Pr_6O_{11}$  in the bulk of the electrode (Figure 12c). However, in this case, these decompositions do not seem to affect the performance of the cells. Indeed, the polarization resistance values before and after aging in SOEC conditions have not changed. These observations were explained by the electrochemically active character of these secondary phases as discussed in the previous section. However, it should be noted that under cathodic polarization, a significant increase in polarization resistance was measured, and this was attributed to the strong delamination of the LPNO electrode at the interface with the electrolyte, as confirmed by SEM images. This observation was not seen when operating in electrolysis mode



Figure 12: XRD-maps of the local distribution of the phases detected in (a) Pristine cell (LPNO electrode deposited on GDC electrolyte) (b) Thermally aged cell (700 °C, 1000 h) and (c) Aged cell in electrolysis mode (700 °C, 960 h at i = - 0.3 A cm<sup>-2</sup>). The color brightness indicates the increase in local intensity of the corresponding compound [112].

Furthermore, La-Pr nickelates exhibited good stability with 8YSZ and GDC electrolyte materials at 700 °C [66,67]. However, chemical reactivities have been observed at the higher temperatures usually required for sintering. For instance, Yaremchenko et al. [64] showed the formation of the insulating phase La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and NiO on mixed LNO/8YSZ powders calcined at 1050 °C for 40 h. Similarly, the LNO/CGO mixture also lead to the formation of NiO. Moreover, for LNO/CGO, the authors also reported a partial incorporation of lanthanum in ceria lattice leading to the formation of Ce(La)O<sub>2-δ</sub>. According to them, despite the ionic conductivity of the latter phase, this decomposition induces a decrease in the electrochemical performance. Besides, Montenegro et al. [67] reported the appearance of insulating phases at even lower temperature (i.e. 900 °C). Although, according to the authors, the preparation method plays an important role since the reactivity seems higher with the batch prepared by the HTMA method which leads to the formation of smaller particles.

#### 4. Conclusion and methodology of this thesis work

As previously discussed, the choice of MIEC materials is favorable for the SOEC operation since the oxygen evolution reaction is expected to be delocalized on the whole gas/electrode interface rather than only at the TPB points in the case of a pure electronic conductor such as LSM. The classical MIEC material is the cobalt-based perovskite,  $La_{1-x}Sr_xCo_{y-1}Fe_yO_{3-\delta}$  (LSCF).

This oxygen-deficient perovskite presents good ionic and electronic conductivity as well as a high oxygen surface exchange rate. However, LSCF suffers from large degradation rates due to chemical decomposition at high operating and reactivity with electrolyte. These degradations induce significant loss in SOCs performances, especially when they are operated in SOEC mode. It has been shown that for this electrode material, the degradation rate is higher under electrolysis mode that could be due to the depletion of oxygen vacancies in LSCF and consequently could drive the Sr segregation. In this context, rare earth nickelates Ln<sub>2</sub>NiO<sub>4+8</sub> (Ln = La, Pr, Nd) appear as good alternative oxygen electrode materials in SOEC mode thanks to their over-stoichiometric property which accommodates interstitial oxygens in excess. From several studies, it has been shown that materials made from a solid solution rich in praseodymium offers better electrochemical performances. However, these materials would be more prone to a phase decomposition. In particular, a decomposition towards the PrO<sub>1.833</sub> (i.e.  $Pr_6O_{11}$ ) phase has been detected by previous studies. Recent attention has been paid to  $PrO_{1.833}$  as an oxygen electrode for solid oxide cells, however, the stability of this material as well as its operating mechanisms under SOEC still need to be understood.

Thus, based on this literature review, two approaches are considered in this thesis work. The first one consists to study the compound  $La_2NiO_{4+\delta}$  (LNO) which presents good chemical stability over a wide range of temperatures and oxygen partial pressures combined with a high MIEC conductivity as well as a fast oxygen reduction reaction kinetics. A coupled experimental and modeling approach will be proposed to study the reaction mechanisms of this material which would then serve as a prerequisite for microstructural optimization. The other approach consists in studying the electrochemical properties of the innovative nanostructured  $PrO_{1.833}$ , and to conduct an in-depth durability study in complete SOEC cells. Through fine structural and microstructural characterizations performed on aged samples and pristine cells, the impact of the microstructure, operating temperature and anodic polarization will be discussed.

## 5. References

- Irvin et al., Evolution of the electrochemical interface in high-temperature fuel cells and electrolysers | Nature Energy, (n.d.). https://www.nature.com/articles/nenergy201514 (accessed November 5, 2020).
- G. Leonzio, Power to Gas Systems Integrated with Anaerobic Digesters and Gasification Systems, Waste Biomass Valor. 12 (2021) 29–64. https://doi.org/10.1007/s12649-019-00914-4.
- [3] S.D. Ebbesen, M. Mogensen, Electrolysis of carbon dioxide in Solid Oxide Electrolysis
  Cells, J. Power Sources. 193 (2009) 349–358. https://doi.org/10.1016/j.jpowsour.2009.02.093.
- [4] W. Dönitz, E. Erdle, High-temperature electrolysis of water vapor—status of development and perspectives for application, International Journal of Hydrogen Energy. 10 (1985) 291–295. https://doi.org/10.1016/0360-3199(85)90181-8.
- [5] M. Yoshikawa, T. Yamamoto, K. Yasumoto, Y. Mugikura, Degradation Analysis of SOFC Stack Performance-Durability Test and Verification of Improved SOFCs-, ECS Trans. 75 (2017) 23. https://doi.org/10.1149/07542.0023ecst.
- [6] K. Kendall, Progress in Microtubular Solid Oxide Fuel Cells, International Journal of Applied Ceramic Technology. 7 (2010) 1–9. https://doi.org/10.1111/j.1744-7402.2008.02350.x.
- [7] T. Suzuki, Z. Hasan, Y. Funahashi, T. Yamaguchi, Y. Fujishiro, M. Awano, Impact of Anode Microstructure on Solid Oxide Fuel Cells, Science. 325 (2009) 852–855. https://doi.org/10.1126/science.1176404.
- [8] J. Schefold, A. Brisse, H. Poepke, 23,000 h steam electrolysis with an electrolyte supported solid oxide cell, International Journal of Hydrogen Energy. 42 (2017) 13415– 13426. https://doi.org/10.1016/j.ijhydene.2017.01.072.
- [9] A. Azim Jais, S.A. Muhammed Ali, M. Anwar, M. Rao Somalu, A. Muchtar, W.N.R. Wan Isahak, C. Yong Tan, R. Singh, N.P. Brandon, Enhanced ionic conductivity of scandia-ceria-stabilized-zirconia (10Sc1CeSZ) electrolyte synthesized by the microwave-assisted glycine nitrate process, Ceramics International. 43 (2017) 8119– 8125. https://doi.org/10.1016/j.ceramint.2017.03.135.
- [10] A. Hauch, Solid Oxide Electrolysis Cells: Performance and Durability, Risø National Laboratory, Roskilde, Denmark, 2008.
- [11] S.C. Singhal, K. Kendall, High-temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications, Elsevier, 2003.

- [12] V.V. Kharton, F.M.B. Marques, A. Atkinson, Transport properties of solid oxide electrolyte ceramics: a brief review, Solid State Ionics. 174 (2004) 135–149. https://doi.org/10.1016/j.ssi.2004.06.015.
- [13] A. Nakamura, J.B. Wagner, Defect Structure, Ionic Conductivity, and Diffusion in Yttria Stabilized Zirconia and Related Oxide Electrolytes with Fluorite Structure, J. Electrochem. Soc. 133 (1986) 1542. https://doi.org/10.1149/1.2108965.
- [14] A. Weber, E. Ivers-Tiffée, Materials and concepts for solid oxide fuel cells (SOFCs) in stationary and mobile applications, Journal of Power Sources. 127 (2004) 273–283. https://doi.org/10.1016/j.jpowsour.2003.09.024.
- [15] E. Lay-Grindler, J. Laurencin, G. Delette, J. Aicart, M. Petitjean, L. Dessemond, Micro modelling of solid oxide electrolysis cell: From performance to durability, International Journal of Hydrogen Energy. 38 (2013) 6917–6929. https://doi.org/10.1016/j.ijhydene.2013.03.162.
- J.W. Fergus, Electrolytes for solid oxide fuel cells, Journal of Power Sources. 162 (2006) 30–40. https://doi.org/10.1016/j.jpowsour.2006.062.
- [17] J.A. Kilner, R.J. Brook, A study of oxygen ion conductivity in doped non-stoichiometric oxides, Solid State Ionics. 6 (1982) 237–252. https://doi.org/10.1016/0167-2738(82)90045-5.
- [18] O. Yamamoto, Y. Arachi, H. Sakai, Y. Takeda, N. Imanishi, Y. Mizutani, M. Kawai, Y. Nakamura, Zirconia based oxide ion conductors for solid oxide fuel cells, Ionics. 4 (1998) 403–408. https://doi.org/10.1007/BF02375884.
- [19] S.M. Haile, Fuel cell materials and components☆☆☆The Golden Jubilee Issue— Selected topics in Materials Science and Engineering: Past, Present and Future, edited by S. Suresh., Acta Materialia. 51 (2003) 5981–6000. https://doi.org/10.1016/j.actamat.2003.08.004.
- [20] S.P.S. Badwal, F.T. Ciacchi, D. Milosevic, Scandia–zirconia electrolytes for intermediate temperature solid oxide fuel cell operation, Solid State Ionics. 136–137 (2000) 91–99. https://doi.org/10.1016/S0167-2738(00)00356-8.
- [21] H. Shi, C. Su, R. Ran, J. Cao, Z. Shao, Electrolyte materials for intermediate-temperature solid oxide fuel cells, Progress in Natural Science: Materials International. 30 (2020) 764–774. https://doi.org/10.1016/j.pnsc.2020.09.003.
- [22] B.C.H. Steele, Appraisal of  $Ce_{1-y}Gd_yO_{2-y/2}$  electrolytes for IT-SOFC operation at 500°C, Solid State Ionics. 129 (2000) 95–110. https://doi.org/10.1016/S0167-2738(99)00319-7.
- [23] B.C.H. Steele\*, Materials for IT-SOFC stacks: 35 years R&D: the inevitability of gradualness?, Solid State Ionics. 134 (2000) 3–20. https://doi.org/10.1016/S0167-2738(00)00709-8.

- [24] N. Grunbaum, L. Dessemond, J. Fouletier, F. Prado, A. Caneiro, Electrode reaction of  $Sr_{1-x}La_xCo_{0.8}Fe_{0.2}O_{3-\delta}$  with x=0.1 and 0.6 on  $Ce_{0.9}Gd_{0.1}O_{1.95}$  at  $600 \le T \le 800$  °C, Solid State Ionics. 177 (2006) 907–913. https://doi.org/10.1016/j.ssi.2006.02.009.
- [25] G. Constantin, C. Rossignol, J.-P. Barnes, E. Djurado, Interface stability of thin, dense CGO film coating on YSZ for solid oxide fuel cells, Solid State Ionics. 235 (2013) 36– 41. https://doi.org/10.1016/j.ssi.2013.01.015.
- [26] H.J. Ko, J. Myung, J.-H. Lee, S.-H. Hyun, J.S. Chung, Synthesis and evaluation of  $(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_3$  (LSCF) $-Y_{0.08}Zr_{0.92}O_{1.96}$  (YSZ) $-Gd_{0.1}Ce_{0.9}O_{2-\delta}$  (GDC) dual composite SOFC cathodes for high performance and durability, International Journal of Hydrogen Energy. 37 (2012) 17209–17216. https://doi.org/10.1016/j.ijhydene.2012.08.099.
- [27] J.W. Yan, Z.G. Lu, Y. Jiang, Y.L. Dong, C.Y. Yu, W.Z. Li, Fabrication and testing of a doped lanthanum gallate electrolyte thin-film solid oxide fuel cell, J. Electrochem. Soc. 149 (2002) A1132. https://doi.org/10.1149/1.1496485.
- [28] H. Kim, C. Lu, W.L. Worrell, J.M. Vohs, R.J. Gorte, Cu-Ni cermet anodes for direct oxidation of methane in solid-oxide fuel cells, J. Electrochem. Soc. 149 (2002) A247. https://doi.org/10.1149/1.1445170.
- [29] X.-F. Ye, S.R. Wang, J. Zhou, F.R. Zeng, H.W. Nie, T.L. Wen, Assessment of the performance of Ni-yttria-stabilized zirconia anodes in anode-supported Solid Oxide Fuel Cells operating on H2–CO syngas fuels, J. Power Sources. 195 (2010) 7264–7267. https://doi.org/10.1016/j.jpowsour.2010.04.016.
- [30] S.P. Jiang, S.H. Chan, A review of anode materials development in solid oxide fuel cells, Journal of Materials Science. 39 (2004) 4405–4439. https://doi.org/10.1023/B:JMSC.0000034135.52164.6b.
- [31] C. Sun, R. Hui, J. Roller, Cathode materials for solid oxide fuel cells: a review, J Solid State Electrochem. 14 (2010) 1125–1144. https://doi.org/10.1007/s10008-009-0932-0.
- [32] J. Fleig, H.L. Tuller, J. Maier, Electrodes and electrolytes in micro-SOFCs: a discussion of geometrical constraints, Solid State Ionics. 174 (2004) 261–270. https://doi.org/10.1016/j.ssi.2004.07.035.
- [33] S.B. Adler, Factors governing oxygen reduction in solid oxide fuel cell cathodes, Chem. Rev. 104 (2004) 4791–4844. https://doi.org/10.1021/cr0207240.
- [34] A. Hauch, S. Dalgaard Ebbesen, S. Højgaard Jensen, M. Mogensen, Highly efficient high temperature electrolysis, Journal of Materials Chemistry. 18 (2008) 2331–2340. https://doi.org/10.1039/B718822F.

- [35] S.P. Jiang, Development of lanthanum strontium manganite perovskite cathode materials of solid oxide fuel cells: a review, J Mater Sci. 43 (2008) 6799–6833. https://doi.org/10.1007/s10853-008-2966-6.
- [36] M. Keane, M.K. Mahapatra, A. Verma, P. Singh, LSM–YSZ interactions and anode delamination in solid oxide electrolysis cells, International Journal of Hydrogen Energy. 37 (2012) 16776–16785. https://doi.org/10.1016/j.ijhydene.2012.08.104.
- [37] A. Mahata, P. Datta, R.N. Basu, Microstructural and chemical changes after high temperature electrolysis in solid oxide electrolysis cell, Journal of Alloys and Compounds. 627 (2015) 244–250. https://doi.org/10.1016/j.jallcom.2014.11.230.
- [38] W. Wang, Y. Huang, S. Jung, J.M. Vohs, R.J. Gorte, A Comparison of LSM, LSF, and LSCo for solid oxide electrolyzer anodes, J. Electrochem. Soc. 153 (2006) A2066. https://doi.org/10.1149/1.2345583.
- [39] Q. Liu, C. Yang, X. Dong, F. Chen, Perovskite Sr<sub>2</sub>Fe<sub>1.5</sub>Mo<sub>0.5</sub>O<sub>6-δ</sub> as electrode materials for symmetrical solid oxide electrolysis cells, International Journal of Hydrogen Energy. 35 (2010) 10039–10044. https://doi.org/10.1016/j.ijhydene.2010.08.016.
- [40] D. Marinha, L. Dessemond, E. Djurado, Comparison of electrochemical performances of electrosprayed LSCF cathode films for IT-SOFCs for different morphologies and cobalt contents, ECS Trans. 35 (2011) 2283. https://doi.org/10.1149/1.3570224.
- [41] H. Ullmann, N. Trofimenko, F. Tietz, D. Stöver, A. Ahmad-Khanlou, Correlation between thermal expansion and oxide ion transport in mixed conducting perovskite-type oxides for SOFC cathodes, Solid State Ion. 138 (2000) 79–90. https://doi.org/10.1016/S0167-2738(00)00770-0.
- [42] A. Petric, P. Huang, F. Tietz, Evaluation of La–Sr–Co–Fe–O perovskites for solid oxide fuel cells and gas separation membranes, Solid State Ionics. 135 (2000) 719–725. https://doi.org/10.1016/S0167-2738(00)00394-5.
- [43] L.-W. Tai, M.M. Nasrallah, H.U. Anderson, D.M. Sparlin, S.R. Sehlin, Structure and electrical properties of La<sub>1-x</sub>Sr<sub>x</sub>Co<sub>1-y</sub>FeyO<sub>3</sub>. Part 2. The system La<sub>1-x</sub>Sr<sub>x</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub>, Solid State Ionics. 76 (1995) 273–283. https://doi.org/10.1016/0167-2738(94)00245-N.
- [44] C.E. Frey, Q. Fang, D. Sebold, L. Blum, N.H. Menzler, A Detailed Post Mortem Analysis of Solid Oxide Electrolyzer Cells after Long-Term Stack Operation, J. Electrochem. Soc. 165 (2018) F357. https://doi.org/10.1149/2.0961805jes.
- [45] J. Laurencin, M. Hubert, D.F. Sanchez, S. Pylypko, M. Morales, A. Morata, B. Morel, D. Montinaro, F. Lefebvre-Joud, E. Siebert, Degradation mechanism of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub>/Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2-δ</sub> composite electrode operated under solid oxide electrolysis and fuel cell conditions, Electrochimica Acta. 241 (2017) 459–476. https://doi.org/10.1016/j.electacta.2017.05.011.

- [46] D. The, S. Grieshammer, M. Schroeder, M. Martin, M. Al Daroukh, F. Tietz, J. Schefold, A. Brisse, Microstructural comparison of solid oxide electrolyser cells operated for 6100 h and 9000 h, J. Power Sources. 275 (2015) 901–911. https://doi.org/10.1016/j.jpowsour.2014.10.188.
- [47] F. Tietz, D. Sebold, A. Brisse, J. Schefold, Degradation phenomena in a solid oxide electrolysis cell after 9000 h of operation, J. Power Sources. 223 (2013) 129–135. https://doi.org/10.1016/j.jpowsour.2012.09.061.
- [48] Z. Pan, Q. Liu, M. Ni, R. Lyu, P. Li, S.H. Chan, Activation and failure mechanism of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> air electrode in solid oxide electrolyzer cells under high-current electrolysis, International Journal of Hydrogen Energy. 43 (2018) 5437–5450. https://doi.org/10.1016/j.ijhydene.2018.01.181.
- [49] O. Celikbilek, C.-A. Thieu, F. Agnese, E. Calì, C. Lenser, N.H. Menzler, J.-W. Son, S.J. Skinner, E. Djurado, Enhanced catalytic activity of nanostructured, A-site deficient (La<sub>0.7</sub>Sr<sub>0.3</sub>)<sub>0.95</sub>(Co<sub>0.2</sub>Fe<sub>0.8</sub>)O<sub>3-δ</sub> for SOFC cathodes, J. Mater. Chem. A. 7 (2019) 25102–25111. https://doi.org/10.1039/C9TA07697B.
- [50] F. Tietz, Thermal expansion of SOFC materials, Ionics. 5 (1999) 129–139. https://doi.org/10.1007/BF02375916.
- [51] M. Mori, N.M. Sammes, E. Suda, Y. Takeda, Application of La<sub>0.6</sub>AE<sub>0.4</sub>MnO<sub>3</sub> (AE=Ca and Sr) to electric current collectors in high-temperature solid oxide fuel cells, Solid State Ionics. 164 (2003) 1–15. https://doi.org/10.1016/S0167-2738(03)00303-5.
- [52] Z. Naiqing, S. Kening, Z. Derui, J. Dechang, Study on Properties of LSGM Electrolyte Made by Tape Casting Method and Applications in SOFC, Journal of Rare Earths. 24 (2006) 90–92. https://doi.org/10.1016/S1002-0721(07)60331-7.
- [53] X.-D. Zhou, J.W. Templeton, Z. Nie, H. Chen, J.W. Stevenson, L.R. Pederson, Electrochemical performance and stability of the cathode for solid oxide fuel cells: V. high performance and stable Pr<sub>2</sub>NiO<sub>4</sub> as the cathode for solid oxide fuel cells, Electrochimica Acta. 71 (2012) 44–49. https://doi.org/10.1016/j.electacta.2012.03.067.
- [54] A. Flura, S. Dru, C. Nicollet, V. Vibhu, S. Fourcade, E. Lebraud, A. Rougier, J.-M. Bassat, J.-C. Grenier, Chemical and structural changes in Ln<sub>2</sub>NiO<sub>4</sub> (Ln=La, Pr or Nd) lanthanide nickelates as a function of oxygen partial pressure at high temperature, J. Solid State Chem. 228 (2015) 189–198. https://doi.org/10.1016/j.jssc.2015.04.029.
- [55] S. Takahashi, S. Nishimoto, M. Matsuda, M. Miyake, Electrode Properties of the Ruddlesden–Popper Series, La<sub>n+1</sub>Ni<sub>n</sub>O<sub>3n+1</sub> (n=1, 2, and 3), as intermediate-temperature solid oxide fuel cells, Journal of the American Ceramic Society. 93 (2010) 2329–2333. https://doi.org/10.1111/j.1551-2916.2010.03743.x.

- [56] G. Amow, S.J. Skinner, Recent developments in Ruddlesden–Popper nickelate systems for solid oxide fuel cell cathodes, J Solid State Electrochem. 10 (2006) 538–546. https://doi.org/10.1007/s10008-006-0127-x.
- [57] B. Aissa, A. Ali, F. El-Mellouhi, Oxide and organic–inorganic halide perovskites with plasmonics for optoelectronic and energy applications: a contributive review, Catalysts. 11 (2021) 1057. https://doi.org/10.3390/catal11091057.
- [58] M. Greenblatt, Ruddlesden-Popper Ln<sub>n+1</sub>Ni<sub>n</sub>O<sub>3n+1</sub> nickelates: structure and properties, Current Opinion in Solid State and Materials Science. 2 (1997) 174–183. https://doi.org/10.1016/S1359-0286(97)80062-9.
- [59] M. Ceretti, O. Wahyudi, A. Cousson, A. Villesuzanne, M. Meven, B. Pedersen, J.M. Bassat, W. Paulus, Low temperature oxygen diffusion mechanisms in Nd2NiO4+δ and Pr<sub>2</sub>NiO<sub>4+δ</sub> via large anharmonic displacements, explored by single crystal neutron diffraction, J. Mater. Chem. A. 3 (2015) 21140–21148. https://doi.org/10.1039/C5TA05767A.
- [60] V. Vibhu, A. Rougier, C. Nicollet, A. Flura, J.-C. Grenier, J.-M. Bassat, La<sub>2-x</sub>Pr<sub>x</sub>NiO<sub>4+δ</sub> as suitable cathodes for metal supported SOFCs, Solid State Ionics. 278 (2015) 32–37. https://doi.org/10.1016/j.ssi.2015.05.005.
- [61] R. K. Sharma, M. Burriel, L. Dessemond, J. M. Bassat, E. Djurado, Design of interfaces in efficient Ln<sub>2</sub>NiO<sub>4+δ</sub> (Ln = La, Pr) cathodes for SOFC applications, J. Mater. Chem. A. 4 (2016) 12451–12462. https://doi.org/10.1039/C6TA04845E.
- [62] A. Montenegro-Hernández, L. Mogni, A. Caneiro, Microstructure and reactivity effects on the performance of Nd2NiO4+δ oxygen electrode on Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> electrolyte, International Journal of Hydrogen Energy. 37 (2012) 18290–18301. https://doi.org/10.1016/j.ijhydene.2012.09.071.
- [63] S.J. Kim, K.J. Kim, A.M. Dayaghi, G.M. Choi, Polarization and stability of La2NiO4+δ in comparison with La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> as air electrode of solid oxide electrolysis cell, Int. J. Hydrog. Energy. 41 (2016) 14498–14506. https://doi.org/10.1016/j.ijhydene.2016.05.284.
- [64] A. Yaremchenko, B.I. Arias-Serrano, K. Zakharchuk, J.R. Frade, Perovskite-like LaNiO <sub>3-δ</sub> as oxygen electrode material for solid oxide electrolysis cells, ECS Trans. 91 (2019) 2399–2408. https://doi.org/10.1149/09101.2399ecst.
- [65] E. Boehm, J.-M. Bassat, P. Dordor, F. Mauvy, J.-C. Grenier, Ph. Stevens, Oxygen diffusion and transport properties in non-stoichiometric Ln<sub>2-x</sub>NiO<sub>4+δ</sub> oxides, Solid State Ionics. 176 (2005) 2717–2725. https://doi.org/10.1016/j.ssi.2005.06.033.
- [66] R.K. Sharma, S.-K. Cheah, M. Burriel, L. Dessemond, J.-M. Bassat, E. Djurado, Design of La<sub>2-x</sub>Pr<sub>x</sub>NiO<sub>4+δ</sub> SOFC cathodes: a compromise between electrochemical performance and thermodynamic stability, J. Mater. Chem. A. 5 (2017) 1120–1132.

- [67] A. Montenegro-Hernández, J. Vega-Castillo, L. Mogni, A. Caneiro, Thermal stability of Ln<sub>2</sub>NiO<sub>4+δ</sub>(Ln: La, Pr, Nd) and their chemical compatibility with YSZ and CGO solid electrolytes, International Journal of Hydrogen Energy. 36 (2011) 15704–15714. https://doi.org/10.1016/j.ijhydene.2011.08.105.
- [68] V. Vibhu, J.-M. Bassat, A. Flura, C. Nicollet, J.-C. Grenier, A. Rougier, Influence of La/Pr ratio on the ageing properties of La<sub>2-x</sub>Pr<sub>x</sub>NiO<sub>4+δ</sub> as cathodes in IT-SOFCs, ECS Trans. 68 (2015) 825.
- [69] F. Mauvy, J.-C. Grenier, J. Vulliet, J.-M. Bassat, A. Rougier, Lanthanum nickelate as an efficient oxygen electrode for solid oxide electrolysis cell, Fuel Cells. 22 (2022) 48– 56. https://doi.org/10.1002/fuce.202200013.
- [70] B.G. Hyde, D.J.M. Bevan, L. Eyring, On the Praseodymium+Oxygen System, Phil. Trans. R. Soc. Lond. A. 259 (1966) 583–614. https://doi.org/10.1098/rsta.1966.0025.
- [71] D.A. Burnham, L. Eyring, Phase transformations in the praseodymium oxide-oxygen system: high-temperature x-ray diffraction studies, J. Phys. Chem. 72 (1968) 4415– 4424. https://doi.org/10.1021/j100859a010.
- [72] A. Abrutis, M. Lukosius, Z. Saltyte, R. Galvelis, P.K. Baumann, M. Schumacher, J. Lindner, Chemical vapour deposition of praseodymium oxide films on silicon: influence of temperature and oxygen pressure, Thin Solid Films. 516 (2008) 4758–4764. https://doi.org/10.1016/j.tsf.2007.08.097.
- [73] A. Netz, W.F. Chu, V. Thangadurai, R.A. Huggins, W. Weppner, Investigations of praseodymium oxide electrodes in lithium concentration cells, Ionics. 5 (1999) 426– 433. https://doi.org/10.1007/BF02376009.
- [74] C. Nicollet, A. Flura, V. Vibhu, A. Rougier, J.-M. Bassat, J.-C. Grenier, An innovative efficient oxygen electrode for SOFC: Pr<sub>6</sub>O<sub>11</sub> infiltrated into Gd-doped ceria backbone, Int. J. Hydrog. Energy. 41 (2016) 15538–15544. https://doi.org/10.1016/j.ijhydene.2016.04.024.
- [75] V. Thangadurai, R.A. Huggins, W. Weppner, Mixed ionic-electronic conductivity in phases in the praseodymium oxide system, J Solid State Electrochem. 5 (2001) 531– 537.
- [76] G.V.S. Rao, S. Ramdas, P.N. Mehrotra, C.N.R. Rao, Electrical Transport in Rare-Earth Oxides, J. Solid State Chem. 2 (1970) 377–384, https://doi.org/10.1016/0022-4596(70)90095-2.
- [77] M. Shamshi Hassan, M. Shaheer Akhtar, K.-B. Shim, O.-B. Yang, Morphological and electrochemical properties of crystalline praseodymium oxide nanorods, Nanoscale Res Lett. 5 (2010) 735–740. https://doi.org/10.1007/s11671-010-9547-8.

- [78] R.K. Sharma, N.I. Khamidy, L. Rapenne, F. Charlot, H. Moussaoui, J. Laurencin, E. Djurado, Highly efficient architectured Pr<sub>6</sub>O<sub>11</sub> oxygen electrode for solid oxide fuel cell, J. Power Sources. 419 (2019) 171–180.
- [79] H. Taguchi, R. Chiba, T. Komatsu, H. Orui, K. Watanabe, K. Hayashi, LNF SOFC cathodes with active layer using Pr<sub>6</sub>O<sub>11</sub> or Pr-doped CeO<sub>2</sub>, J. Power Sources. 241 (2013) 768–775. https://doi.org/10.1016/j.jpowsour.2013.04.141.
- [80] M. Khoshkalam, M.A. Faghihi-Sani, X. Tong, M. Chen, P.V. Hendriksen, Enhanced Activity of Pr<sub>6</sub>O<sub>11</sub> and CuO Infiltrated Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2</sub> Based Composite Oxygen Electrodes, J. Electrochem. Soc. 167 (2020) 024505. https://doi.org/10.1149/1945-7111/ab6821.
- [81] R. Chiba, H. Aono, K. Kato, An SOFC cathode infiltrated with Pr<sub>6</sub>O<sub>11</sub>, ECS Trans. 57 (2013) 1831–1840. https://doi.org/DOI 10.1149/05701.1831ecst.
- [82] E. Dogdibegovic, R. Wang, G.Y. Lau, M.C. Tucker, High performance metal-supported solid oxide fuel cells with infiltrated electrodes, J. Power Sources. 410–411 (2019) 91– 98. https://doi.org/10.1016/j.jpowsour.2018.11.004.
- [83] R.K. Sharma, E. Djurado, An efficient hierarchical nanostructured Pr<sub>6</sub>O<sub>11</sub> electrode for solid oxide fuel cells, J. Mater. Chem. A. 6 (2018) 10787–10802. https://doi.org/10.1039/C8TA00190A.
- [84] J. Grimes, S.A. Barnett, Effect of pressurization on solid oxide cell oxygen electrodes: the role of PrOx nanoparticle infiltration, J. Electrochem. Soc. 168 (2021) 084514. https://doi.org/10.1149/1945-7111/ac1faf.
- [85] X. Ding, W. Zhu, G. Hua, J. Li, Z. Wu, Enhanced oxygen reduction activity on surfacedecorated perovskite La0.6Ni0.4FeO3 cathode for solid oxide fuel cells, Electrochimica Acta. 163 (2015) 204–212. https://doi.org/10.1016/j.electacta.2015.02.084.
- [86] L. Ge, K. Sun, Y. Gu, Q. Ni, X. Huang, Boosting the performance of conventional air electrodes for solid oxide cells by in-situ loading of nano praseodymium oxide, Energy Conversion and Management. 249 (2021) 114873. https://doi.org/10.1016/j.enconman.2021.114873.
- [87] R. Wang, E. Dogdibegovic, G.Y. Lau, M.C. Tucker, Metal-Supported Solid Oxide Electrolysis Cell with Significantly Enhanced Catalysis, Energy Technol. 7 (2019) 1801154. https://doi.org/10.1002/ente.201801154.
- [88] P. Sonström, J. Birkenstock, Y. Borchert, L. Schilinsky, P. Behrend, K. Gries, K. Müller, A. Rosenauer, M. Bäumer, Nanostructured Praseodymium Oxide: Correlation Between Phase Transitions and Catalytic Activity, ChemCatChem. 2 (2010) 694–704. https://doi.org/10.1002/cctc.200900311.

- [89] B.L. Treu, W.G. Fahrenholtz, M.J. O'Keefe, Thermal decomposition behavior of praseodymium oxides, hydroxides, and carbonates, Inorg Mater. 47 (2011) 974–978. https://doi.org/10.1134/S0020168511090214.
- [90] M.F. Gazulla, M.J. Ventura, C. Andreu, J. Gilabert, M. Orduña, M. Rodrigo, Praseodymium oxides. Complete characterization by determining oxygen content, Microchem. J. 148 (2019) 291–298. https://doi.org/10.1016/j.microc.2019.05.013.
- [91] G.A.M. Hussein, Formation of praseodymium oxide from the thermal decomposition of hydrated praseodymium acetate and oxalate, J Anal Appl Pyrolysis. 29 (1994) 89–102. https://doi.org/10.1016/0165-2370(93)00782-I.
- [92] J. Schefold, A. Brisse, M. Zahid, Non-Ionic Conduction Phenomena in Yttria Stabilised Zirconia Electrolyte in SOFC operated in the Electrolysis Mode, ECS Trans. 25 (2009) 1021. https://doi.org/10.1149/1.3205627.
- [93] R. Knibbe, M.L. Traulsen, A. Hauch, S.D. Ebbesen, M. Mogensen, Solid Oxide Electrolysis Cells: Degradation at High Current Densities, J. Electrochem. Soc. 157 (2010) B1209. https://doi.org/10.1149/1.3447752.
- [94] H. Kishimoto, K. Yashiro, T. Shimonosono, M.E. Brito, K. Yamaji, T. Horita, H. Yokokawa, J. Mizusaki, In situ analysis on the electrical conductivity degradation of NiO doped yttria stabilized zirconia electrolyte by micro-Raman spectroscopy, Electrochimica Acta. 82 (2012) 263–267. https://doi.org/10.1016/j.electacta.2012.04.148.
- [95] T. Shimonosono, H. Kishimoto, M.E. Brito, K. Yamaji, T. Horita, H. Yokokawa, Phase transformation related electrical conductivity degradation of NiO doped YSZ, Solid State Ionics. 225 (2012) 69–72. https://doi.org/10.1016/j.ssi.2012.05.023.
- [96] X. Sun, M. Chen, Y.-L. Liu, P. Hjalmarsson, S.D. Ebbesen, S.H. Jensen, M.B. Mogensen, P.V. Hendriksen, Durability of Solid Oxide Electrolysis Cells for Syngas Production, J. Electrochem. Soc. 160 (2013) F1074. https://doi.org/10.1149/2.106309jes.
- [97] S.-D. Kim, D.-W. Seo, A.K. Dorai, S.-K. Woo, The effect of gas compositions on the performance and durability of solid oxide electrolysis cells, International Journal of Hydrogen Energy. 38 (2013) 6569–6576. https://doi.org/10.1016/j.ijhydene.2013.03.115.
- [98] E. Lay-Grindler, J. Laurencin, J. Villanova, P. Cloetens, P. Bleuet, A. Mansuy, J. Mougin, G. Delette, Degradation study by 3D reconstruction of a nickel-yttria stabilized zirconia cathode after high temperature steam electrolysis operation, Journal of Power Sources. 269 (2014) 927–936. https://doi.org/10.1016/j.jpowsour.2014.07.066.
- [99] M. Hubert, J. Laurencin, P. Cloetens, B. Morel, D. Montinaro, F. Lefebvre-Joud, Impact of Nickel agglomeration on Solid Oxide Cell operated in fuel cell and electrolysis

modes, J. Power Sources. 397 (2018) 240–251. https://doi.org/10.1016/j.jpowsour.2018.06.097.

- [100] A. Hauch, M. Mogensen, A. Hagen, Ni/YSZ electrode degradation studied by impedance spectroscopy — Effect of p(H<sub>2</sub>O), Solid State Ionics. 192 (2011) 547–551. https://doi.org/10.1016/j.ssi.2010.01.004.
- [101] G. Chen, G. Guan, Y. Kasai, A. Abudula, Nickel volatilization phenomenon on the Ni-CGO anode in a cathode-supported SOFC operated at low concentrations of H<sub>2</sub>, International Journal of Hydrogen Energy. 37 (2012) 477–483. https://doi.org/10.1016/j.ijhydene.2011.09.007.
- [102] Q. Fang, C.E. Frey, N.H. Menzler, L. Blum, Electrochemical performance and preliminary post-mortem analysis of a solid oxide cell stack with 20,000 h of operation, Journal of The Electrochemical Society. 165 (2018) F38.
- [103] M. Trini, A. Hauch, S. De Angelis, X. Tong, P.V. Hendriksen, M. Chen, Comparison of microstructural evolution of fuel electrodes in solid oxide fuel cells and electrolysis cells, J. Power Sources. 450 (2020) 227599. https://doi.org/10.1016/j.jpowsour.2019.227599.
- [104] J. Kim, H.-I. Ji, H.P. Dasari, D. Shin, H. Song, J.-H. Lee, B.-K. Kim, H.-J. Je, H.-W. Lee, K.J. Yoon, Degradation mechanism of electrolyte and air electrode in solid oxide electrolysis cells operating at high polarization, International Journal of Hydrogen Energy. 38 (2013) 1225–1235. https://doi.org/10.1016/j.ijhydene.2012.10.113.
- [105] J.X. Sierra, H.F. Poulsen, P.S. Jørgensen, C. Detlefs, P. Cook, H. Simons, A.C. Jakobsen, J.R. Bowen, In-operando observation of microstructural evolution in a solid oxide cell electrolyte operating at high polarization, J. Power Sources. 413 (2019) 351–359. https://doi.org/10.1016/j.jpowsour.2018.12.057.
- [106] K. Chen, Failure mechanism of (La,Sr)MnO3 oxygen electrodes of solid oxide electrolysis cells, Int. J. Hydrog. Energy. 36 (2011) 10541–10549. doi:10.1016/j.ijhydene.2011.05.103.
- [107] G.-B. Jung, J.-Y. Chen, C.-Y. Lin, S.-Y. Sun, Fabrication of hydrogen electrode supported cell for utilized regenerative solid oxide fuel cell application, International Journal of Hydrogen Energy. 37 (2012) 15801–15807. https://doi.org/10.1016/j.ijhydene.2012.02.188.
- [108] H. Wang, S.A. Barnett, Degradation Mechanisms of Porous La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> Solid Oxide Fuel Cell Cathodes, J. Electrochem. Soc. 165 (2018) F564. https://doi.org/10.1149/2.1211807jes.
- [109] D. Kim, J.W. Park, B.-H. Yun, J.H. Park, K.T. Lee, Correlation of Time-Dependent Oxygen Surface Exchange Kinetics with Surface Chemistry of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub>
Catalysts, ACS Appl. Mater. Interfaces. 11 (2019) 31786–31792. https://doi.org/10.1021/acsami.9b06569.

- [110] M.R. Ardigò, A. Perron, L. Combemale, O. Heintz, G. Caboche, S. Chevalier, Interface reactivity study between La0.6Sr0.4Co0.2Fe0.8O3-δ (LSCF) cathode material and metallic interconnect for fuel cell, J. Power Sources. 196 (2011) 2037–2045. https://doi.org/10.1016/j.jpowsour.2010.09.063.
- [111] J.R. Mawdsley, J. David Carter, A. Jeremy Kropf, B. Yildiz, V.A. Maroni, Post-test evaluation of oxygen electrodes from solid oxide electrolysis stacks, Int. J. Hydrog. Energy. 34 (2009) 4198–4207. https://doi.org/10.1016/j.ijhydene.2008.07.061.
- [112] N.I. Khamidy, J. Laurencin, D. Ferreira Sanchez, F. Monaco, F. Charlot, E. Djurado, Durability of nanostructured LaPrNiO<sub>4+δ</sub> electrode for solid oxide cells: Electrochemical, microstructural, and structural investigation, J. Power Sources. 450 (2020) 227724. https://doi.org/10.1016/j.jpowsour.2020.227724.

# Chapter II Materials and methods

# **Chapter II: Materials and methods**

This chapter provides a detailed explanation of the fabrication and characterization techniques used in this study. It starts with a description of the two main coating techniques that have been used for the oxygen electrode manufacturing, i.e. electrostatic spray deposition (ESD) and screen-printing (SP). The parameters optimized for the development of each of the two materials selected for this work (La<sub>2</sub>NiO<sub>4+ $\delta$ </sub> (LNO) and Pr<sub>6</sub>O<sub>11</sub>) are detailed subsequently. The second part is devoted to the description of the various techniques which allowed us to characterized the materials before and after ageing. Scanning electron microscopy (SEM) is mainly used for microstructural observations. Laboratory X-ray diffraction (XRD) are complemented with synchrotron  $\mu$ -X-ray diffraction and  $\mu$ -X-ray fluorescence for the structural and chemical characterizations. The preparation of the lamellae by plasma-focused ion beam (p-FIB) for synchrotron analyses is explained in detail. The last part is dedicated to electrochemical characterizations. The principle of the electrochemical impedance spectroscopy (EIS) is first reminded. Then, the experimental setups for the electrochemical characterizations, i.e. the 3-electrode setup for the symmetrical cell and the test bench for the long-term durability study on complete cell are presented. The as well as the experimental measurements for each of the materials are detailed. The experimental conditions for the measurements are also given.

## **1.** Fabrication techniques

## 1.1 Electrostatic spray deposition

Electrostatic spray deposition (ESD) is a unique and versatile film preparation technique for the processing of hierarchical and fine microstructures from tenth of nanometers to tenth of micrometers [1]. This process, which obeys electro-hydrodynamic laws of liquids, consists of the atomization of an aerosol from a solution of precursors directed on a heated substrate, in high electrical voltage. This deposition technique offers many advantages such as (i) a good adhesion of the deposited film into the substrate at a low deposition temperature, (ii) a good homogeneity in composition and in grain size, (iii) a good reproducibility, and (iv) the possibility to design different microstructures (Figure) with specific porosities and small particle sizes in the nanometric scale with large surface areas. Moreover, ESD, which is an alternative method to the common screen-printing one, is a low-cost and non-vacuum process. It has been mostly and extensively studied by Prof. Schoonman (Delft University of Technology) and Prof. Djurado (Université Grenoble Alpes) groups for various components in energy devices such as batteries [2] and fuel cells [3–5] The resulting electrodes could be dense, porous, thick-film, and thin-film, all of which can be controlled by varying deposition conditions [6].



Figure 1: Different microstructures that can be obtained by ESD, a) dense b) columnar and c) coral [7] and d) coral-type microstructure with plate-like grains [8]

The ESD setup is represented in Figure 2. A syringe is connected to a needle through which the precursor solution is injected. The flow rate is controlled with a syringe pump. The needle is directed to a heating plate, on which the sample holder is placed. A K-type thermocouple is used to control the effective temperature of the sample before the deposition. Depending on the required film diameter, several sample holders are available with different hole sizes. A power supply is used to apply a positive high voltage (several kV) between the needle and the grounded substrate, inducing an electric field at the origin of the spray.



Figure 2: Scheme of electrostatic spray deposition (ESD) [9] and image of the jet-mode cone.

The electrostatic spray deposition can be decomposed in five steps. The first one is the atomization of the precursor solution occurring at the tip of the needle. Indeed, under the effect of the applied electric field, the solution becomes polarized. The drops are thus subjected to the the electrostatic force which opposes the hydrodynamic one. This creates instabilities and distortion of the liquid which forms a stable jet-cone called a "Taylor-cone" at the tip of the needle. When the applied voltage is high enough, the jet bursts into small charged drops that are attracted to the substrate. This second step of droplet transport is accompanied by evaporation during the flight (Figure 3). Then, the third and fourth steps consist of the droplets impact with the substrate followed by spreading and drying. In the last fifth step, decomposition and reaction of the droplets occurs at the surface of the substrate (Figure 3). The morphology of the deposited film is mainly dependent on the physicochemical parameters of the precursor solution (i.e. the surface tension ( $\gamma$ ), the electrical conductivity ( $\sigma$ ), and the density of the solution ( $\rho$ )) as well as the deposition parameters (the flow rate (Q), the distance between the needle and the substrate (d), and the temperature of the substrate (T), time (h)).



Figure 3: ESD deposition stages with the sequential ESD stages: 1 - aerosol formation; 2 - droplet transport; 3 - droplet impact; 4 - spreading and drying; 5 - decomposition and reaction (adapted from [2]).

#### **Designed microstructure by ESD**

A wide variety of film morphologies ranging from dense to porous can be designed by ESD. The formation of dense or reticular films occurs when the droplets are still liquid when they reach the substrate (Figure 1a,b and 4a). Dense films can be obtained if the droplets retain enough of liquid to avoid cracking during the drying step. The reticular film can growth if the liquid spread and dry simultaneously on the substrate. On the other hand, if the droplets have completely dried when they impact the substrate, the deposition mechanism leads to the formation of porous coral-type microstructures (Figure 1c and 4b). Indeed, the evaporation of the solvent during the flight induces the formation of solid particles. These charged particles are electrically attracted to each other by the closest curvatures point on the surface. Consequently, this accumulation of solid particles by so-called "preferential" attraction leads to the formation of a highly porous microstructure.



Figure 4: Schematic representation of the microstructures developed by ESD [10]. (a) Spreading of a liquid droplet leading to the formation of a dense to reticulated coating (b) Growth of solid particles by preferential attraction leading to "Coral" type microstructure.

Thus, it appears that the size of the arriving droplets on the surface of the substrate has a significant role in the microstructure and the thickness of the films. This arriving droplet size can be estimated by Gañán-Calvo equation (Eq. 1) [11] which links the droplets size (d) to several parameters such as to the solution density ( $\rho$ , in g cm<sup>-3</sup>), vacuum permeability ( $\varepsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$ ), flow rate (Q, mL h<sup>-1</sup>), solution surface tension ( $\gamma$ , N m<sup>-1</sup>) and solution electrical conductivity ( $\sigma$ , S m<sup>-1</sup>), as the following :

$$d_{size} \propto \left(\frac{\rho \varepsilon_0 Q^3}{\gamma \sigma}\right)^{1/6}$$
 Eq. 1

Therefore, in order to promote the formation of "coral" type microstructure for example, it would be necessary to decrease the size of the droplets by either decreasing the flow rate of the solution, and/or increasing the surface tension and/or the conductivity of the precursors solution according to Gañán-Calvo equation. Moreover, it appears that it is also possible to vary the droplet size by adjusting several other process parameters namely, the nature of the solvent, the temperature of the substrate ( $T_s$ ) the distance between the needle and the substrate ( $d_{n-s}$ ). Indeed, the boiling point of the solvent in the precursor solution is also significant because it determines the evaporation rate of the solvent.

For example, the boiling point of ethanol is 78 °C while the one of butyl carbitol is 231 °C. Therefore, a solvent with a lower boiling point will promote the formation of solid particles due to a strong evaporation of the solvent. Similarly, the increase of the temperature of the substrate or a larger needle-substrate distance leads to an increase of the evaporation of the solvent during

the flight and thus a decrease of the size of the particles. However, according to Neagu et al [10], all these parameters are dependent on each other and it is necessary to find a balance in order to avoid the mechanical stresses and to optimize the deposition.

## 1.2 Screen-printing (SP)

The screen-printing (SP) is a versatile printing technique that has been widely used in different areas from garment printing to circuit board printing. It is also a classical technique for the deposition of uniformly distributed SOC electrodes on a series of continuously processed samples. The procedure consists of spreading an ink of the studied material on the surface of the substrate through a mesh screen (Figure 5). The screen is a sheet of polymer resin into which perforations have been made for a fixed diameter. The ink is then spread across the perforated area by a squeegee connected to a mechanical system that controls the pressure and speed of the passage. The density and thickness of the deposited film depend on the size of the mesh aperture, the viscosity of the ink, and the speed and force of the passing squeegee.



Figure 5: Schematic representation of the screen printing process [12].

The ink used for screen printing is obtained by mixing a powder of the studied material, a solvent and an organic binder. For screen printing film deposition, the solvent is completely removed after sintering while the binder ensures the cohesion with the functional phase grains. It has been shown that the choice of these starting materials have a direct influence on the

rheology of the ink and on the thickness and quality of the deposited film [13]. Indeed, when the initial quantity of solvent is overweight, the ink obtained is liquid and sinks through the screen support even before the squeegee sweeps. Conversely, if the quantity of solvent is insufficient, the ink has a high viscosity that could not allow a sufficient transfer through the interstices of the screen. Moreover, it has been reported that if the quantity of binder exceeds a threshold amount, the ink become steaky whereas a low quantity of binder leads to the scratching of the film after sintering. It is therefore necessary to find a balance between the different elements, which also depends on the size of the powder used. In this work, the initial powders have been either directly purchased or synthesized in the laboratory. The powders produced in the laboratory was generally ground in order to break the agglomerates or to homogenize the particle size.

Once the elements are mixed together, it is necessary to perform an additional grinding process through a triple-roll mill to break the remaining aggregates and to homogenize the ink. An illustration of the device is shown in Figure 6. It consists of three horizontal rolls with the same size and that turns in opposite directions. Levers on the sides of the machine are used to change the spacing between the rollers and the rotation speed. Finally, a scraper is used to recover the ink which can be directly used for the SP process. Depending on the size of the substrate, parameters such as squeegee pressure, squeegee speed and the gap between the screen and the substrate must be adjusted.



Figure 6: Schematic representation of the working mechanism of a triple roll mill [14].

The subsequent thermal annealing to remove the organic solvent was carried out in air at 450 °C for 2 h followed by sintering at temperature  $\geq$  800 °C depending on the type of the samples and the experiments which will be detailed in each chapter regarding the experimental results. These values were defined depending on the studied compounds (i.e. solvent, binder and

powder grain size) as well as to the nature of the material. However, these high temperatures can cause reactivity or inter-diffusion between the different layers of the materials [15–17]. It is therefore necessary to find a compromise between chemical stability and an appropriate sintering temperature to ensure the formation of the active phase and a good mechanical resistance.

1.3 Influence of the microstructure and the architecture on the electrode performances

The previous work carried out on the ESD has shown that the microstructure and the architecture play a key role on the electrode performances. These performances have been optimized from the previous students for several oxygen electrode materials (i.e.  $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$  (LSCF), nickelates  $Ln_2NiO_{4+\delta}$  (Ln = La, Pr),  $PrO_{1.833}$  ...). For instance, D. Marinha [18] measured the evolution of the performances of single LSCF electrode of around 15 µm thickness deposited by ESD on each side of GDC electrolyte. A polarization resistance of 1.2  $\Omega$  cm<sup>2</sup> at 600 °C (measured at Open Circuit Voltage (OCV) with symmetrical cells) has been reached for the columnar type microstructure against 9.5  $\Omega$  cm<sup>2</sup> for the coraltype microstructure. On the other hand, for the La<sub>2</sub>NiO<sub>4+ $\delta$ </sub>, R. Sharma reported lower polarization resistance with the coral microstructure. Moreover, in his thesis work, R. Sharma [19] compared the polarization resistance of single and double layer LNO electrode. The double layer electrodes in symmetrical cell configuration have been elaborated by both ESD and screen-printing (SP). For the ESD layer, the particle size is about 100 nm while with screenprinting it achieves 450 nm. From the Figure 7, it can be observed that for temperatures above 600 °C, the polarization resistance is lower for the screen-printed sample (cathode 3). This behavior is explained by a better current collection for this cell provided due to the thick SP current collector that ensures a more homogeneous distribution of the current at the electrolyte interface. Thus, the addition of a screen-printed layer on the top of the ESD (cathode 4) induces a strong decrease of the polarization resistance.



Figure 7: Arrhenius plot of various LNO electrodes architectures [19]

O. Celikbilek [20] studied the influence of the thickness of the functional (AFL for active functional layer) and collecting layer (CCL for current collecting layer) in the electrode performances with LSCF double-layer electrode deposited on a gadolinia-doped ceria (Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2- $\delta$ </sub>, GDC) electrolyte. Figure 8a shows the evolution of the polarization resistance (R<sub>pol</sub>) value for double-layer electrode with an AFL of 6 µm thickness, and CCL varying from 20 to 50 µm. It appears that the lowest R<sub>pol</sub> of 0.06  $\Omega$  cm<sup>2</sup> at 600 °C has been obtained with the CCL of 30 µm. Subsequently, for fixed CCL thickness, it has been shown (Figure 8b) that R<sub>pol</sub> decreases when increasing the AFL thickness from 0.5 to 5 µm. Then, the performances remain roughly the same with thicker functional layer. Therefore, in the following study, thicknesses of 5 to 6 µm for the AFL and 30 µm for the CCL have been retained as optimized values for the elaboration of the double-layer electrodes.



Figure 8: Arrhenius plot of double layer LSCF electrode with various thicknesses of (a) CCL and (b) AFL [20]

## 1.4 Physical vapor deposition sputtering process (PVD)

Physical vapor deposition (PVD) technique, the DC Magnetron Sputtering technique (Figure 9) consists on the elaboration of thin films from the extracted vapor provided by a solid target source. The process is performed in a low-pressure chamber supplied by inert gas which is usually Argon (Ar) following the DC magnetron sputtering method. A high voltage is applied between a cathode (target) and an anode (substrate) leading to the formation of plasma. Thus, under the effect of this electric field, the plasma ions (ex: Ar<sup>+</sup>) will collide the surface of the cathode coated by the material to be deposited. This material converted into a vapor is then transported from the cathode to the substrate. Finally, the condensation of the vapor will lead to the formation of a thin film on the surface of the substrate. The thickness of the deposit can vary from tens of nanometers to micrometers. In this study, the PVD deposition has been performed by Forschungszentrum Jülich GmbH institute (FZJ) as described in the following article [21].



Figure 9: Schematic representation of the physical vapor deposition sputtering process.

#### 2. Cell preparation

As discussed in the previous chapter, two oxygen electrode materials have been investigated in this work. The first part of this work focused on the performant RP phase, namely lanthanum nickelate, La<sub>2</sub>NiO<sub>4+ $\delta$ </sub> (LNO) through an experimental and modeling approach to understand the underlying reaction mechanisms of this oxygen electrode. For this, electrochemical measurements in symmetric cells are necessary. For the second part of this work, an electrochemical, chemical and microstructural study has been carried out on an alternative PrO<sub>1.833</sub> (i.e. Pr<sub>6</sub>O<sub>11</sub>) oxygen electrode which is a decomposition product of LPNO after operation as previously shown in Nur Istiqomah Khamidy's thesis [22,23]. Measurements of PrO<sub>1.833</sub> ageing in a complete cell accompanied by *ante* and *post-mortem* analyses have been performed. The cells manufacturing is presented below.

2.1  $La_2NiO_{4+\delta}$  (LNO)

The electrochemical measurements have been performed with La<sub>2</sub>NiO<sub>4+ $\delta$ </sub> (LNO) electrodes deposited by screen-printing on each side of a circular and dense 8YSZ electrolyte (thickness = 260 µm, diameter = 25 mm, Neyco). In order to prevent the reactivity with YSZ that leads to the formation of insulating phases, a Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>2- $\delta$ </sub> (CGO) barrier layer of 2 µm of thickness was added in between the electrodes and the electrolyte. For the screen-printing deposition, a commercial GDC (Solvay) powder has been mixed with a terpineol-based solvent and an organic binder. After deposition, a sintering step at 1200°C for 1 h in air have been performed. For the LNO, the powder, which was used for the ink preparation, has been obtained by mixing

La<sub>2</sub>O<sub>3</sub> (Strem Chemical, 99,99%) and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Acros Organics, 99%) precursors via the citrate-nitrate route (modified Pechini method) [24]. The La<sub>2</sub>O<sub>3</sub> was initially pre-annealed at 900 °C for 12 hours followed by annealing step at 1200 °C for 12 hours for phase formation. A grinding step has been performed to reduce the average particle size of LNO to 0.5 - 1  $\mu$ m. The SP layer has been sintered in air subsequently at 400 °C for 1 h, with a heating rate of 1 °C min<sup>-1</sup> to remove the organic solvent and 1150 °C for 1 h with a heating rate of 2 °C min<sup>-1</sup> for the phase formation. The obtained electrode has a surface area of 1 cm<sup>2</sup> (diameter  $\approx 11.3$ mm) and a thickness of around 30  $\mu$ m. SEM image of a cross-section of the cell is shown in Figure 10.



Figure 10: SEM image of the LNO electrode on 8YSZ electrolyte with GDC barrier layer.

## 2.2 $PrO_{1.833}$ (i.e. $Pr_6O_{11}$ )

In a previous study, R. Sharma [25] optimized the microstructure of the  $PrO_{1.833}$  electrode by varying ESD deposition parameters as well as the nature of the solvent for the precursor solution. From this study, a low polarization resistance of 0.02  $\Omega$  cm<sup>2</sup> at 600 °C was obtained for a double-layer architecture electrode composed of an ESD columnar-type active layer topped by LSCF current collecting layer. This columnar type microstructure is obtained using a needle-to-substrate distance of 20 mm, flow rate of 1.5 mL h<sup>-1</sup>, a substrate temperature of 300 °C and a deposition time of 3 h. The precursor solution was obtained from praseodymium nitrate hexahydrate powder (Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Aldrich, 99 %) dissolved in a mixture of ethanol (EtOH, CH<sub>3</sub>CH<sub>2</sub>OH, 99 %, Fisher) and butyl carbitol (BC, diethylene glycol monobutyl ether CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>(OC<sub>2</sub>H<sub>4</sub>)<sub>2</sub>OH), i.e. (EtOH:BC, 1:2) in 0.02 M. Moreover, he also studied the

influence of the CCL by testing LSCF ( $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ ), LSM ( $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ ) and  $PrO_{1.833}$  (i.e.  $Pr_6O_{11}$ ) [26]. He measured a high polarization resistance of 0.101  $\Omega$  cm<sup>2</sup> at 600 °C for the cell with  $Pr_6O_{11}$  used as current collecting layer. On the other hand, the results obtained for LSM are similar to the values obtained for the LSCF.

For the sake of consistency, a 2-electrode symmetrical cell test has been performed to confirm the reproducibility of the measurements obtained by R. Sharma. Thus, a double-layer electrode with  $PrO_{1.833}$  electrode topped with LSM current collecting layer has been deposited on a gadolinium-doped ceria ( $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ , GDC) electrolyte of 1.1 mm thick and 19.6 mm in diameter. A polarization resistance of 0.032  $\Omega$  cm<sup>2</sup> at 600 °C has been measured. The elaboration procedure is thus verified and the durability measurements in complete cells have been initiated. The complete cell study has been carried out by using half cells provided by Forschungszentrum Jülich GmbH institute (FZJ). The half cells are composed with a NiO-YSZ cermet and 8 mol% yttria-stabilized zirconia (8YSZ) electrolyte topped by a thin GDC barrier layer (600 - 700 nm). The FZJ supported cells is 50 mm in diameter and the deposited double layer oxygen electrode is 34 mm in diameter.



Figure 11: Schematic representation of the studied complete cell (Ni-YSZ/YSZ/GDC/PrO<sub>1.833</sub>/LSM).

The ESD used in LEPMI moves along the X-Y directions so that the spray covers the whole surface homogeneously. Thus, the deposition time and the number of steps has been adjusted to ensure a reproducibility between the samples. The deposition time was about 3 h for the symmetrical cell electrode of 1 mm diameter. It was increased up to 8 h in order to achieve 34

mm diameter required for the complete cell. The deposition is followed by an annealing step of 600 °C for 2 h in air. The SEM image of the columnar  $PrO_{1.833}$  microstructure is shown in Figure 12. The current collecting layer has been added by screen-printing (SP) through a mesh screen (inox 18/0 mesh 90°, JFP Microtechnic, mesh size 20 µm) on the top of the  $Pr_6O_{11}$ . For the SP ink preparation, commercial LSM powder (SSC Inc.) has been mixed to an organic solvent (KD2921, Zschimmer, and Schwarz) with the mass ratio of 1:1. A polyvinyl butyral ((C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>)<sub>n</sub>, Aldrich) in 1 wt. % is added as a binder. The mixture has been then stirred using three cylinders by following a rigorous protocol that lasts 45 minutes to progressively tighten the rollers until a fluid and homogeneous ink is obtained. As previously discussed around 30 µm thickness is aimed for the current collecting layer (CCL). For this purpose, the ink has been then deposited on the sample in several passes, with drying steps at 80 °C in between, until the required thickness is achieved. Then, the SP deposition has been sintered first at 450 °C for 2 h in air with a ramp of 0.5 °C min<sup>-1</sup>. SEM image of this double-layer electrode is shown in Figure 12.



Figure 12: SEM micrograph of double layer oxygen electrode (PrO<sub>1.833</sub>-ESD topped by LSM-SP) deposited in Ni-YSZ/YSZ/GDC half-cell provided by Forschungszentrum Jülich GmbH Institute (FZJ).

Long-term test has been conducted in this FZJ/  $PrO_{1.833}/LSM$  complete cell for 1000 h at 700 °C under electrolysis mode (- 0.5 A cm<sup>-2</sup>). These measurements have been accompanied by *ante* and *post-mortem* analyses. To better understand the influence of the temperature and the

current on the material stability, two samples composed with  $PrO_{1.833}$  topped with LSM electrode deposited on GDC electrolyte were thermally aged (without current). The first sample was maintained at 700 °C for 1000 h and the second at 800 °C for 700 h. The results of this work will be discussed in the chapter IV.

## 3. Characterization techniques

#### 3.1 SEM observations

Scanning electron microscopy has been used in this work for morphological, topological and chemical characterization of studied samples. The basic principle of a scanning electron microscope (SEM) consists to scan the surface of a material with an electron beam produced by an electron gun. The electron beam is accelerated and focused on the sample by electromagnetic lenses. The radiation resulting from the interactions between the sample and a high-energy electron beam (namely secondary electrons, backscattered electrons, Auger electrons and X-rays) is then collected through detectors. Secondary electrons (SE) result from the inelastic interaction with the electrons of the atoms in the sample. The number of secondary electrons varies with the surface and the nature of the material. Thus, by sweeping the electron beam, it is possible to obtain the topography of the sample surface. The backscattered electrons (BSE) result from the elastic scattering of primary electrons with atomic nuclei. This elastic scattering occurs with a low energy loss, so their mean free path is higher than that of SE and are therefore emitted from deeper position in the sample. Moreover, since the BSE are correlated to the atomic number of the sample, the difference in the contrast on the acquired images gives information on the distribution of the elements in the sample. Both of these acquisition types have been used in this work.

When the SEM is coupled with energy-dispersive X-ray spectroscopy (EDX), it is possible to have structural analysis of the sample. Indeed, the electronic transitions that take place during the inelastic impact causes the emission of a photon, with characteristic energy related to the nature of the element. Thus, SEM-EDX has been used to collect X-ray spectrum in order to identify the elemental composition of the sample.

In this work, the microstructural observation was carried out both on the surface and the crosssection of the prepared electrode. To observe the cross-section, the sample was cut by a diamond pen. The samples were prepared for the characterization by placing them on small aluminum blocks. Electrically conducting carbon tape was used to fix the samples in place. The silver paste was then applied to connect the samples with the aluminum blocks and left to completely dry at least for several hours to prevent outgassing inside the sample chamber of SEM. Since the electrolyte was not electrically conducting, 1 nm-thin Au/Pd was deposited by vacuum metallization on the surface/cross-section of the samples to obtain a conducting surface. The particle size and the thickness of the electrodes were then estimated from the SEM cross-sections of the cell using an image analysis tool (ImageJ software). Two devices have been used in this work located in Consortium des Moyens Technologiques Communs (CMTC) platform (Grenoble-INP) and MINATEC.

## 3.2 Laboratory X-ray diffraction at room temperature

X-ray diffraction is a non-destructive analysis method used for the structural characterization of crystalline materials: in this work, it is based on crystalline oxides as powders and films.

The acquisition of diffraction patterns has been performed on a laboratory diffractometer PANalytical X'pert Pro MPD at room temperature. The diffractometer is equipped with an anticathode of copper with the wavelength ( $\lambda$ ) of 1.5419 Å in Bragg-Brentano geometry in 20 range from 20 ° to 130 °. The phase identification has been carried out by the powder diffraction file (PDF) from International Centre for Diffraction Data (ICDD). The positions of the X-ray diffraction peaks and the cell parameters have been obtained by Rietveld refinement using Fullprof software [27].

Since it is not possible to differentiate with the laboratory XRD the diffraction patterns of the ESD and SP layers in double layer electrode, synchrotron  $\mu$ -X-ray diffraction has been used for the study on PrO<sub>1.833</sub>. Indeed, synchrotron  $\mu$ -X-ray diffraction provide a resolution at the micrometer scale of the elements and phases distribution all over the electrode, at a much larger resolution than the one of the laboratory XRD equipment.

## 3.3 Synchrotron-based X-ray: $\mu$ -XRD and $\mu$ -XRF characterization

For the characterization along the electrode thickness, local  $\mu$ -X-ray diffraction and  $\mu$ -X-ray fluorescence have been performed at microXAS beamline on the Swiss Light Source (SLS),

Paul Scherrer Institute (PSI), Switzerland. For this purpose, thin lamella of  $Pr_6O_{11}$  (i.e.  $PrO_{1.833}$ ) oxygen electrode were harvested from the studied samples by a plasma-focused ion beam (p-FIB) Vion (FEI<sup>TM</sup>) using Xe<sup>+</sup> ion source. First, a cell fragment is placed in the vacuum chamber of the machine, on a 5-axial motorized stage. Adjustments of the height and the tilting of the sample are then made to determine the position of the eucentric point. Afterwards, a protective layer of platinum (Pt), with a thickness of 10 µm, has been deposited along the region of interest (ROI) using a current of 59 nA (Figure 13a). The areas on each side of the ROI were then milled as shown in Figure 13b. In order to prevent the damage of the sample, a current of 180 nA has been chosen for the area close to the ROI and 470 nA at the furthest. The isolated lamella was then detached from the sample with a micromanipulator using a low ion current of 180 nA. The detached portion was then placed on an aluminum pin and fixed to it by a platinum deposit before to be removed from the p-FIB chamber. As shown in the Figure 13c, the lamella dimensions are approximately  $80 \times 20 \times 20 \mu m^3$  for the width, height and depth, respectively.



Figure 13: Schematic representation of the PFIB sample preparation (a) Pt deposition (b) FIB milling (c) Extracted lamella from the cell mounted on the Al pin.

The prepared lamellae were used for synchrotron X-ray characterization at  $\mu$ -XAS beamline on the Swiss Light Source (SLS), Paul Scherrer Institute (PSI), Switzerland. Synchrotron radiation is a very high energy light emitted by the acceleration of electrons by intense electric and magnetic fields through concentric tunnels. The  $\mu$ -XAS beamline provides high resolution chemical imaging of materials, reaching a spatial resolution in the range of 1  $\mu$ m. Therefore,  $\mu$ -X-ray diffraction ( $\mu$ -XRD) and  $\mu$ -X-ray fluorescence ( $\mu$ -XRF) measurements have been performed simultaneously on the studied samples. The XRF allows identifying the elemental chemical composition of the material.

A schematic of the  $\mu$ -XAS beamline setup is shown in Figure 14. The lamella is illuminated by an X-ray incident beam with a high energy of 17.2 keV, focused by a Kirkpatrick-Baez (KB)

mirror system to a spot size of  $1 \times 0.5 \ \mu\text{m}^2$  (horizontal by vertical dimension). The sample is positioned at a focal plane of the X-ray beam and 2D raster scans on horizontal (X) and vertical (Y) directions have been performed all over the lamella using a step size of 500 nm. Thanks to the high energy of the beam and the small size of the samples, the X-ray is able to penetrate and cross the lamella. Therefore, a 2D diffraction detector is positioned behind the samples to record the XRD patterns. In addition, a silicon drift diode detector (SDD; Ketek GmbH, Germany) is positioned at 50° of the beam to record the fluorescence spectrum. A classical 1D diffractogram has been obtained by azimuthal integration of the 2D diffraction rings measured in each point, by using pyFAI [28]. The XRD data were then integrated over the horizontal direction (Xdirection) for each vertical position of the sample. The Rietveld refinement and the fitting of the diffractograms have been carried out by using the software XRDUA [29]. The fluorescence spectra have been fitted using pyMCA [30]. Thus, 2D images of each detected element have been generated. The images were then treated by using Image J software.



Figure 14: Schematic representation of  $\mu$ -XRF and  $\mu$ -XRD characterization at  $\mu$ -XAS beamline, SLS, PSI, Switzerland [22].

#### 4. Electrochemical measurements and characterization

### 4.1 Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectroscopy (EIS) is a characterization technique used to study the behavior of electrochemical systems such as the solid oxide cells. This technique consists of applying a small perturbation (voltage or current) and to measure the response of the studied system (respectively current or tension), over a wide range of frequencies (10 mHz to 10 kHz). The ratio of these input and output data gives key information about the electrochemical phenomena associated to the system. Indeed, thanks to this technique, it is possible to extract some physical values such as conductivity, diffusion coefficients... Moreover, it is possible to separate the contributions associated with each of the interfaces through the associated frequency ranges and thus determine the different electrochemical processes occurring within the electrode. The evolution of the electrodes can thus be studied at different conditions of applied current, temperature and oxygen partial pressure.

For the operating, the measurement consists of applying a sinusoidal voltage  $V(t) = V_0 \cos(i\omega t)$  (or current  $I(t) = I_0 \sin(i\omega t)$ ) across the cell over a frequency range ( $f = \omega/(2\pi)$ ) and to measure the response in current  $I(t) = I_0 \sin(i\omega t + \varphi)$  with a a phase shift  $\varphi$  (or in tension  $V(t) = V_0 \sin(i\omega t + \varphi)$ ). For a small applied perturbation, the system can be considered as being in a linear response domain. The complex impedance can thus be defined as follows:

$$Z(\omega) = \frac{V_0}{I_0} e^{i\varphi(\omega)} = Z' + iZ''$$
 Eq. 1

where Z' is the real part and Z'' is the imaginary part which can be presented in Nyquist plot (Figure 15a) or Bode plot (Figure 15b).



Figure 15: Representation of the impedance spectra: a) Nyquist plot – b) Bode plot.

The interpretation of these diagrams gives information about the electrochemical processes occurring in the cell. From the Nyquist plot, it is possible to extract the series resistance ( $R_s$ ) and the polarization resistance ( $R_{pol}$ ).

- The series resistance (R<sub>s</sub>) defined as the ohmic resistance of the cell originating mainly from the electrolyte and the current collection. This value is identified as the intercept at high frequency with the real axis.
- The polarization resistance (*R*<sub>pol</sub>) is related to all the resistive processes involved in the electrode. It is calculated as the difference between the series resistance R<sub>s</sub> and the total resistance R<sub>t</sub>. Moreover, the shape of the impedance spectra can give also key information about the reaction mechanisms that take place in the cell [31–33]. Besides, these kinetics processes are assigned to a well-defined frequency range. Therefore, the representation in Bode diagrams allows the deconvolution in different peaks associated to the different rate-determining steps in the electrodes.

In order to analyze and discriminate the electrochemical behavior involved in the studied system, the main approach consists of simulating the impedance spectra. For this purpose, it is possible to fit the diagram using electric equivalent circuit model (ECM) [33]. In this approach, the model is based on an electric circuit composed with different electrical elements (such as resistance, inductance, capacitance ...) to simulate the phenomena involved. An alternative approach consists to build a physics-based model for the impedance. The experimental spectra together with the electrode polarization curves recorded under different operating conditions (T, pO<sub>2</sub>) can be used to validate the model. Once validated, sensitivity analyses performed with the model allows identifying the activated reaction mechanism and the rate-determining steps. This methodology has been implemented to study the electrochemical behavior of LNO

electrodes under anodic and cathodic polarizations (cf. chapter III).

## 4.2 Symmetrical cell measurements for LNO

In order to study the impact of the temperature and the pO<sub>2</sub> on the reaction mechanisms of the LNO oxygen electrode material, electrochemical characterizations have been carried on symmetrical cells (Figure 16) tested in a 3-electrodes setup. A reference electrode (RE), consisting of a platinum wire, was deposited around the periphery of the electrolyte (i.e. platinum ~ 25 mm in diameter) by taking care of respecting the positioning rules [34]. Two platinum grids with a mesh of 3600 meshes cm<sup>-2</sup> and a surface equal to that of the electrode were used as current collectors on both the working (WE) and counter (CE) electrodes. A  $\approx$  1 mm thick disk in porous gold was also added between the ceramic housing and the platinum grids so that each electrode surface can be considered as equipotential. In order to improve the electrical contact between the current collector grids and the electrodes, a weight of 0.7 kg was also applied to the setup to ensure the electric contact between the metallic grids and the electrodes. The cells have been heated at a temperature of 800 °C, with a heating rate of 1°C min<sup>-1</sup>. This temperature has been maintained during several hours on which EIS measurements have then recorded at OCV periodically until the stabilization of the diagrams.

Electrochemical measurements were then carried out at a temperature of 750, 700 and 650 °C under air condition, with a gas flow rate of  $\approx 2$  NL min<sup>-1</sup>. For each temperature, polarization curves have been recorded. The current density-voltage (i-V) curves were measured in potentiostatic mode with a step of 2 mV s<sup>-1</sup>. EIS measurements were also performed at OCV, in a frequency range of 10<sup>6</sup> to 10<sup>-2</sup> Hz, with a signal amplitude of  $\pm$  10 mA cm<sup>-2</sup>. For the reference temperature of 700 °C, complementary EIS measurements were added. EIS diagrams were acquired under anodic and cathodic current, with  $i_{dc} = \pm$  100 mA cm<sup>-2</sup> for LNO electrode. Finally, EIS were carried out by adjusting the O<sub>2</sub> and N<sub>2</sub> flow rate in order to vary the oxygen partial pressure in a range from 0.15 to 1 atm. The measurements have been acquired by using an autolab potentiostat-galvanostat (PGSTAT 302N) equipped with a frequency response analyzer (FRA).



Figure 16: Schematic representation of the 3-electrodes setup with a symmetrical cell configuration [35].

# 5. Long-term test on complete cell

## 5.1 Description of the test bench

The electrochemical characterizations on complete cell have been performed to study the  $Pr_6O_{11}$  oxygen electrode described in section 2.2. The scheme of the test bench is shown in Figure 17.



Figure 17: Schematic representation of the experimental test bench for complete cell measurement.

On the lower side, two ceramic tubes are connected to the alumina cell housing. The chambers are supplied with air, oxygen, nitrogen and hydrogen through metallic pipes connected to flowmeters located upstream. In this test bench, the steam is produced through a combustion chamber. A controlled amount of H<sub>2</sub> and O<sub>2</sub> is supplied into the chamber in such way that the oxy-combustion reaction can produce the desired amount of water. On the oxygen electrode side, air is blown into the cell through a diffuser. It is composed of a metal tube connected to a cylinder with the same diameter of the cell (34 mm). These tubes are used for the gas supply as well as for routing the gold wires for the current collection. On both sides, these wires are connected to metallic grids in contact with the cell. At the H<sub>2</sub> electrode a nickel grid (100 mesh cm<sup>-2</sup>) of 50 mm in diameter is used. On the oxygen electrode side, the current collection is performed with a platinum grid (3600 mesh cm<sup>-2</sup>) topped by a gold grid (100 mesh cm<sup>-2</sup>). A compressive load of 600 g cm<sup>-2</sup> is applied on the assembly in order to improve the contacts between these different layers. A glass-ceramic paste is added at the cell periphery to ensure the tightness of hydrogen electrode compartment (Figure 17). The formation of this glassceramic seal is done during a heating step before the beginning of the electrochemical characterizations. The temperature is regulated by means of a thermocouple in contact with the furnace. Another thermocouple is placed near the cell to control its temperature. The whole input parameters (e.g. gas flow, furnace temperature, current ...) are controlled by a software called RSview. Data are recorded every second for continuous monitoring.

Polarization curves (i-V) and EIS spectra have been recorded using an autolab potentistatgalvanostat (FRA-PGSTAT302N). A power supply is used to impose the current to the cell during the long-term test conducted in galvanostatic mode.

## 5.2 Testing protocol

The electrochemical test of the complete cell starts with a heating step required for the glass seal formation to ensure the gas tightness between the two chambers. The glass seal is conducted at more than 800 °C, with a heating rate of 1 °C min<sup>-1</sup> to avoid any thermal damage. The heating is performed under nitrogen sweep on the hydrogen electrode side and air on the oxygen electrode side. A flow rate of 0.5 Nl h<sup>-1</sup> is used on each side. Once the seal is formed, the bench is cooled to a cell temperature of 800 °C for the reduction step of NiO to Ni on the hydrogen electrode. The reduction starts with a pure N<sub>2</sub> in a total flow rate of 4 Nl h<sup>-1</sup> which is progressively replaced by H<sub>2</sub>. Once the cell is under pure hydrogen atmosphere, the OCV value

is compared to the Nernst voltage to verify the gas tightness. Afterwards, the electrochemical characterization of the cell can start.

In this work, the initial performances of the cells are measured under electrolysis mode, at 700 °C, with 90 vol. %  $H_2O + 10$  vol. %  $H_2$  in the hydrogen side and air in the oxygen side. The polarization curves were obtained in galvanostatic mode by applying a current with a ramp rate of 20 mA s<sup>-1</sup> until a maximum voltage fixed at 1.6 V. The cell voltage curve is then plotted against the current density. The EIS spectra were acquired at OCV, in a frequency range of  $10^6$  to  $10^{-2}$  Hz, with an amplitude of  $\pm$  10 mA. Both polarization curves and EIS measurements were carried out before and after durability test. The long-term test was conducted in galvanostatic mode at 700 °C by imposing a current density of - 0.5 A cm<sup>-2</sup> under SOEC mode, with H<sub>2</sub>O/H<sub>2</sub> ratio of 90/10 and a steam conversion (SC) of 25 %. Once finished, the cell is cooled at room temperature by supplying the hydrogen electrode with a mixture of nitrogen and hydrogen to maintain the cermet in a reduced state.

## 5.3 Polarization curves (i-V)

If a cell is subjected to an electric current, irreversible processes occur. These phenomena result in the increase of the cell voltage in SOEC mode. The shape of an i-V curve gives information about the performance of the cell (Figure 18). Indeed, for an applied current density, the cell voltage can be decomposed according to the following equation

$$U_{cell}(i) = U_{i=0} \pm R \times i \pm \eta_{act}^{cath} \pm \eta_{act}^{anode} \pm \eta_{conc}^{cath} \pm \eta_{conc}^{anode} \qquad Eq. \ 2$$

The sign convention is as follows: i > 0 in SOFC mode while i < 0 since it is supplied by an external power.

(i)  $U_{i=0}$  corresponds to the cell voltage at open circuit. This voltage is related to the difference in oxygen activity at the two electrodes. The value can be calculated by the Nernst equation

$$U_{i=0} = \frac{RT}{4F} \ln \frac{p O_2^{O2 \ electrode}}{p O_2^{H2 \ electrode}}$$
Eq. 3

where R is the gas constant, T is the temperature, F is the Faraday constant and  $pO_2^i$  is the oxygen partial pressure at each electrode "i".

The other terms in the equation correspond to the energy dissipation when a current is applied as followed

(ii) Ohmic losses,  $R \times i$ 

It is related to the resistance of the electrolyte and the contact resistances between the grids and the electrodes. For a single cell, the resistance can be thus decomposed as follows

$$\eta_{ohm} = (R_{electrolyte} + R_{contact}) \times i$$
 Eq. 4

The ohmic losses due to the ionic resistance of the electrolyte to the diffusion of oxygen ions are dependent on the electrolyte material and the temperature. The contact resistance  $R_{contact}$  depends on the nature of the materials and also parameters such as the surface of the contacts or the compressive forces applied on the assembly to ensure the tightening.

#### (iii) The activation overpotentials, $\eta_{act}$

The activation overpotentials represent all the processes arising in the active layer for each electrode. They combine a mass and charge transfer with the set of reactions that occurs within the active layers. They are dependent on several parameters such as reaction kinetic rates (i.e. electrocatalytic activity of the material, temperature, microstructure of the active layer, etc...).

For a macroscopic and simplified approach, the activation overpotentials can be roughly estimated for each electrode using a Butler-Volmer formalism

$$\eta_{act}^{electrode} = \frac{RT}{F} \sin^{-1} \left( \frac{i}{2i_0^{electrode}} \right)$$
 Eq. 5

Where i the current density and  $i_0$  the 'apparent' exchange current density of the considered electrode.

(iv) The concentration overpotentials,  $\eta_{conc}$ 

The concentration overpotentials reflect the losses related to the depletion or accumulation of gas at the reaction sites. They can be further decomposed in two contributions:  $\eta_{conc} = \eta_{rev} + \eta_{diff}$ . On the one hand, the change of gas at the reaction site due the reactions along the length of the cell induces reversible losses, which are referred to as the gas conversion overpotentials  $\eta_{rev}$ .

These thermodynamic losses are more important at high current density because of the high steam conversion rate in SOEC mode or the high fuel utilization in SOFC mode. On the other hand, the gas diffusion especially through the thick cermet support induces some diffusion overpotentials  $\eta_{diff}$ .

The polarization curves also give quantitative information about the cell performance by measuring the current density reached by the cell at a reference voltage. From the i-V curve, it is also possible to estimate the Area Specific Resistance (ASR) defined as follows

$$ASR = \frac{dU}{di}$$
 ( $\Omega \,\mathrm{cm}^2$ ) Eq. 6

In general, the ASR is determined by the slope of the i-V curve in its linear part.

In this work, the i-V curves have been measured in the galvanostatic mode. The current can be applied in static mode, i.e. by time step, or in dynamic mode, by applying a ramp speed. A maximum voltage of 1.4 V will be fixed in order not to damage the cell.



Figure 18: Typical i-V curve for SOC indicating the performances losses.

## 5.4 Degradation rate

By monitoring the evolution of the cell voltage during operation, it is possible to estimate the degradation rate. In this study, an in-situ monitoring of the cell voltage evolution has been

performed during the durability tests. The degradation rate has been estimated using the following relation

$$\frac{\Delta U}{\Delta t} = \frac{U(i,t) - U(i,t_0)}{t - t_0} \qquad (\text{mV h}^{-1}) \qquad \text{Eq. 7}$$

It is possible to express the degradation rate by normalizing it with respect to the initial cell voltage.

$$\frac{\Delta U \times 100}{\Delta t \times U(i, to)} \qquad (\% h^{-1}) \qquad Eq. 8$$

This rate is usually standardized for 1000 hours of operation.



Figure 20: Evolution of voltage versus time for a typical cell

## 6. Conclusion

This chapter was devoted to present the main fabrication and characterization techniques that have been used to study mainly  $La_2NiO_{4+\delta}$  (LNO) and PrO<sub>1.833</sub> as oxygen electrode materials for high temperature electrolyzers.

The study of the LNO required the acquisition of electrochemical data required for the electrochemical model that is presented in Chapter III. For this purpose, LNO electrode has been produced by classical screen-printing technique. Then, electrochemical measurements have been performed on a symmetrical cell (LNO//GDC//8YSZ) using a 3-electrodes setup. The study of the performance and stability of a nanostructured PrO<sub>1.833</sub> electrode is based on an

experimental work. The fabrication of this nanostructured electrode has been obtained thanks to electrostatic spray deposition and screen-printing techniques. The electrochemical measurements have been performed through a complete cell under SOEC mode. Thanks to a numerous of characterizations techniques (SEM, XRD, synchrotron), a better understanding of the behavior of  $PrO_{1.833}$  has been obtained. All these results are discussed in Chapter IV for this electrode.

## 7. References

- [1] C. Chen, Thin-Film Components for Lithium-Ion Batteries, Delft University of Technology, 1998.
- [2] C.H. Chen, E.M. Kelder, M.J.G. Jak, J. Schoonman, Electrostatic spray deposition of thin layers of cathode materials for lithium battery, Solid State Ionics. 86–88 (1996) 1301– 1306. https://doi.org/10.1016/0167-2738(96)00305-0.
- [3] I. Taniguchi, R.C. van Landschoot, J. Schoonman, Electrostatic spray deposition of Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.95</sub> and La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>2.87</sub> thin films, Solid State Ionics. 160 (2003) 271–279. https://doi.org/10.1016/S0167-2738(03)00149-8.
- [4] G. Constantin, C. Rossignol, J.-P. Barnes, E. Djurado, Interface stability of thin, dense CGO film coating on YSZ for solid oxide fuel cells, Solid State Ionics. 235 (2013) 36–41. https://doi.org/10.1016/j.ssi.2013.01.015.
- [5] R. K. Sharma, M. Burriel, L. Dessemond, J. M. Bassat, E. Djurado, Design of interfaces in efficient  $Ln_2NiO_{4+\delta}$  (Ln = La, Pr) cathodes for SOFC applications, J. Mater. Chem. A. 4 (2016) 12451–12462. https://doi.org/10.1039/C6TA04845E.
- [6] R. Neagu, D. Perednis, A. Princivalle, E. Djurado, Influence of the process parameters on the ESD synthesis of thin film YSZ electrolytes, Solid State Ionics. 177 (2006) 1981– 1984. https://doi.org/10.1016/j.ssi.2006.05.052.
- [7] D. Marinha, Nouvelles électrodes à architecture contrôlée pour piles à combustible à oxydes solides fonctionnant à température intermédiaire, These de doctorat, Grenoble INPG, 2010. https://www.theses.fr/2010INPG0110 (accessed March 29, 2023).
- [8] E. Djurado, A. Salaün, G. Mignardi, A. Rolle, M. Burriel, S. Daviero-Minaud, R.N. Vannier, Electrostatic spray deposition of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9+δ</sub> layers to be used as cathode materials for IT-SOFC, Solid State Ionics. 286 (2016) 102–110. https://doi.org/10.1016/j.ssi.2016.01.021.
- [9] G. Constantin, C. Rossignol, P. Briois, A. Billard, L. Dessemond, E. Djurado, Efficiency of a dense thin CGO buffer layer for solid oxide fuel cell operating at intermediate temperature, Solid State Ionics. 249–250 (2013) 98–104. https://doi.org/10.1016/j.ssi.2013.07.004.
- [10] R. Neagu, D. Perednis, A. Princivalle, E. Djurado, Zirconia coatings deposited by electrostatic spray deposition. Influence of the process parameters, Surf. Coat. Technol. 200 (2006) 6815–6820. https://doi.org/10.1016/j.surfcoat.2005.10.014.
- [11] A.M. Gañán-Calvo, J. Davila, A. Barrero, Current and droplet size in the electrospraying of liquids. Scaling laws, Journal of Aerosol Science. 28 (1997) 249–275.
- [12] C.W. Foster, R.O. Kadara, C.E. Banks, Fundamentals of Screen-Printing Electrochemical Architectures, in: C.E. Banks, C.W. Foster, R.O. Kadara (Eds.), Screen-Printing Electrochemical Architectures, Springer International Publishing, Cham, 2016: pp. 13– 23. https://doi.org/10.1007/978-3-319-25193-6\_2.
- [13] M.R. Somalu, A. Muchtar, W.R.W. Daud, N.P. Brandon, Screen-printing inks for the fabrication of solid oxide fuel cell films: A review, Renewable and Sustainable Energy Reviews. 75 (2017) 426–439. https://doi.org/10.1016/j.rser.2016.11.008.
- [14] EXAKT, EXAKT Advanced Technologies | Präzision für unsere Kunden, (n.d.). https://www.exakt.de/startseite/ (accessed November 10, 2022).

- [15] S. Uhlenbruck, T. Moskalewicz, N. Jordan, H.-J. Penkalla, H.P. Buchkremer, Element interdiffusion at electrolyte–cathode interfaces in ceramic high-temperature fuel cells, Solid State Ion. 180 (2009) 418–423. https://doi.org/10.1016/j.ssi.2009.01.014.
- [16] S.P.S. Badwal, Stability of solid oxide fuel cell components, Solid State Ionics. 143 (2001) 39–46. https://doi.org/10.1016/S0167-2738(01)00831-1.
- [17] G. Constantin, Interfaces et durabilité d'un cœur de pile à combustible à oxyde solide fonctionnant à température intermédiaire, n.d.
- [18] D. Marinha, C. Rossignol, E. Djurado, Influence of electrospraying parameters on the microstructure of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> films for SOFCs, J. Solid State Chem. 182 (2009) 1742–1748. https://doi.org/10.1016/j.jssc.2009.04.018.
- [19] R. Sharma, Innovative design of rare earth nickelates as cathodes for solid oxide fuel cells, (n.d.) 217.
- [20] O. Celikbilek, L. Dessemond, E. Djurado, State-of-the-Art La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-δ</sub> Cathode for SOFC: Microstructural and Electrochemical Properties, ECS Trans. 78 (2017) 747–758. https://doi.org/10.1149/07801.0747ecst.
- [21] Q. Fang, L. Blum, N.H. Menzler, Performance and Degradation of Solid Oxide Electrolysis Cells in Stack, J. Electrochem. Soc. 162 (2015) F907. https://doi.org/10.1149/2.0941508jes.
- [22] N.I. Khamidy, J. Laurencin, D. Ferreira Sanchez, F. Monaco, F. Charlot, E. Djurado, Durability of nanostructured LaPrNiO<sub>4+δ</sub> electrode for solid oxide cells: Electrochemical, microstructural, and structural investigation, J. Power Sources. 450 (2020) 227724. https://doi.org/10.1016/j.jpowsour.2020.227724.
- [23] N.I. Khamidy, Microstructure and durability of praseodymium-doped lanthanum nickelate for solid oxide cells, (n.d.) 184.
- [24] P. Courty, H. Ajot, C. Marcilly, B. Delmon, Powder Technology. (1973) 21-38.
- [25] R.K. Sharma, E. Djurado, An efficient hierarchical nanostructured Pr6O11 electrode for solid oxide fuel cells, J. Mater. Chem. A. 6 (2018) 10787–10802. https://doi.org/10.1039/C8TA00190A.
- [26] R.K. Sharma, N.I. Khamidy, L. Rapenne, F. Charlot, H. Moussaoui, J. Laurencin, E. Djurado, Highly efficient architectured Pr6O11 oxygen electrode for solid oxide fuel cell, J. Power Sources. 419 (2019) 171–180.
- [27] J. Rodriguez-Carvajal, Recent developments of the program FULLPROF, Comm. Powder Diffr. (2001) 12–19.
- [28] G. Ashiotis, A. Deschildre, Z. Nawaz, J.P. Wright, D. Karkoulis, F.E. Picca, J. Kieffer, The fast azimuthal integration Python library: pyFAI, J Appl Cryst. 48 (2015) 510–519. https://doi.org/10.1107/S1600576715004306.
- [29] W. De Nolf, F. Vanmeert, K. Janssens, XRDUA: crystalline phase distribution maps by two-dimensional scanning and tomographic (micro) X-ray powder diffraction, J Appl Cryst. 47 (2014) 1107–1117. https://doi.org/10.1107/S1600576714008218.
- [30] W. De Nolf, K. Janssens, Micro X-ray diffraction and fluorescence tomography for the study of multilayered automotive paints, Surf Interface Anal. 42 (2010) 411–418. https://doi.org/10.1002/sia.3125.

- [31] H. Schichlein, A.C. Müller, M. Voigts, A. Krügel, E. Ivers-Tiffée, Deconvolution of electrochemical impedance spectra for the identification of electrode reaction mechanisms in solid oxide fuel cells, Journal of Applied Electrochemistry. 32 (2002) 875–882. https://doi.org/10.1023/A:1020599525160.
- [32] A. Bertei, G. Arcolini, J.P. Ouweltjes, Z. Wuillemin, P. Piccardo, C. Nicolella, Physicallybased deconvolution of impedance spectra: interpretation, fitting and validation of a numerical model for lanthanum strontium cobalt ferrite-based solid oxide fuel cells, Electrochim. Acta. 208 (2016) 129–141. https://doi.org/10.1016/j.electacta.2016.04.181.
- [33] A. Nechache, M. Cassir, A. Ringuedé, Solid oxide electrolysis cell analysis by means of electrochemical impedance spectroscopy: A review, J. Power Sources. 258 (2014) 164– 181. https://doi.org/10.1016/j.jpowsour.2014.01.110.
- [34] J. Rutman, I. Riess, Placement of reference electrode in solid state electrolyte cells, Solid State Ionics. 179 (2008) 913–918. https://doi.org/10.1016/j.ssi.2008.01.071.
- [35] G. Sdanghi, L. Yefsah, F. Mauvy, E. Djurado, T. David, J.-M. Bassat, J. Laurencin, Reaction mechanisms of La<sub>2</sub>NiO<sub>4+δ</sub> oxygen electrodes operated in electrolysis and fuel cell mode, J. Electrochem. Soc. 169 (2022) 034518. https://doi.org/10.1149/1945-7111/ac58c3.

# Chapter III Reaction mechanisms of $La_2NiO_{4+\delta}$ oxygen electrode for SOCs
# Chapter III: Reaction mechanisms of La<sub>2</sub>NiO<sub>4+δ</sub> oxygen electrode for SOCs

The present chapter aims to provide a better understanding of the reaction mechanism for *over-stoichiometric* oxygen electrode material such as  $La_2NiO_{4+\delta}$  (LNO). For this purpose, a micro-scale model has been proposed to describe the kinetic of the oxygen oxidation/reduction reaction. It is based on an existing model developed and available at the laboratory for the classical *under-stoichiometric*  $La_{1-x}Sr_xCo_{y-1}Fe_yO_{3-\delta}$  (LSCF) [1-2]. The proposed stationary and dynamic numerical model is able to predict the experimental curves at the open circuit potential (OCP) but also under polarization. Electrochemical measurement and advanced 3D characterizations have been used for model calibration and validation. This work is divided into two parts:

#### Part I

This section introduces the basic numerical model to study the electrochemical behavior of LNO oxygen electrode. Electrochemical measurements performed in a 3-electrode setup including i-V curves and impedance spectra at various operating conditions (T = 650-750 °C,  $pO_2 = 0.15 - 1$  atm, and  $\pm 100$  mA cm<sup>-2</sup>) are also detailed. Microstructural data collected through a 3D reconstruction of the electrode by FIB-SEM tomography are also reported. These data are used as input parameters for model calibration and validation. The implemented model considers main reaction pathways, i.e. (i) the oxygen incorporation/excorporation at the gas/electrode interface for the "bulk path" and (ii) the direct charge transfer at the TPBIs for the "surface path" is described. Finally, the behavior of the LNO electrode is discussed for both anodic and cathodic polarization. This part of the work was done in a collaboration with Giuseppe Sdanghi, a post-doctorate who was in charge of the cell manufacturing as well as the development, calibration and validation of the LNO model published in the Journal of The Electrochemical Society (2022) [3].

#### Part II

In this section, it is proposed to compare the reaction mechanisms of the over-stoichiometric LNO material to the classical oxygen-deficient LSCF electrode. Indeed, in a previous study, Elisa Effori [4] extended a simplified LSCF model into a full elementary model, decomposed into six reaction steps, which take into account the oxygen species likely to be found on the

electrode surface [5]. This elementary model allowed us to go further in the analysis of the reaction phenomena by taking into account the impact of the oxygen partial pressure (pO2) on the electrode kinetics. Thus, notwithstanding the fact that the basic LNO model was able to reproduce the electrode performance, it has been extended to an elementary model in order to make a valid comparison between the two materials. For that purpose, the same set of input data used in the previous section has been used. The given equations for the LNO elementary model are detailed in Appendix I.

#### References

- [1] J. Laurencin, M. Hubert, K. Couturier, T.L. Bihan, P. Cloetens, F. Lefebvre-Joud, E. Siebert, Reactive mechanisms of LSCF single phase and LSCF-CGO composite electrodes operated in anodic and cathodic polarisations, Electrochim. Acta. 174 (2015) 1299–1316. https://doi.org/10.1016/j.electacta.2015.06.080.
- M. Hubert, J. Laurencin, P. Cloetens, J.C. da Silva, F. Lefebvre-Joud, P. Bleuet, A. [2] Nakajo, E. Siebert, Role of microstructure on electrode operating mechanisms for mixed ionic electronic conductors: synchrotron-based From 3D reconstruction to electrochemical 90-107. modeling, Solid State Ion. 294 (2016)https://doi.org/10.1016/j.ssi.2016.07.001.
- [3] G. Sdanghi, L. Yefsah, F. Mauvy, E. Djurado, T. David, J.-M. Bassat, J. Laurencin, Reaction mechanisms of La<sub>2</sub>NiO<sub>4+δ</sub> oxygen electrodes operated in electrolysis and fuel cell mode, J. Electrochem. Soc. 169 (2022) 034518. https://doi.org/10.1149/1945-7111/ac58c3.
- [4] E. Effori, J. Laurencin, E.D.R. Silva, M. Hubert, T. David, M. Petitjean, G. Geneste, L. Dessemond, E. Siebert, An elementary kinetic model for the LSCF and LSCF-CGO electrodes of solid oxide cells: impact of operating conditions and degradation on the electrode response, J. Electrochem. Soc. 168 (2021) 044520. https://doi.org/10.1149/1945-7111/abf40a.
- [5] J. Fleig, On the current–voltage characteristics of charge transfer reactions at mixed conducting electrodes on solid electrolytes, Phys. Chem. Chem. Phys. 7 (2005) 2027–2037. https://doi.org/10.1039/B501086A.

# Part I

# Reaction mechanisms of $La_2NiO_{4+\delta}$ oxygen electrodes operated in electrolysis and fuel cell mode

G. Sdanghi<sup>a,b\*</sup>, L. Yefsah<sup>b,c</sup>, F. Mauvy<sup>a</sup>, E. Djurado<sup>c</sup>, T. David<sup>b</sup>, J-M. Bassat<sup>a</sup>, J. Laurencin<sup>b</sup>

<sup>a</sup>CNRS, Univ. Bordeaux, ICMCB, 87 Av. Dr. Schweitzer, 33608 Pessac, France
 <sup>b</sup>Univ. Grenoble Alpes – CEA, LITEN, DTCH, 17 rue des Martyrs, 38054, Grenoble, France
 <sup>c</sup>CNRS, Univ. Grenoble Alpes, LEPMI, 1130 Rue de la Piscine, 38402, Saint Martin d'Hères, France

#### Abstract

The reaction mechanisms governing the electrochemical behavior of  $La_2NiO_{4+\delta}$  (LNO) oxygen electrodes for Solid Oxide Cells have been investigated through a coupled experimental and modeling approach. In this frame, a set of experiments was performed on a symmetrical cell using a three-electrode setup. A micro-scale electrode model considering two reaction pathways, i.e. bulk and surface paths, has been developed to describe the experimental results. The microstructural parameters of the electrode were obtained by FIB-SEM tomography. The model was calibrated using the experimental polarization curves measured at different temperatures, and it was validated using electrochemical impedance diagrams recorded at open circuit potential (OCP) and under polarization for different oxygen partial pressures.

It has been evidenced that the LNO reaction mechanism depends on both the temperature and the polarization. At OCP, the reaction mechanism is controlled by the bulk path at 650 °C and by the surface path at higher temperatures. A transition from the bulk path towards the surface path was observed under cathodic polarizations. These results have been interpreted by considering the evolution of the LNO over stoichiometry with the electrode polarization. The evolution of the electrode polarization resistance with the oxygen partial pressure has been also investigated.

Keywords: Oxygen electrode reaction, nickelates, SOFC, SOEC, Modeling, EIS, polarization curves.

\*Corresponding author: Telephone: +33 4 38 78 61 97, E-mail: giuseppe.sdanghi@cnrs.fr

#### 1. Introduction

Solid Oxide Cells (SOCs) are electrochemical devices that can be used either in fuel cell (SOFCs for Solid Oxide Fuel Cells) or electrolysis modes (SOECs for Solid Oxide Electrolysis Cells). Thanks to their high operating temperature (750°C-850°C), they can reach high electrical efficiencies without using expensive electrocatalysts [1]. The SOCs are composed of a thin and dense electrolyte classically made of Yttria Stabilized Zirconia (YSZ), which is sandwiched between two porous electrodes. The hydrogen electrode is usually a porous cermet of nickel and YSZ (Ni-YSZ), while Mixed Ionic and Electronic Conductors (MIECs) are currently used for the oxygen electrodes. Indeed, MIEC electrodes lead to improve the electrochemical properties of the SOCs [2,3] if compared to other types of the electrode [3–5]. In this frame, the lanthanum doped strontium cobalt ferrite La<sub>1-x</sub>Sr<sub>x</sub>Co<sub>y-1</sub>Fe<sub>y</sub>O<sub>3-δ</sub> (LSCF) is nowadays the most classical material employed as an oxygen electrode in commercial cells [6-9]. LSCF materials are oxygen deficient oxides, with a high electronic conductivity occurring by hole hopping and non-negligible ionic conduction involving oxygen vacancies. Although LSCF is well-suited for SOCs applications, this material suffers from chemical decomposition, consisting in migration and segregation of  $Sr'_{La}$  from the perovskite lattice resulting in the formation of a SrO insulating film at the LSCF surface, blocking the reactions of oxygen exchange herein [10,11]. These phenomena are known to decrease the SOC lifetime especially under electrolysis mode [11].

Considering another type of MIEC oxides, rare earth nickelates Ln<sub>2</sub>NiO<sub>4+δ</sub> (Ln = La, Pr, Nd), belong to an alternative promising family of materials with oxygen over stoichiometry [12]. The oxygen-excess crystalline structure of nickelates, which consists of alternating rock salts LnO and perovskite LnNiO<sub>3</sub> layers, can provide a very high mixed oxygen ionic and electronic conductivity ( $\approx$  100 S cm<sup>-1</sup> at 700 °C) [2,13] with fast oxygen reduction reaction kinetics [14– 19]. This structure has a strong ability to accept interstitial oxygen even at high temperature, which is located in the LnO rock-salt interlayers, thus maintaining structural stability [20]. The aforementioned features allow significantly improving the cell electrochemical performance, especially at intermediate temperatures (600-700°C). Out of all nickelates electrodes, La<sub>2</sub>NiO<sub>4+δ</sub> (LNO) is the most chemically stable in a wide range of temperature and oxygen partial pressure. Indeed, LNO always keeps a K<sub>2</sub>NiF<sub>4</sub>-type structure, the symmetry only changing from orthorhombic to tetragonal around 150 °C under air or 400 °C at *p*O<sub>2</sub>=10<sup>-4</sup> atm, as shown by Flura et al. [21]. Conversely, solid oxide materials rich in praseodymium were found to be chemically unstable in the temperature range 600-800 °C, since they progressively decompose into various perovskite-derived components, such as  $Pr_6O_{11}$ ,  $PrNiO_{3-\delta}$ ,  $Pr_4Ni_3O_{10+\delta}$ , and NiO [22,23]. Among the different studied nickelates,  $La_2NiO_{4+\delta}$  can be thus considered as the reference material.

In addition, both the electrode architecture and its microstructure play a key role in the electrochemical behavior of the MIEC-type electrodes. Therefore, several recent experimental studies have been devoted to optimize the LNO material [14,24-29]. Sayers et al. [24] have obtained a polarization resistance ( $R_{pol}$ ) value equal to 1  $\Omega$  cm<sup>2</sup> at 700 °C under air and at zero dc current for screen printed (SP) electrodes deposited on a dense Gadolinium-doped Ceria (GDC) electrolyte. Vibhu et al. [14] reported in the same experimental condition  $R_{pol} = 0.3 \Omega$ cm<sup>2</sup> for a SP electrode layered on a YSZ electrolyte. Besides, Nicollet et al. [25] have shown that preparing composite electrodes *via* the infiltration of LNO in a GDC backbone is a very promising manufacturing route to increase significantly the electrochemical performance of the SOFC cathodes. Indeed, the authors obtained  $R_{pol} = 0.38 \ \Omega \text{ cm}^2$  at 600 °C (under air and zero dc current) when using a YSZ electrolyte. Furthermore,  $R_{pol}$  decreased down to 0.29  $\Omega$  cm<sup>-2</sup> at 600°C when adding a GDC interlayer between the composite electrode and the YSZ electrolyte. Such a difference arises from the formation of a thick insulating La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> layer when the electrode is directly in contact with the electrolyte, downgrading the ionic transfer at the electrode/electrolyte interface. Sharma et al. [26] have measured  $R_{pol} = 0.42 \ \Omega \ \text{cm}^2$  at 600°C (under air and at zero dc current) when using LNO electrodes deposited on GDC electrolyte by Electrostatic Spray Deposition (ESD) topped by a SP LNO current collector. When a composite interface LNO/GDC was designed between this previous double-layered LNO electrode and GDC, a decrease of  $R_{pol}$  value down to 0.16  $\Omega$  cm<sup>2</sup> at 600°C was recorded [27].

The performances of the LNO oxygen electrode can thus be significantly improved by microstructural optimization. In this objective, a deep knowledge of the reaction mechanisms is necessary to identify the most adapted microstructure enhancing the electrode response. Therefore, several theoretical and experimental studies have been dedicated to investigating the electrochemical mechanisms of MIEC electrodes, especially for the LSCF material [30–34].

A general modeling framework describing the electrochemical behavior of MIEC oxygen electrodes (*i.e.* working either in fuel cell and electrolysis modes) has been already developed by our research group [32,35,36]. In the recent past, it has been applied to propose a microscale physically based model for both LSCF and composite LSCF-CGO electrodes. Such a model has been found to predict accurately the electrochemical response of the LSCF and LSCF-CGO porous electrodes, giving a thorough description of the reaction mechanism taking place herein.

Conversely to LSCF, the reaction mechanisms of LNO oxygen electrodes operating in both fuel cell and electrolysis modes are still not precisely understood [37,38]. Indeed, only a few experimental studies dealing with the electrochemical behavior of this electrode material under polarization are currently available in the literature [39]. Moreover, to the best of our knowledge, electrochemical models have not yet been proposed for over-stoichiometric materials such as nickelates.

The present work aims to better understand the reaction mechanisms occurring in LNO oxygen electrodes operating under both anodic and cathodic polarization through the aforementioned modeling approach adapted for the LNO material. For this purpose, experiments have been firstly performed by using a three electrodes setup. Polarization curves  $(\eta - i)$  have been recorded at different temperatures (650 – 750 °C) under air. EIS diagrams were also measured at the OCP and under both anodic and cathodic polarization. In addition, the impact of the oxygen partial pressures on the electrode performance has been also investigated at 700°C. The electrode microstructural properties have been extracted from 3D reconstruction obtained by Focused Ion Beam – Scanning Electron Microscopy (FIB-SEM) tomography. The polarization curves and the EIS diagrams at OCP and under cathodic and anodic polarization have been then simulated with the model. The impact of the temperature and the polarization on the reaction pathway have been investigated. The model has been also used to simulate the variation of the electrode polarization resistance with respect to the oxygen partial pressure.

#### 2. Materials and methods

#### 2.1 Description of the electrochemical cell

A symmetrical button cell (Figure 1) was manufactured with La<sub>2</sub>NiO<sub>4+ $\delta$ </sub> electrodes deposited by Screen-Printing (SP) on each side of a circular and dense 8YSZ electrolyte (diameter: 25 mm, thickness: 260 µm, provider: Neyco). The LNO powder was first prepared *via* the citratenitrate route (modified Pechini method) [40], from La<sub>2</sub>O<sub>3</sub> (Strem Chemical, 99,99%) and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Acros Organics, 99%) precursors. La<sub>2</sub>O<sub>3</sub> was pre-fired in the first step at 900 °C for 12 hours to remove the water content. Final annealing was performed at 1200 °C for 12 hours in the air to form the crystalline phase. A milling step by attrition was carried out to decrease the mean particle size of the powder to reach a particle size distribution ranging from 0.5 µm to 1 µm. Then, screen-printing terpineol-based slurries were prepared using LNO as well as Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>2- $\delta$ </sub> (CGO) powders (provided by Solvay company in this latter case). Indeed, a CGO barrier layer of 2  $\mu$ m of thickness was previously added by screen printing between LNO and 8YSZ to limit the formation of the insulating phase La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> between the electrode and the electrolyte (the sintering of the CGO layer was performed at 1300°C for 1h under air). The LNO containing slurry was used to deposit the electrodes on each side of the 8YSZ membrane. A two-step sintering process under air was then performed: (i) 400 °C for 1 h, with a heating rate of 1 °C min<sup>-1</sup>, which allowed removing the organic solvent; and (ii) 1150 °C for 1 h with a heating rate of 2 °C min<sup>-1</sup> to ensure the sintering on YSZ / CGO. The good adhesion between the cell layers has been checked on a cell cross-section observed by Scanning Electron Microscopy (SEM) (Figure S1a). To avoid any misalignment between the working and counter electrodes (WE and CE, respectively), special attention was paid to ensure the electrodes positioned on the electrolyte center. This feature is fundamental to avoid any perturbation and errors on the EIS measurements [41]. After manufacturing, the thickness of the LNO electrode was around 35 µm, while its diameter was ≈ 11.3 mm (thus the obtained surface area was around 1 cm<sup>2</sup>).



Figure 1: Three electrode setup with a symmetrical cell configuration

#### 2.2 Experimental setup and testing conditions

The electrochemical characterization of the symmetrical cell has been performed using a three electrodes setup, as shown in Figure 1. A platinum wire ring, used as a reference electrode (RE), was positioned on the upper surface of the electrolyte, on the periphery of the membrane (*i.e.*, the diameter of the Pt wire ring was  $\approx 25$  mm). To avoid as much as possible measurement artifacts due to the influence of the equipotential lines through the electrolyte on the RE, the distance between the WE and RE must be higher than three times the electrolyte thickness [42]. This requirement has been largely satisfied in the present work since the distance between the WE and RE is around 7 mm for an electrolyte thickness of 260 µm (Figure 1).

Two platinum grids with a mesh of 3600 meshes cm<sup>-2</sup> and a surface equal to that of the symmetrical electrodes were used as current collectors on both the WE and CE. A  $\approx$  1 mm thick disk in porous gold was also inserted between the ceramic housing and the platinum grids so that each electrode surface can be considered as equipotential. A weight of 0.7 kg was also applied to the setup. This assembly aimed to ensure the electric contact between the metallic grids and the ceramic electrodes.

To optimize the electric contacts and to stabilize the electrochemical response, the cell was first heated up to 800 °C with a heating rate of 1 °C min<sup>-1</sup> and then maintained at this temperature for 24 h, under air. The electrochemical measurements were carried out at 650 °C, 700 °C, and 750°C. A high inlet flow rate (total flow rate ~ 2 NL min<sup>-1</sup>) was used to avoid oxygen depletion within the electrode under operation. The O<sub>2</sub> and N<sub>2</sub> flow rates were adjusted to make  $pO_2$  varying in the range 0.15-1 atm.

The current density-voltage (*i*-*V*) curves measured between the electrodes and the reference (WE/CE *vs.* RE) were recorded first in SOEC mode, then in SOFC mode. Measurements were carried out from zero dc current to the highest polarization, then back to zero. The *i*-*V* curves were recorded in potentiostatic mode with a step of 2 mV s<sup>-1</sup>. In complementarity to the polarization curves, EIS measurements were performed in galvanostatic mode, *i.e.* at open circuit potential (OCP) and under anodic/cathodic dc current densities. The frequency range was scanned from 10<sup>6</sup> to 10<sup>-2</sup> Hz with a signal amplitude of ± 10 mA cm<sup>-2</sup> using an Autolab potentiostat/impedance frequency analyzer (PGSTAT 302N), equipped with a frequency response analyzer (FRA). The amplitude of the sinusoidal perturbation for the impedance measurements was chosen to remain in the linear regime of the cell response. From the EIS data, the ohmic and polarization resistances ( $R_s$  and  $R_{pob}$  respectively) have been obtained considering the intercepts of the impedance diagram with the real axis at high ( $R_s$ ) and low

frequencies ( $R_{tot} = R_s + R_{pol}$ ). The overpotential of the WE at each current density,  $\eta$ , has been determined by subtracting the ohmic drop to the corresponding dc voltage applied,  $E_{WR}$ . Therefore, the overpotential was calculated as  $\eta = E_{WR} - R_s \times i_{dc}$ . After the measurements, the cell was heated up again to 800 °C, under air, and for 12 hours, to check that no significant degradation (evidenced *via* the EIS characterizations) was induced during the test campaign.

#### 2.3 Microstructural characterization by FIB-SEM reconstruction

The microstructural parameters used in the model have been extracted from 3D reconstruction obtained by Focused Ion Beam - Scanning Electron Microscopy (FIB-SEM) tomography. The samples were first impregnated under vacuum conditions to fill the pores with an epoxy resin. This procedure allowed: (i) minimizing the undesirable damage of the specimen; (ii) avoiding the accumulation of gallium ions in the pores during the FIB milling and; (iii) improving the contrast between the porosity and the solid phases [43]. The serial sectioning and the image acquisition were carried out in a FEG-SEM NVISION 40 from Carl ZEISS® microscope. An energy selective backscatter (ESB) detector with a low acceleration voltage of 1.5 kV was used for the SEM observations. This condition allowed distinguishing the porosity and the solid phases. Then, images with a pixel size of 10 nm were acquired sequentially with a z-axis slice pitch of 10 nm using a milling current of 1.5 nA. After the acquisition, the images in the stack were aligned using the Matlab<sup>®</sup> software. Finally, the raw 3D images were filtered and thresholded as described in previous work [44]. A volume of 14.43  $\times$  18.72  $\times$  10.1  $\mu$ m<sup>3</sup> with a voxel size of 10 nm was selected. This resolution is sufficient to capture the small geometrical features of the electrode. The rendering volume for the reconstruction is shown in Figure 2 while a SEM image taken from the stack is given in the Supplementary Information (Figure S1b). As a first visual inspection, it is evidenced that the LNO microstructure appears homogeneous and quite typical of SOCs electrodes.

The microstructural properties needed for the model have been then computed thanks to a set of numerical tools already presented and thoroughly detailed in [45,46]. In this study, the specific surface area ( $S_p$ ), the phase connectivity ( $\delta$ ), the volume fraction for the percolated phases ( $\varepsilon$ ), the mean phase diameter ( $d_p$ ), the 'apparent' tortuosity factor ( $\tau$ ), and the density of the Triple Phase Boundary lines (TPBIs) ( $\xi_{TPBIs}$ ) have been calculated on the reconstruction. The microstructural properties for the LNO electrode are listed in Table 1. As a general matter, it is worth mentioning that the LNO microstructural properties drop within typical values for the SOCs electrodes [47].



Figure 2: 3D rendering volume for a cube of 10x10x10 µm<sup>3</sup> extracted from the whole LNO reconstruction.

Table 1: Microstructural parameters of the LNO electrode reconstructed via FIB-SEM

LNO electrode										
		Gas phase					MIEC (LNO)			
Properties	S <sub>p</sub> (μm <sup>-1</sup> )	δ <sub>gas</sub> (%)	8 (%)	d <sub>p</sub> <sup>(*)</sup> (μm)	τ <sub>gas</sub> (-)	S <sub>p</sub> (μm <sup>-1</sup> )	δ <sub>lno</sub> (%)	ε (%)	$d_{p}^{(*)}$ (µm)	τ <sub>lno</sub> (-)
FIB-SEM reconstructions	3.83	99.98	38.47	0.308	1.94	3.83	99.99	61.52	-	1.97
$\xi_{TPBls} (\mu m^{-1})$					2	.51				

<sup>(\*)</sup> mean phase diameter taken from the Phase Size Distribution

#### 3. Model description

The electrochemical behavior of the LNO electrode under anodic and cathodic polarization has been simulated by using an in-house model, which considers an equivalent homogenous medium of an isothermal slice (1D) of porous LNO including the CGO barrier. The proposed model can simulate the LNO electrode response for both stationary and dynamic behavior. Because of the importance of the electrode microstructure on its electrochemical behavior, the mass transport phenomena and the kinetic constants of each reaction have been scaled up with the microstructural parameters computed on the 3D reconstruction.

#### 3.1 Reaction mechanisms and kinetic rates

For the sake of clarity, the reaction mechanism is depicted in Figure 3 under anodic polarization (electrolysis mode) and is described hereafter. Regarding the oxygen electrode

reaction in the LNO electrodes, two parallel pathways are considered. Indeed, the oxygen oxidation/reduction reaction can occur at the two-phase (gas/electrode) as well as at the triple-phase (gas/electrode/electrolyte) boundaries lines (TPBIs)[48]. The former case (bulk path) considers an ionic transfer at the electrolyte/electrode interface to form interstitial oxygen,  $O_i$ , in the electrode bulk (R1) (see Table 2), with subsequent diffusion of the latter through the LNO bulk and a final oxygen excorporation (R2). On the other hand, the second scenario (surface path) considers that the charge transfer may proceed by reaction at the TPBIs (R3). Both reaction pathways lead to the formation of adsorbed oxygen atoms on the LNO surface. A final associative desorption step allows releasing oxygen gas molecules O<sub>2</sub> into the electrode porosity (R4). It is worth mentioning that the oxygen mass transfer by solid-state diffusion, the gaseous, and the adsorbed oxygen atom diffusions have been also considered in the model.



Figure 3: Schematic description of the reaction pathway considered in the model (in electrolysis mode).

All the reactions considered in the model and the corresponding kinetic rates are listed in Table 2 using the "Kröger-Vink notation". Each kinetic rate is expressed as the difference between the forward and the backward reactions. The reaction rate for the ionic transfer at the CGO/LNO interface (R1) describes the oxygen exchange from the CGO phase into the LNO electrode. Even if R1 is not an oxidation/reduction reaction, its kinetic rate can be expressed through a Butler-Volmer formalism as discussed in [49]. Indeed, R1 is affected by the electrode potential, E(z) corresponding to the difference in electronic potential  $\varphi_{LNO}(z)$  and ionic potential  $\varphi_{CGO}(z)$ :

$$E(z) = \varphi_{LNO}(z) - \varphi_{CGO}(z) = -\frac{\tilde{\mu}_{e,LNO}}{F} - \frac{\tilde{\mu}_{V_{O,CGO}}}{2F}$$
Eq. 1

where  $\tilde{\mu}_{e_{LNO}}$  and  $\tilde{\mu}_{V_{0,CGO}}$  denote the electrochemical potentials for the oxygen vacancies in CGO and for the electrons in LNO, respectively. In contrast to the ionic transfer, the oxygen exchange at the LNO surface (R2) is an oxidation/reduction reaction. However, as detailed in [32] for the LSCF, its reaction rate can be expressed as a pure chemical reaction since only neutral adsorbed oxygen atoms are considered on the electrode surface [49]. The charge transfer at the TPBIs (R3) is a classical electrochemical reaction and its kinetic rate has been expressed according to the Butler-Volmer formalism. Finally, the associative desorption (R4) generates O<sub>2</sub> gaseous molecules in the pores of the electrode. As it is a pure chemical reaction, its kinetic rate depends only on the activity of the adsorbed species and the oxygen partial pressure. It can be noticed that an ideal solution for the surface species has been assumed in the model. In that condition, the activity of the adsorbed oxygen atoms is given by the product of the number of available sites on the LNO surface,  $\Gamma$ , and the surface coverage,  $\theta_{o_{s,LNO}}$ . In other words, a Langmuir hypothesis is adopted in the model so that  $\theta_{s,LNO} + \theta_{o_{s,LNO}} = 1$ .

All the kinetic rates have been scaled up by considering the electrode morphological properties. For instance, the oxygen excorporation reaction (R2) and the desorption one (R4) are dependent on the LNO/gas specific surface area,  $S_p^{LNO/gas}$ , since they both take place on the electrode surface. Conversely, the charge transfer reaction at TPBIs (R3) is directly proportional to the density of active TPBIs,  $\xi_{TPBIs}$ . Finally, the ionic transfer reaction at the electrode/electrolyte interface (R1) depends on the CGO/LNO specific surface area,  $S_p^{CGO/LNO}$ . All the reactions are supposed to be thermally activated. Therefore, each kinetic constant is supposed to depend on the temperature according to Arrhenius's law.

Table 2: Reactions and expressions of the kinetics rates

]	Reactions	Kinetic rates	
R1	$O_0^{X}(CGO) + V_i^{X}(LNO) \stackrel{k_+}{\leftrightarrow} V_0^{\bullet}(CGO) + O_i^{\prime\prime}(LNO)$ $k$	$ \begin{aligned} \nu_{(1)} &= S_p^{CGO/LNO} \left\{ k_+ \exp\left(\frac{2\alpha_{(1)}^{ox}FE}{RT}\right) \left(1 - \frac{c_{o_l'}}{c_{o_l'}^{max}}\right) \\ &- k \exp\left(\frac{-2\alpha_{(1)}^{red}FE}{RT}\right) \left(\frac{c_{o_l'}}{c_{o_l'}^{max}}\right) \right\} \end{aligned} $	Eq. 2
R2	$\begin{array}{ccc} & & & & & & & & & \\ O_i^{\prime\prime}(LNO) + s_{,LNO} & & & & & & \\ & & & & & & \\ & & & & & $	$\begin{aligned} v_{(2)} &= S_p^{LNO/gas} \left\{ k_{ox}^{LNO/gas} \Gamma(1 - \theta_{O_{s,LNO}}^{eq}) \frac{c_{0''}}{c_{0''}^{max}} \\ &- k_{red}^{LNO/gas} \Gamma \theta_{O_{s,LNO}}^{eq} \left( 1 - \frac{c_{0''}}{c_{0''}^{max}} \right) \right\} \end{aligned}$	Eq. 3
R3	$O_{O}^{X}(CGO) + s_{LNO} \stackrel{k_{OX}^{TPB}}{\underset{k_{red}}{\leftrightarrow}} V_{O}^{\bullet\bullet}(CGO) + 2e^{-}$ $+ O_{s,LNO}$	$v_{(3)} = \xi_{TPBs} \left\{ k_{ox}^{TPB} \exp\left(\frac{2\alpha_{(3)}^{ox}FE}{RT}\right) \Gamma\left(1 - \theta_{o_{s_{LNO}}}^{eq}\right) - k_{red}^{TPB} \exp\left(\frac{-2\alpha_{(3)}^{red}FE}{RT}\right) \Gamma\theta_{o_{s_{LNO}}}^{eq} \right\}$	Eq. 4
R4	$O_{s,LNO} \stackrel{k_{des}}{\underset{k_{ads}}{\leftrightarrow}} \frac{1}{2}O_{2,gas} + s_{LNO}$	$v_{(4)} = S_p^{LNO/gas} \left\{ k_{des} \Gamma \theta_{O_{S_{LNO}}}^{eq} - k_{ads} P_{O_2}^{1/2} \Gamma (1 - \theta_{O_{S_{LNO}}}^{eq}) \right\}$	Eq. 5

#### 3.2 Thermodynamic description

In the model, the forward and backward kinetic constants for each reaction are linked through the thermodynamic equilibrium constants according to the expressions listed in Table 3, which represent the reaction quotients at the equilibrium state. In these equations, the electrode potential at equilibrium,  $E^{eq}$ , is equal to the chemical potential of oxygen in the gas phase taken at the reference electrode (i.e.,  $E^{eq} = \frac{\tilde{\mu}_{O_{2,gas}}^{ref}}{4F}$ , as discussed in [50]). The surface coverage of the adsorbed oxygen atoms at equilibrium,  $\theta_{O_{s,LNO}}^{eq}$ , is considered as a model input parameter at  $pO_2=0.21$  atm, and it is obtained by fitting the experimental polarization curves. Moreover, the oxygen coverage is assumed as independent of the temperature. This hypothesis is justified as long as the oxygen coverage remains low on the surface sites, with no restriction. Knowing  $\theta_{O_{s,LNO}}^{eq}$  at  $pO_2=0.21$  atm, the equilibrium constant  $K_e^{(4)}$  can be determined, and hence, the evolution of  $\theta_{O_{s,LNO}}^{eq}$  as a function of the oxygen partial pressure can be computed with Eq. 9.

To calculate the composition at equilibrium, the concentration of interstitial oxygen  $c_{O''_i}{}^{eq}$  is determined as a function of the temperature using the available data of the oxygen over stoichiometry,  $\delta^{eq}$ , and the volume of the lattice unit-cell,  $V(c_{O''_i}{}^{eq} = \delta^{eq}/V)$  at  $pO_2 = 0.21$  atm [51]. This approach allows calculating the thermodynamic equilibrium constant  $K_e^{(2)}$  at the three

investigated temperatures. Hence, the evolution of  $c_{o''}{}^{eq}$  as a function of the oxygen partial pressure can be computed at each temperature by using Eq. 7.

Finally, the thermodynamic equilibrium constants  $K_e^{(1)}$  and  $K_e^{(3)}$  are calculated with Eqs. 6 and 8 by using the data at equilibrium.

Thern	nodynamic equilibrium constants	
R1	$K_{e}^{(1)} = \frac{k_{+}}{k_{-}} = \frac{c_{O_{i'}}e^{eq}}{\left(c_{O_{i'}}max,eq - c_{O_{i'}}e^{q}\right)}exp\left(\frac{-2FE^{eq}}{RT}\right)$	Eq. 6
R2	$K_{e}^{(2)} = \frac{k_{ox}^{LNO/gas}}{k_{red}^{LNO/gas}} = \frac{\theta_{O_{s_{LNO}}}^{eq}}{1 - \theta_{O_{s_{lNO}}}^{eq}} \frac{\left(c_{O_{i}^{\prime\prime}}^{max,eq} - c_{O_{i}^{\prime\prime}}^{eq}\right)}{c_{O_{i}^{\prime\prime}}^{eq}}$	Eq. 7
R3	$K_e^{(3)} = \frac{k_{ox}^{TPB}}{k_{red}^{TPB}} = \frac{\theta_{O_{s,LNO}}}{1 - \theta_{O_{s,LNO}}} eq exp\left(\frac{-2FE^{eq}}{RT}\right)$	Eq. 8
R4	$K_{e}^{(4)} = \frac{k_{des}}{k_{ads}} = \frac{1 - \theta_{O_{s_{LNO}}}}{\theta_{O_{s_{LNO}}}} (P_{O_{2}}^{eq})^{1/2}$	Eq. 9

Table 3: Equations for the thermodynamic equilibrium constants

#### 3.3 Transport phenomena and conservation equations

The equations related to the fluxes, currents, mass, and charges balances, which are taken into account in the model, are given in Table 4. The ionic current in CGO and the electronic current in LNO have been computed using a classical Ohm's law. Specifically, the electronic conductivity in LNO has been assumed to be independent of the temperature, whereas a power law was considered to take into account its evolution with the  $pO_2$ , i.e.,  $\sigma_{e^-} = \sigma_0 (p_{O_2})^k$ . According to the data reported by Jeon et al. [52], the exponent k of the aforementioned power law is roughly about 1/10 within the range of  $pO_2$  considered in the present study, i.e., 0.15 - 1atm.

The transport of the interstitial oxygen in the LNO lattice has been modeled using a classical Fick's law through chemical diffusivity depending on the oxygen partial pressure:

$$D_{chem} \approx \gamma \cdot D_{O_i''} = -\frac{1}{2} \frac{\partial \ln(p_{O_2})}{\partial \ln(c_o)} \cdot D_{O_i''}$$
 Eq. 10

In Eq. 10,  $\gamma$  is the so-called thermodynamic factor with  $C_o = (4 + \delta^{eq})/V$ . It can be noticed that the oxygen self-diffusion coefficient,  $D_{o''_i}$ , is directly related to the oxygen tracer

coefficient through  $D^* = f \cdot D_{o''_i}$ , where *f* is the correlation factor. When it is assumed that oxygen diffuses *via* an interstitial mechanism, as in the specific case of LNO electrodes, *f* can be approximated to the unity [53]. Therefore,  $D_{chem}$  was calculated through Eq. 10 by using the available data for  $D^*$  provided by Li et al. [54].  $D^*$  is thermally activated, and can be described by an Arrhenius's law. According to the authors, the corresponding activation energy is  $E_a \approx 90$  kJ mol<sup>-1</sup>.

The diffusivity of the oxygen adsorbed on the LNO surface,  $D_{Os}$ , as well as the ionic conductivity of the CGO barrier,  $\sigma_{CGO}$ , have been also supposed to be thermally activated. The evolution of  $\sigma_{CGO}$  as a function of the temperature was taken into account in the model using activation energy of  $E_a = 65$  kJ mol<sup>-1</sup>, as proposed in [55]. On the other hand, there is still a lack of information about the diffusivity of the oxygen atoms adsorbed on the LNO surface. Therefore, it has been considered as a model input parameter and obtained by fitting the experimental polarization curves.

It is important to highlight that all the effective transport parameters (*i.e.*, the effective conductivities and diffusivities) have been expressed as a function of their intrinsic values and the electrode microstructural parameters listed in Table 1.

Finally, the gas transport in the electrode porosity has been computed in the frame of the Dusty Gas Model (DGM), combining the molecular and the Knudsen diffusion. The binary coefficient  $D_{O_2,N_2}$  can be expressed according to Fuller's theory as follows (Eq. 11):

$$D_{O_2,N_2} = \frac{0.00143}{P_{tot} \cdot \left( \left( V_{O_2} \right)^{1/3} + \left( V_{N_2} \right)^{1/3} \right)^2 \cdot \sqrt{\frac{2}{\frac{1}{M_{O_2}} + \frac{1}{M_{N_2}}}} \cdot T^{1.75}$$
Eq. 11

where  $M_i$  is the molar mass for the gas species and  $V_i$  the Fuller diffusion volume, which can be found in [56]. On the other hand, the Knudsen coefficient is given by:

$$D_{k,O_2} = \bar{r}_{pores} \cdot \frac{2}{3} \sqrt{\frac{8 \cdot RT}{\pi M_i}}$$
 Eq. 12

where  $\bar{r}_{pores}$  is the mean pore radius.

The set of equations for the reaction rates (Eqs. 2-5), charge and mass balances (Eqs. 18-22) and the corresponding fluxes (Eqs. 13-17) represents a set of Partial Differential Equations (PDEs) that have been solved in the time domain by the Finite Element Method (FEM). The used boundary conditions for each calculated species are given in Table 5. The methodology for the calculations of the EIS diagrams has been thoroughly described elsewhere [33].

Table 4: Equations of charge and mass conservations associated with the current and fluxes taken into account in the physically-based model

Electrode						
Transport phenomena		Conservation equations				
$\vec{N}_{O_i''} = -\frac{\varepsilon_{LNO}}{\tau_{LNO}} D_{chem} \times \vec{\nabla} c_{O_i''}$	Eq. 13	$\vec{\nabla} \cdot \vec{N}_{O_{i}^{\prime\prime}} = -\nu_{(2)} - \varepsilon_{LNO} \frac{\partial c_{O_{i}^{\prime\prime}}(z,t)}{\partial t}$	Eq. 18			
$\vec{N}_{O_{s_{LNO}}} = -S_p^{LNO/gas} \cdot D_{O_{s_{LNO}}} \cdot \Gamma \cdot \vec{\nabla} \theta_{O_{s_{LNO}}}$	Eq. 14	$\vec{\nabla} \cdot \vec{N}_{O_{s_{LNO}}} = \left(\nu_{(2)} - \nu_{(4)}\right) \\ - S_p^{LNO/gas} \Gamma \frac{\partial \theta_{O_{s_{LNO}}}(z, t)}{\partial t}$	Eq. 19			
$\vec{\nabla}y_{O_2} = -\frac{RT}{P_t} \left( \frac{\vec{N}_{O_2}}{\frac{\varepsilon_{pores}}{\tau_{pores}} D_{k,O_2}} + \frac{\vec{N}_{O_2} y_{N_2}}{\frac{\varepsilon_{pores}}{\tau_{pores}} D_{O_2,N_2}} \right)$	Eq. 15	$\vec{\nabla} \cdot \vec{N}_{O_2} = \frac{1}{2} \nu_{(4)} - \frac{\varepsilon_{pores}}{RT} P_t \frac{\partial y_{O_2}(z,t)}{\partial t}$	Eq. 20			
$\vec{\iota}_{e^-} = -\frac{\varepsilon_{LNO}}{\tau_{LNO}} \sigma_{e^-} \times \vec{\nabla} \varphi_{LNO}$	Eq. 16	$\vec{\nabla} \cdot \vec{N}_{O_2} = \frac{1}{2} \nu_{(4)} - \frac{\varepsilon_{pores}}{RT} P_t \frac{\partial y_{O_2}(z,t)}{\partial t}$	Eq. 21			
	-	Electrolyte				
$\vec{\iota}_{io} = -\sigma_{io,CGO} \times \vec{\nabla} \varphi_{CGO}$	Eq. 17	$\vec{\nabla} \cdot \vec{i}_{io} = 0$	Eq. 22			

Table 5: Boundary conditions for the simulations

Species		Boundary	Conditions			
	z = 0	$z = \ell_{CGO}$		$z = \ell_{LNC}$	)	
<i>O</i> ''	n.a.*	$N_{O_i''} = v_{(1)}$	Eq. 23	$N_{O_i'' z=L} = 0$	Eq. 28	
O <sub>SLNO</sub>	n.a.	$N_{O_{S_{LNO}}, local} = v_{(3)}$	Eq. 24	$N_{O_{S_{LNO}} z=L} = 0$	Eq. 29	
02	n.a.	$N_{O_2,local} = 0$	Eq. 25	$C_{O_2 z=L} = \frac{P_{O_2}}{RT}$	Eq. 30	
Electronic current in LNO, e <sup>-</sup>	n.a.	$i_{e^{-,local}}$ $= -2Fv_{(3)} + S_p^{CGO/LNO}C_{dl}\frac{\partial E}{\partial t}$	Eq. 26	$\varphi_{e^- z=L}=0$	Eq. 31	

		i <sub>io,local</sub>			
Ionic current in CGO,	imposed	$= +2F(\nu_{(1)} + \nu_{(3)})$	Ea 27	na	Ea 32
$i_0$	mposed	$\delta E^{CGO/LNO} \partial E$	Eq. 27	11.0.	Eq. 52
		$-S_p$ $C_{dl} \frac{\partial t}{\partial t}$			

\*n.a. = Not applicable

#### 4. Experimental results and model validation

#### 4.1Experimental results

The experimental electrode polarization curves  $\eta = f(i)$  measured at 650 °C, 700 °C and 750 °C under air are shown in Figurea. As expected, the electrode overpotential significantly decreases when increasing the temperature for a given current density, meaning that the LNO performance is strongly thermally activated. Indeed, under SOEC conditions, an overpotential equal to +0.055 V/Pt/air was recorded at 650 °C and 0.1 A cm<sup>-2</sup>, whereas a value of +0.02 V/Pt/air was obtained in the same condition at 750 °C. Hence, a relative decrease of about 64% was achieved. A higher improvement can be observed under cathodic polarization (SOFC mode). The overpotential obtained at 750 °C and -0.1 A cm<sup>-2</sup> is about four times lower than that obtained at 650 °C (-0.021 vs. -0.091 V/Pt/air, thus giving a decrease of around 77%).

The polarization curves present a dissymmetry with respect to the OCP at 700 °C and 650°C, in full agreement with the results reported by Tong et al. [39] for LNO electrodes. In other words, the performance of the LNO electrode is higher in anodic conditions, thus for electrolysis application. On the other hand, the polarization curve exhibits an almost linear behavior at 750 °C. This result is likely due to the narrow investigated overpotentials range, which is not sufficiently extended to detect a change in the slope. The strong dissymmetry of the polarization curve detected at 650°C is better highlighted in the  $R_{pol} = f(\eta)$  plot (Figureb). This behavior may suggest a change either in the reaction mechanism or in the rate-determining step under these conditions, which would be triggered under cathodic polarization. On the other hand, the linearity of the polarization curve observed at 750 °C and in the range of considered overpotentials may suggest the presence of a unique dominant mechanism with the same co-limitations whatever the polarization.



Figure 4: a) Experimental (marks) and simulated (solid lines) polarization curves obtained at 650, 700, and 750 °C under air for LNO electrodes. b) Experimental LNO electrode polarization resistance plotted a function of the electrode overpotential for the three investigated temperatures

To go further in the analysis, EIS diagrams have been acquired at OCP under air for the three investigated temperatures (Figure 5). The measured electrode polarization resistance was found to decrease from 0.78  $\Omega$  cm<sup>2</sup> at 650°C down to 0.20  $\Omega$  cm<sup>2</sup> at 750°C, in good agreement with the polarization curves. The obtained EIS diagrams present a kind of Gerischer-type element at 650 °C, whereas they exhibit a more depressed semi-circle at higher temperatures (700 and 750°C). The recorded change in the shape of the open circuit EIS diagrams when increasing the temperature is in full agreement with the results of Tong et al. [39]. This evolution suggests that the reaction mechanism at zero dc current is significantly affected by the temperature. Indeed, the characteristic frequency also increases when increasing the temperature (i.e.,  $f_c \approx 11$  Hz, 19 Hz, and 46 Hz at 650 °C, 700 °C, and 750 °C, respectively), as shown in the diagrams reported in Figure 5d to 5f. This behavior has been also observed with LSCF oxygen electrodes [9,35,57].



Figure 5: Experimental (marks) and simulated (solid lines) EIS diagrams for the LNO electrodes at OCP under air. Nyquist plots for: (a) 650 °C, (b) 700 °C and (c) 750 °C. Bode plot for: (d) 650 °C, (e) 700 °C and (f) 750 °C.

The EIS diagrams were also recorded under both anodic and cathodic polarization at intermediate temperature, *i.e.* at 700 °C (Figure 6). Although the EIS diagram recorded under "high" anodic polarization (+100 mA cm<sup>-2</sup>) appears to be slightly depressed, the global shape does not completely change in the investigated range of overpotentials. The values for the characteristic frequencies under cathodic polarization were only slightly higher than those obtained under anodic polarization (i.e.  $f_c \approx 23$  Hz at  $i_{dc} = -100$  A cm<sup>-2</sup> and  $f_c \approx 19$  Hz at  $i_{dc} = +100$  A cm<sup>-2</sup>). However, these values remain quite close to each other. These observations may suggest that no changes in the reaction mechanism arise at an intermediate temperature in LNO electrodes in the range of investigated polarizations ( $i_{dc} = +/-100$  mA cm<sup>-2</sup>). It is worth mentioning that the aforementioned behavior observed for the LNO electrode is radically different from that observed for the LSCF electrodes [36]. In the latter case, the shape of the EIS diagrams was found to change from a well-defined Gerischer element at OCP towards a semi-circle under anodic current. Hence, this change was explained by a modification of the dominant reaction mechanism.



Figure 6: Experimental (marks) and simulated (solid lines) EIS diagrams at 700 °C under air for  $i_{dc} = -100 \text{ mA cm}^{-2}$ ,  $-50 \text{ mA cm}^{-2}$ ,  $+50 \text{ mA cm}^{-2}$  and  $+100 \text{ mA cm}^{-2}$ . (a-d) Nyquist plots and (e-h) Bode plots.

In addition to the experimental characterization previously described, the effect of the oxygen partial pressure on the LNO electrode response has been also investigated. Figure 7a shows the impedance diagrams in the Nyquist plots obtained at intermediate temperature (700°C) and OCP recorded in the  $pO_2$  range of 0.15 - 1 atm and from  $10^{-1}$  to  $10^3$  Hz. As expected, the electrode polarization resistance decreases when increasing the oxygen partial pressure. For instance, a value of about 0.41  $\Omega$  cm<sup>2</sup> was obtained at  $pO_2 = 0.21$ , whereas a lower value (0.28  $\Omega$  cm<sup>2</sup>) was measured at  $pO_2$  of 1 atm. Based on kinetic considerations, the relationship between the electrode polarization resistance,  $R_{pol}$ , and the oxygen partial pressure has been considered, using the following power law:

$$\frac{1}{R_{pol}} \propto p_{O_2}^{n}$$
 Eq. 33

When plotting  $R_{pol}$  as a function of  $pO_2$ , a power law with an exponent *n* close to 1/4 ( $\approx 0.23$ ) was obtained at 700°C and OCP (Figure 7b). To the best of our knowledge, no values of the

exponent *n* were reported for the LNO oxygen electrode yet. Indeed, only a few experimental studies dealing with the electrochemical behavior of this electrode material at OCP are currently available in the literature. Very few studies consist in fitting the impedance diagrams using an equivalent circuit with several contributions in series, each composed of resistance in parallel with a constant phase element (R//CPE) [37,38]. This approach is different than the one used in the present study. Therefore, the results obtained cannot be directly compared.



Figure 7: a) Impedance diagrams (Nyquist plots) recorded for the LNO electrode at 700°C for the investigated range of oxygen partial pressure (marks = experimental; solid lines = simulation).
b) Experimental and simulated polarization resistance plotted as a function of the oxygen partial pressure in logarithmic coordinates (at 700°C).

#### 4.2 Calibration and validation of the electrochemical model

For the electrochemical simulations, all the microstructural parameters were obtained from the 3D reconstruction of the LNO electrode (Table 1).

Concerning the transport properties for the mass and the charge transfer, the oxygen molecular diffusion, as well as the Knudsen diffusion coefficient, were calculated as a function of the temperature by using Equations 11 and 12, respectively. The evolution of the chemical diffusivity  $D_{chem}$  as a function of the oxygen partial pressure was calculated using Eq. 10 while its temperature dependence was evaluated with the activation energy reported in [54]. The evolution of the electronic conductivity in LNO,  $\sigma_{e^-}$ , as a function of the oxygen partial pressure was obtained from the available data in [52]. Specifically, a pre-factor  $\sigma_0 \approx 86$  S cm<sup>-</sup>

<sup>1</sup> and an exponent k of 0.07 were used. The evolution of the ionic conductivity in CGO with temperature was taken from [55] with an activation energy of 65 kJ mol<sup>-1</sup>. Conversely, the diffusivity of the adsorbed oxygen on the LNO surface was considered as a model input parameter.

Concerning the thermodynamic calculation, the LNO oxygen over stoichiometry data,  $\delta^{eq}$ , as a function of the temperature and at  $pO_2 = 0.21$  atm were taken from Nakamura et al. [51]. The lattice unit cell volume, V, was taken from Flura et al. [21]. The resulting data for  $c_{O_i'}{}^{eq}$  at the three investigated temperatures and  $pO_2 = 0.21$  atm are provided in Table 4. On the other hand, the maximum amount of over-stoichiometric oxygen in LNO was calculated through the balance of the oxygen and interstitial sub-lattice sites as proposed in [58–60]. Hence, it was supposed that the LNO saturation in interstitial oxygen is reached when  $\delta^{max} \approx 2$ .

For the transient simulations, the CGO/LNO double-layer capacitance,  $C_{dl}$ , has been fixed at 50 µF cm<sup>-2</sup>, as estimated by Monaco et al. [36] for LSCF electrodes. Indeed, there is still a lack of information about the  $C_{dl}$  for LNO electrodes.

Regarding the kinetic parameters, the ionic transfer reaction at the CGO/LNO interface (R1) has been considered as not limiting ( $k_+ \gg 0$ ) (see Table 4). On the other hand, the kinetic constants for the oxygen incorporation/excorporation reaction (R2), the direct oxidation/reduction reaction at the TPBIs (R3), and the adsorption/desorption reaction (R4) are unknown.

As a summary, the undetermined parameters are the pre-exponential factor and the activation energy of the Arrhenius law for the three kinetic constants and the oxygen surface diffusivity along with the surface coverage of the adsorbed oxygen atoms at equilibrium,  $\theta_{O_{s,LNO}}^{eq}$ , at  $pO_2 =$ 0.21 atm. These unknown parameters were determined by fitting the simulated data on the experimental polarization curves at the three investigated temperatures. All the model input and fitted values of the different parameters are listed in Table 4.

The polarization curves computed with the input parameters listed in Table 4 are compared to the experimental data in Figure 4a. As a general comment, a quite good agreement was achieved between the simulations and the experiments for each temperature. To validate the model, EIS diagrams were computed in the same conditions as the experiments without additional fitting. The calculated and experimental EIS diagrams are compared in the Nyquist plot at OCP and under polarization in Figure 5a-c and Figure 6a-d, respectively. It can be observed that the model can reproduce quite accurately the shape of the experimental EIS diagrams whatever the temperature or the polarization.

In addition, for the impedance spectra in the Bode plots, the computed and experimental frequency distributions at 700°C are compared in Figure 5d-f at OCP and in Figure 6e-h under polarization. Concerning the measurements at OCP, it can be observed that the model can reproduce the increase of the characteristic frequency with the temperature. On the other hand, the slight increase of the characteristic frequency when shifting from anodic towards cathodic polarization is also well retrieved with the model. Both behaviors can be explained by the larger contribution of the direct oxidation/reduction at TPBIs over the excorporation/incorporation reactions when increasing the temperature and when increasing the dc current in the sense of cathodic polarization. This behavior will be discussed in the next section. Nevertheless, a frequency lag is observed between the simulated and the experimental diagrams. The same behavior has been also observed for LSCF electrodes [36]. The origin of this discrepancy is still not completely understood. It might be due to the uncertainty in the determination of the microstructural parameters by the 3D reconstruction. Indeed, it has been shown that the electrode microstructure can have an important impact on the frequency response [9,61]. Moreover, the frequency lag between the simulations and the experiments could be also due to the impact of the contact resistances, which are attributed to non-optimal contact between the electrode and the current collector, on the polarization resistance. This possibility is discussed in the next section.

To go further in the validation, the model has been also used to simulate the LNO electrode response when operated under different oxygen partial pressures. With this aim, EIS diagrams have been computed at OCP and intermediate temperature (700 °C) in the range of pressures of 0.15 - 1 atm. The simulated electrode polarization resistance,  $R_{pol}$ , has been plotted as a function of  $pO_2$  in logarithmic coordinates and compared to the experimental results (Figure 7a. It can be seen that the model predicts accurately the decrease of  $R_{pol}$  when increasing the oxygen partial pressure. This good agreement is also found for the exponent of the power-law used to fit both the experimental and the simulated data (Eq. 33), even if a slight difference between the two values has been found (0.21 vs. 0.23 for the simulated and experimental n, respectively). This slight discrepancy may be due to the model assumptions considering only atomic oxygen adsorbates on the electrode surface. Indeed, according to Fleig et al. [62], the prediction of the electrode response as a function of  $pO_2$  is particularly improved by taking into account charge species on the MIEC surface with a full elementary description of the reaction mechanism.

As a general comment, the polarization curves for the LNO electrode have been accurately fitted by the model for the determination of the missing parameters. Once calibrated, the model was able to predict quite accurately the EIS diagrams at different temperatures ( $650 - 750^{\circ}$ C) and polarization (between – 100 mA cm<sup>-2</sup> and + 100 mA cm<sup>-2</sup>), without any additional fitting. Moreover, the electrochemical response of the LNO with the change of *pO*<sub>2</sub> has been also predicted in good agreement with the experimental results. Despite a systematic lag in the frequency distribution, the capacity of the model to reproduce the response of the LNO electrode allows validating the main model assumptions.

INPUT PARAMETERS						
Parameter		650 °C	700 °C	750 °C		
<i>c<sub>0''</sub></i> <sup>eq</sup>	/ mol m <sup>-3</sup>	450.64	427.78	405.98		
$C_{O_i''}^{max,eq}$	/ mol m <sup>-3</sup>	8118.52	8127.44	8134.54		
$\sigma_{el}$	/ S m <sup>-1</sup>	7706.85	7706.85	7706.85		
$\sigma_{CGO}$	/ S m <sup>-1</sup>	1.95	2.87	4.05		
Γ	/ mol m <sup>-2</sup>	1.10-5	1.10-5	1.10-5		
$C_{dl}$	/ F m <sup>-2</sup>	0.5	0.5	0.5		
$D_{chem}$	$/ m^2 s^{-1}$	$2.04 \cdot 10^{-10}$	$3.7 \cdot 10^{-10}$	$6.37 \cdot 10^{-10}$		

Table 6: Input parameters used to fit the experimental data ( $pO_2 = 0.21$  atm)

FITTED PARAMETERS							
Parameter	650 °C	700 °C	750 °C	E <sub>a</sub> [kJ mol <sup>-1</sup> ]			
$ heta^{eq}_{O_{S_{LNO}}}$ / -	4.6.10-5	4.6.10-5	4.6·10 <sup>-5</sup>	-			
$D_{Os}$ / m <sup>2</sup> s <sup>-1</sup>	$4 \cdot 10^{-6}$	6·10 <sup>-6</sup>	9·10 <sup>-6</sup>	63			
$k_{+}$ / mol m <sup>-2</sup> s <sup>-1</sup>	NOT	NOT	NOT	_			
	LIMITING	LIMITING	LIMITING				
$k_{ox}^{LNO/gas}$ / m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	34	43	75	62			
$k_{ox}^{TPB}$ / m s <sup>-1</sup>	6·10 <sup>-5</sup>	$1.5 \cdot 10^{-4}$	$3.7 \cdot 10^{-4}$	142			
$k_{ads}$ / atm <sup>-0.5</sup> s <sup>-1</sup>	$8 \cdot 10^4$	$2 \cdot 10^{5}$	$4 \cdot 10^5$	126			

#### 5. Discussion

### 5.1Effect of polarization and temperature on the reaction mechanism

To analyze the reaction mechanisms taking place in the LNO electrodes, the relative proportion of the surface to the bulk path has been expressed through the ratio  $\xi$  between the kinetic rates of direct oxidation/reduction at TPBIs and that of the oxygen excorporation/incorporation:

$$\xi = \frac{v_{R3}}{\int_{z=\ell_{CGO}}^{z=\ell_{LNO}} v_{R2}}$$
 Eq. 34

It is reminded that the charge transfer at TPBIs takes place only at the gas/electrode/electrolyte interface, whereas the oxygen excorporation/incorporation reaction occurs all over the electrode thickness. Both the kinetic rates  $v_{R2}$  and  $v_{R3}$  are a result of the simulations. Once they are calculated, it is possible to evaluate the ratio  $\xi$ . Therefore, a value of  $\xi$  lower than the unity ( $\xi < 1$ ) means that the bulk path dominates the reaction mechanism while a ratio higher than one ( $\xi > 1$ ) corresponds to a mechanism controlled by the surface path.

The ratio  $\xi$  is plotted as a function of the electrode overpotential in Figure 8a. Whatever the investigated temperature,  $\xi$  was found to increase while decreasing the overpotential from anodic to cathodic polarization. This behavior can be interpreted through the dependence with the electrode overpotential of both the kinetic rates of oxygen excorporation/incorporation reaction (integrated over the whole electrode thickness) and charge transfer at TPBIs (at the CGO/LNO interface) (Figure 8b). Indeed, as shown in Figure 8b, the oxygen exchange reaction becomes bounded under cathodic polarization. This behavior is related to the evolution of the oxygen over-stoichiometry in the LNO lattice with the polarization. Indeed, the electrode material is progressively depleted in interstitial oxygen from anodic to cathodic polarization, as illustrated in Figure 8c. In these conditions, the concentration of interstitial oxygen becomes nil at the electrolyte/electrode interface under cathodic polarization, so that the bulk path is limited. This behavior is explained since the rate of oxygen incorporation, which supplies the material in oxygen, is lower than the fast ionic transfer at the electrolyte interface. On the other hand, the charge transfer at TPBIs is found to remain strongly activated under cathodic polarization. Nevertheless, it can be noticed that the surface path is likely to be limited at very high cathodic polarization, because of the evolution of the oxygen atoms adsorbed on the LNO surface. Indeed, the surface coverage at the LNO surface decreases with increasing the absolute value of the cathodic polarization. This evolution is explained by the limitation of the adsorption of oxygen on the LNO surface to its incorporation. Therefore, the surface path is also expected to be bounded once  $\theta_{O_{s,LNO}}^{eq}$  falls to zero. However, according to Figure 8c, this condition is not reached in the investigated range of overpotentials. As a result, the surface path is strongly promoted even at the highest overpotentials investigated in the present study.

On the other hand, the two pathways remain activated under anodic polarization (Figure 8b). Indeed, the concentration of interstitial oxygen in the LNO bulk is increased from equilibrium under this polarization. Nevertheless, it is found that the oxygen over-stoichiometry remains always much lower than the saturating estimated value  $\delta_{max} = 2$  [58–60] for which the bulk path is bounded. Therefore, according to the model, the bulk path will be never limited if considering reasonable anodic polarization. On the other hand, the surface coverage is also increased with increasing the anodic polarization. Nevertheless, since the oxygen coverage is very low at equilibrium, the adsorption sites are never saturated, even at very high anodic polarization. Summarizing, the higher performances of the LNO electrode in electrolysis mode compared to the fuel cell conditions (cf. section 4.1) are explained by the limitation of the bulk path under cathodic polarizations while both paths remain activated under anodic polarization.

Figure 8a also shows the impact of the temperature on the ratio of the surface to the bulk path at the three investigated temperatures. For the OCP condition, the bulk path appears to be the dominant pathway at 650 °C, whereas the reaction mechanism is controlled by the surface path at higher temperatures, i.e., at 700 °C and 750 °C. This evolution allows claiming that the contribution of the charge transfer at the TPBIs in the global reaction mechanism is enhanced when increasing the temperature. This electrode behavior at OCP can be explained by the thermal activation of the reaction kinetics. According to the fitted parameters reported in Table VI, the activation energy for the charge transfer at TPBIs is found to be roughly equal to 142 kJ mol<sup>-1</sup>, whereas the one for the oxygen incorporation/excorporation reaction is about 62 kJ mol<sup>-1</sup>. Therefore, the kinetics for the charge transfer at TPBIs is strongly thermally-activated as expected [36]. These results are also confirmed by the EIS diagrams at OCP and the three investigated temperatures (Figure 5). Indeed, a Gerischer-type element has been obtained at 650 °C, whereas a more depressed semicircle can be observed at 700 °C and 750 °C. This change in the shape of the EIS diagrams for LNO electrodes when increasing the temperature at OCP was also observed by Tong et al. [39]. According to Adler et al. [30], the presence of a Gerischer-type element in the impedance diagrams of MIEC electrodes suggests that the global reaction mechanism is dominated by the bulk path. Moreover, it has been shown for the LSCF that a change from the Gerischer-type impedance towards a depressed semi-circle must be ascribed to a transition from the bulk to the surface path [36,57]. All these statements are in full agreement with the present results obtained for the LNO material and reinforce the claim of a higher contribution of the surface path when increasing the temperature.

A transition from the bulk to surface path occurs under cathodic polarization at 650 °C ( $\xi = 1$  at  $\eta \approx -0.01$  V/Pt/Air) and under anodic polarization at 700 °C ( $\xi = 1$  at  $\eta \approx +0.04$  V/Pt/Air). Concerning the results at 750 °C, no transition is observed in the range of investigated overpotentials. Hence, the reaction mechanism is entirely controlled by the surface path under these conditions. The dissymmetry of the polarization curves with respect to the OCP observed at 650°C and 700°C (Figure 5a) is thus explained by the transition in the reaction pathway. Moreover, it is essential to remind that the almost linear behavior of the polarization curve observed at 750 °C is due to the limited range of overpotential considered in the present study, which is not sufficiently extended to detect a change in the slope. As a proof of the matter, Figure 8a shows that a change in the reaction mechanism would occur at anodic polarization higher than  $\eta \approx +0.1$  V/Pt/Air.



Figure 8: a) Ratio of the surface to the bulk path under air for the LNO electrode at 650°C, 700 °C and 750 °C plotted as a function of the electrode overpotential. b) Kinetics rates for the oxygen excorporation/incorporation reaction and the oxidation/reduction reaction at the TPBIs as a function of the electrode overpotential at 700 °C b) Oxygen over stoichiometry in the electrode thickness at different polarization, under air and 700 °C.

#### 5.2 Effect of the oxygen partial pressure on the reaction mechanism

In Figure b, it is shown that the model can reproduce quite accurately the response of the electrode LNO when changing the oxygen partial pressure. Indeed, a reaction order n of about

0.23 was obtained at 700 °C and OCP from both experimental measurements and simulations. Thus, the model developed in the present work has been used to identify the rate-determining steps in the oxygen evolution reaction for n = 0.23 (at OCP and 700°C). It was found that the oxygen reaction is mainly co-limited by the charge transfer reactions at both the gas/electrode interface (cf. R2, Table 2) and at the Triple Boundary Phase lines (cf. R3, Table 3). To a lesser extent, it has been found that the oxygen diffusion in the LNO bulk also participate to the co-limitation. These results are in full agreement with other works, for which the charge transfer is the rate-determining step when  $n \approx 0.25$  [63].

The effect of the oxygen partial pressure on the reaction mechanism in such electrode material has been also investigated at OCP and 700 °C. The range of investigated  $pO_2$  is 0.15 - 1 atm. Figure 9a shows that the bulk path is promoted when increasing the oxygen partial pressure. Indeed, the ratio of the surface to bulk path globally decreases when  $pO_2$  is increased. For instance, the ratio  $\xi$  close to the OCP is about 2 at  $pO_2 = 0.15$  atm, compared to 0.8 at  $pO_2 = 1$  atm.

Figure 9a evidences that the surface path remains the predominant reaction mechanism at OCP for  $pO_2$  lower than 0.6 atm, while the bulk path controls the reaction mechanism at higher oxygen partial pressures. To interpret this result, the kinetic rates of charge transfer at TPBIs and oxygen exchange at the LNO surface (integrated along the electrode thickness) have been calculated close to the OCP and plotted as a function of the oxygen partial pressure in Figure 9b. It can be noticed that the kinetic rate of the oxygen exchange reaction increases with increasing the oxygen partial pressure. This behavior can be explained by the increase of the LNO over stoichiometry,  $\delta_{LNO}$ , when increasing the oxygen partial pressure, as it has been observed by Nakamura et al. [64]. Indeed, the high concentration of interstitial oxygen in the LNO lattice at high  $pO_2$  favors the bulk path in the reaction mechanism. On the other hand, the kinetic rate for the charge transfer at the TPBIs at OCP is not affected by the change of  $pO_2$ . As a result, it can be noticed that the sum of the two contributions globally increases with  $pO_2$ , which explains the decrease of the electrode polarization resistance as shown in Figure a.



Figure 9: a) Ratio of the surface to bulk path as a function of the electrode overpotential at OCP and 700 °C for different oxygen partial pressures. b) Kinetic rates of the oxygen excorporation/incorporation reaction and the charge transfer at TPBIs as a function of pO<sub>2</sub> computed close to the OCP ( $i_{dc} \approx 0.002$  A cm<sup>-2</sup>).

#### 5.3 Effect of the contact resistance on the electrode response

The non-optimal contact between the electrode and the current collector is an important factor that can significantly affect the cell performances [65]. Indeed, it is well known that a low density of contact points at the interface between the electrode and the current collector can induce high ohmic contact resistances [66]. Besides, it also affects the current distribution in the electrode [67], thus inducing a significant increase in the electrode polarization resistance [67,68]. Moreover, this effect can be exacerbated by a low electronic conductivity of the electrode material [67]. It is worth noting that the frequency distribution in the impedance diagram should not be strongly impacted by the inhomogeneous distribution of current in the electrode. Indeed, the inhomogeneous current distribution will decrease the 'effective' surface area in the electrodes where the reactions occur [69] while the overall reaction mechanism must remain identical. In other words, a non-optimal current collection will increase both the ohmic and electrode polarization resistances while the frequency response should be not changed significantly.

In the present work, the contact resistances were evaluated by removing the ohmic losses due to the electrolyte from the experimental series resistances measured on the impedance diagrams. For example, a contact resistance of  $1.72 \ \Omega.cm^2$  was found at 700°C. This high value is explained on one hand by a very rough electrode surface limiting the density of contacts with the grid, and on the other hand, by the relative low electric conductivity of LNO compared to

other electrode materials (*e.g.* LSCF, LSM) [13]. Therefore, it is reasonable to consider that the electrode polarization resistance obtained in the present work may be significantly overestimated by the contact resistances. Thereby, the model developed in the present work has been used to minimize the influence of the contact resistance on the electrode behavior. With this aim, the model has been calibrated by fitting the experimental frequency distributions instead of the polarization curves. This approach allows identifying the electrode polarization resistances without any influence of the contact resistances. Thus, it is assumed that the electrode is governed by the same reaction mechanisms as previously described in section 5.1. The same trends of the surface-to-bulk ratio as a function of the polarization and the temperature have been retained.

By following this approach, the frequency lag shown in the previous section tends to disappear, allowing obtaining lower  $R_{pol}$  than those recorded experimentally (Figure 10 and Figure S2). According to the results reported in Figure 10, a correction factor  $\approx 0.12$  should be used to correct the  $R_{pol}$  recorded experimentally, confirming that the contribution of the contact resistances to the obtained experimental measurements is effectively quite large. By fitting the experimental frequency distribution, new values of the missing model parameters (i.e., i) the pre-exponential factor and ii) the activation energy of the Arrhenius law for the three kinetic constants, and iii) the oxygen surface diffusivity along with the surface coverage of the adsorbed oxygen atoms at equilibrium,  $\theta_{O_{s,INO}}^{eq}$ , at  $pO_2 = 0.21$  atm) were obtained (Table S1, Supplementary Information). The obtained values of the kinetic parameters are higher than those obtained through the fitting of the experimental polarization curves listed in Table 4 (while the oxygen surface diffusivity remains identical). Indeed, a significant enhancement of the electrode performance is obtained, as shown in the polarization curves reported in Figure S3. Thus, these results could be representative of the ideal case in which the electrode behavior is not affected by any contact resistances. In other words, the kinetic constants obtained by following this approach could be considered as the intrinsic properties of the LNO material according to the reaction mechanisms considered in the present work and described in section 3. Moreover, the effect of the oxygen partial pressure on the electrode performance is also unchanged (Figure S4).



Figure 10: EIS diagrams for the LNO electrodes at OCP under air obtained by fitting the frequency distribution. Nyquist plots for: (a) 650 °C, (b) 700 °C and (c) 750 °C. Bode plot for: (d) 650 °C, (e) 700 °C and (f) 750 °C.

To validate the aforementioned model calibration method based on the fitting of the frequency distribution, the global chemical constant of the oxygen exchange,  $k_{chem}$ , has been calculated using the expression from the Adler model as presented in [70] and by using the polarization resistance,  $R_{pol}$  taken from the corrected impedance diagrams:

$$k_{chem} = \left(\frac{RT}{4F^2 c_{O_i'}{}^{eq}}\right)^2 \cdot \frac{1}{\frac{\varepsilon_{LNO}}{\tau_{LNO}} D_{chem} \cdot S_p^{LNO/gas} \cdot R_{pol}{}^2}$$
Eq. 35

Using the values reported in Table 1 and 6 for the microstructural and input parameters, respectively, and the  $R_{pol}$  obtained by fitting the frequency distribution,  $k_{chem}$  was found to be around  $1.06 \cdot 10^{-5}$ ,  $2.73 \cdot 10^{-5}$  and  $6.57 \cdot 10^{-5}$  m s<sup>-1</sup> at 650, 700 and 750°C, respectively. These values are in full agreement with the data of  $k_{chem}$  measured through electrical conductivity relaxation and reported in the literature [54,71]. For the sake of comparison, it is worth mentioning that the values of  $k_{chem}$  evaluated using the polarization resistances recorded experimentally are two order of magnitude lower than those of  $k_{chem}$  reported in the literature. Therefore, this discussion suggests that the frequency lag between the simulations and the experiments reported in section

4 is related to the impact of the current collection on the polarization resistance. Nevertheless, the reaction mechanism for the LNO material remains unchanged.

#### 6. Conclusion

In this study, a coupled experimental and modeling approach has been used to investigate the reaction mechanisms of the La<sub>2</sub>NiO<sub>4+ $\delta$ </sub> (LNO) oxygen electrodes.

A set of experiments has been performed by using a three-electrode setup. Polarization curves ( $\eta$ -*i*) have been recorded in the temperature range of 650-750 °C and under air. Impedance diagrams have been also recorded in the temperature range of 650-750°C, at OCP and under air. A decrease of the electrode polarization resistance from about 0.78  $\Omega$  cm<sup>2</sup> at 650°C down to 0.20  $\Omega$  cm<sup>2</sup> at 750°C was obtained. The shape of the EIS diagram changed from a Gerischer-like element at 650 °C and OCP towards a depressed semicircle at higher temperatures. The effect of the oxygen partial pressure on the LNO electrode response in the range of 0.15 - 1 atm has been also investigated.

To analyse the experimental results, a physically-based electrode model has been developed. It considers two parallel pathways, *i.e.*: (i) the oxygen incorporation/excorporation at the gas/electrode interface for the bulk path and; (ii) the direct charge transfer at the TPBIs for the surface path. A 3D electrode reconstruction obtained by FIB-SEM tomography allowed determining the microstructural properties required for the simulations. With a reduced number of unknown parameters, the model has been found to reproduce the dissymmetry of the electrode polarization curves. Furthermore, without any additional fitting, the model can reproduce correctly the shape of the experimental EIS diagram at OCP and under polarization whatever the temperature. The evolution of the electrode polarization resistance with the oxygen partial pressure is also well described by the model. Nevertheless, a frequency lag was systematically obtained for the impedance diagrams. This discrepancy has been attributed to the impact of the current collection on the polarization resistance.

Once validated, the model has been used to analyze the LNO reaction mechanisms. The contribution of the charge transfer at the TPBIs (surface path) over the excorporation/incorporation reaction (bulk path) was found to increase with the cathodic dc current. This evolution has been explained by the limitation of the bulk path caused by the interstitial oxygen depletion in LNO arising under cathodic current. Regarding the anodic polarization, the two pathways remain activated explaining the higher performances obtained

in this condition. Moreover, the bulk path controls the reaction mechanism at OCP and 650 °C, whereas the contribution of the surface path increases while increasing the operating temperature (700 and 750 °C). A transition from the bulk to surface path occurs under cathodic polarization at 650 °C  $\eta \approx$  -0.01 V/Pt/Air) and under anodic polarization at 700 °C ( $\eta \approx$  +0.04 V/Pt/Air), in full agreement with the dissymmetry of the polarization curves recorded experimentally. Finally, the dependence of the LNO electrode response with *pO*<sub>2</sub> has been explained since the bulk path is promoted when increasing the oxygen partial pressures.

#### Acknowledgements

This study was supported by the French National Research Agency (ANR) project "ECOREVE", reference ANR-18-CE05-0036, and by the GENVIA company. The authors thank the company SRT Microcéramique for the screen-printing of the CGO barrier onto the YSZ electrolyte.

## 7. Supplementary Information

FITTED PARAMETERS							
Parameter		650 °C	700 °C	750 °C	E <sub>a</sub> [kJ mol <sup>-1</sup> ]		
$\theta^{eq}_{O_{S_{LNO}}}$	/ -	4.6·10 <sup>-3</sup>	4.6.10-3	$4.6 \cdot 10^{-3}$	-		
$D_{Os}$	$/ m^2 s^{-1}$	$4 \cdot 10^{-6}$	6·10 <sup>-6</sup>	9·10 <sup>-6</sup>	63		
<i>k</i> <sub>+</sub>	$/ \text{ mol } \text{m}^{-2} \text{ s}^{-1}$	NOT	NOT	NOT			
		LIMITING	LIMITING	LIMITING	-		
$k_{ox}^{LNO/gas}$	$/ m^{3} mol^{-1} s^{-1}$	$1.5 \cdot 10^3$	$2.2 \cdot 10^3$	$3.5 \cdot 10^3$	66		
$k_{ox}^{TPB}$	/ m s <sup>-1</sup>	4.5.10-4	$1.17 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$	134		
k <sub>ads</sub>	$/ \text{ atm}^{-0.5} \text{ s}^{-1}$	$8 \cdot 10^{6}$	$2.10^{7}$	$4 \cdot 10^{7}$	126		

Table S1: Input parameters used to fit the experimental frequency distribution data ( $pO_2 = 0.21$  atm)



Figure S1: SEM observations for the studied cell: a) cross-section including the LNO electrode, the CGO barrier layer and a part of the 8YSZ electrolyte and b) image of the LNO electrode taken from the stack of images used for the electrode reconstructions.



Figure S2: EIS diagrams obtained by fitting the frequency distribution at 700 °C under air for  $i_{dc} = -100 \text{ mA cm}^{-2}$ ,  $-50 \text{ mA cm}^{-2}$ ,  $+50 \text{ mA cm}^{-2}$  and  $+100 \text{ mA cm}^{-2}$ . (a-d) Nyquist plots and (e-h) Bode plots.


Figure S3: Polarization curves obtained at 650, 700, and 750 °C under air for LNO electrodes obtained by fitting the experimental frequency distribution.



Figure S4: Experimental (corrected) and simulated polarization resistance plotted as a function of the oxygen partial pressure in logarithmic coordinates (at 700°C) when fitting the frequency distribution.

## 8. References

- N. Minh, J. Mizusaki, S.C. Singhal, Advances in solid oxide fuel cells: review of progress through three decades of the international symposia on solid oxide fuel cells, ECS Trans. 78 (2017) 63. https://doi.org/10.1149/07801.0063ecst.
- [2] E. Boehm, J.-M. Bassat, M.C. Steil, P. Dordor, F. Mauvy, J.-C. Grenier, Oxygen transport properties of La<sub>2</sub>Ni<sub>1-x</sub>Cu<sub>x</sub>O<sub>4+δ</sub> mixed conducting oxides, Solid State Sci. 5 (2003) 973–981. https://doi.org/10.1016/S1293-2558(03)00091-8.
- [3] I. Riess, Mixed ionic–electronic conductors—material properties and applications, Solid State Ion. 157 (2003) 1–17. https://doi.org/10.1016/S0167-2738(02)00182-0.
- [4] A. R. West, Solid electrolytes and mixed ionic–electronic conductors: an applications overview, J. Mater. Chem. 1 (1991) 157–162. https://doi.org/10.1039/JM9910100157.
- [5] A. Barbucci, P. Carpanese, G. Cerisola, M. Viviani, Electrochemical investigation of mixed ionic/electronic cathodes for SOFCs, Solid State Ion. 176 (2005) 1753–1758. https://doi.org/10.1016/j.ssi.2005.04.027.
- [6] A. Ahuja, M. Gautam, A. Sinha, J. Sharma, P.K. Patro, A. Venkatasubramanian, Effect of processing route on the properties of LSCF-based composite cathode for IT-SOFC, Bull Mater Sci. 43 (2020) 129. https://doi.org/10.1007/s12034-020-2075-y.
- [7] A. Donazzi, G. Cordaro, A. Baricci, Z.-B. Ding, M. Maestri, A detailed kinetic model for the reduction of oxygen on LSCF-GDC composite cathodes, Electrochim. Acta. 335 (2020) 135620. https://doi.org/10.1016/j.electacta.2020.135620.
- [8] H.J. Hwang, J.-W. Moon, S. Lee, E.A. Lee, Electrochemical performance of LSCF-based composite cathodes for intermediate temperature SOFCs, J. Power Sources. 145 (2005) 243–248. https://doi.org/10.1016/j.jpowsour.2005.02.063.
- [9] J. Nielsen, T. Jacobsen, M. Wandel, Impedance of porous IT-SOFC LSCF:CGO composite cathodes, Electrochim. Acta. 56 (2011) 7963–7974. https://doi.org/10.1016/j.electacta.2011.05.042.
- [10] G.Ch. Kostogloudis, G. Tsiniarakis, Ch. Ftikos, Chemical reactivity of perovskite oxide SOFC cathodes and yttria stabilized zirconia, Solid State Ion. 135 (2000) 529–535. https://doi.org/10.1016/S0167-2738(00)00433-1.
- [11] J. Laurencin, M. Hubert, D.F. Sanchez, S. Pylypko, M. Morales, A. Morata, B. Morel, D. Montinaro, F. Lefebvre-Joud, E. Siebert, Degradation mechanism of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub>/Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2-δ</sub> composite electrode operated under solid oxide electrolysis and fuel cell conditions, Electrochim. Acta. 241 (2017) 459–476. https://doi.org/10.1016/j.electacta.2017.05.011.
- [12] V. Vibhu, A. Rougier, C. Nicollet, A. Flura, J.-C. Grenier, J.-M. Bassat, La<sub>2-x</sub>Pr<sub>x</sub>NiO<sub>4+δ</sub> as suitable cathodes for metal supported SOFCs, Solid State Ion. 278 (2015) 32–37. https://doi.org/10.1016/j.ssi.2015.05.005.
- [13] E. Boehm, J.-M. Bassat, P. Dordor, F. Mauvy, J.-C. Grenier, Ph. Stevens, Oxygen diffusion and transport properties in non-stoichiometric Ln<sub>2-x</sub>NiO<sub>4+δ</sub> oxides, Solid State Ion. 176 (2005) 2717–2725. https://doi.org/10.1016/j.ssi.2005.06.033.

- [14] V. Vibhu, A. Rougier, J.-C. Grenier, J.-M. Bassat, Mixed Nickelates  $Pr_{2-x}La_xNiO_{4+\delta}$ Used as Cathodes in Metal Supported SOFCs, ECS Trans. 57 (2013) 2093. https://doi.org/10.1149/05701.2093ecst.
- [15] Y. Lee, H. Kim, Electrochemical performance of La<sub>2</sub>NiO<sub>4+δ</sub> cathode for intermediatetemperature solid oxide fuel cells, Ceramics International. 41 (2015) 5984–5991. https://doi.org/10.1016/j.ceramint.2015.01.037.
- [16] S.J. Skinner, J.A. Kilner, Oxygen diffusion and surface exchange in  $La_{2-x}Sr_xNiO_{4+\delta}$ , Solid State Ionics. 135 (2000) 709–712. https://doi.org/10.1016/S0167-2738(00)00388-X.
- [17] A.D. Rougier, A. Flura, C. Nicollet, V. Vibhu, S. Fourcade, E. Lebraud, J.-M. Bassat, J.-C. Grenier, Ln2NiO4+δ (Ln = La, Pr) As Suitable Cathodes for Metal Supported Cells, ECS Trans. 68 (2015) 817. https://doi.org/10.1149/06801.0817ecst.
- [18] A. Montenegro-Hernández, J. Vega-Castillo, L. Mogni, A. Caneiro, Thermal stability of Ln<sub>2</sub>NiO<sub>4+δ</sub> (Ln: La, Pr, Nd) and their chemical compatibility with YSZ and CGO solid electrolytes, Int. J. Hydrog. Energy. 36 (2011) 15704–15714. https://doi.org/10.1016/j.ijhydene.2011.08.105.
- [19] K. Zhao, Y.-P. Wang, M. Chen, Q. Xu, B.-H. Kim, D.-P. Huang, Electrochemical evaluation of La2NiO4+δ as a cathode material for intermediate temperature solid oxide fuel cells, Int. J. Hydrog. Energy. 39 (2014) 7120–7130. https://doi.org/10.1016/j.ijhydene.2014.02.106.
- [20] V.V. Vashook, S.P. Tolochko, I.I. Yushkevich, L.V. Makhnach, I.F. Kononyuk, H. Altenburg, J. Hauck, H. Ullmann, Oxygen nonstoichiometry and electrical conductivity of the solid solutions  $La_{2-x}Sr_xNiO_y$  ( $0 \le x \le 0.5$ ), Solid State Ion. 110 (1998) 245–253. https://doi.org/10.1016/S0167-2738(98)00134-9.
- [21] A. Flura, S. Dru, C. Nicollet, V. Vibhu, S. Fourcade, E. Lebraud, A. Rougier, J.-M. Bassat, J.-C. Grenier, Chemical and structural changes in  $Ln_2NiO_{4+\delta}$  (Ln=La, Pr or Nd) lanthanide nickelates as a function of oxygen partial pressure at high temperature, Journal of Solid State Chemistry. 228 (2015) 189–198. https://doi.org/10.1016/j.jssc.2015.04.029.
- [22] V. Vibhu, A. Flura, A. Rougier, C. Nicollet, S. Fourcade, T. Hungria, J.-C. Grenier, J.-M. Bassat, Electrochemical ageing study of mixed lanthanum/praseodymium nickelates La<sub>2-x</sub>Pr<sub>x</sub>NiO<sub>4+δ</sub> as oxygen electrodes for solid oxide fuel or electrolysis cells, Journal of Energy Chemistry. 46 (2020) 62–70. https://doi.org/10.1016/j.jechem.2019.10.012.
- [23] N.I. Khamidy, J. Laurencin, D. Ferreira Sanchez, F. Monaco, F. Charlot, E. Djurado, Durability of nanostructured LaPrNiO<sub>4+δ</sub> electrode for solid oxide cells: electrochemical, microstructural, and structural investigation, Journal of Power Sources. 450 (2020) 227724. https://doi.org/10.1016/j.jpowsour.2020.227724.
- [24] R. Sayers, M. Rieu, P. Lenormand, F. Ansart, J.A. Kilner, S.J. Skinner, Development of lanthanum nickelate as a cathode for use in intermediate temperature solid oxide fuel cells, Solid State Ion. 192 (2011) 531–534. https://doi.org/10.1016/j.ssi.2010.02.014.
- [25] C. Nicollet, A. Flura, V. Vibhu, A. Rougier, J.M. Bassat, J.C. Grenier, La<sub>2</sub>NiO<sub>4+δ</sub> infiltrated into gadolinium doped ceria as novel solid oxide fuel cell cathodes: Electrochemical performance and impedance modelling, J. Power Sources. 294 (2015) 473–482. https://doi.org/10.1016/j.jpowsour.2015.06.077.

- [26] R.K. Sharma, M. Burriel, L. Dessemond, V. Martin, J.-M. Bassat, E. Djurado, An innovative architectural design to enhance the electrochemical performance of  $La_2NiO_{4+\delta}$  cathodes for solid oxide fuel cell applications, J. Power Sources. 316 (2016) 17–28. https://doi.org/10.1016/j.jpowsour.2016.03.067.
- [27] R.K. Sharma, M. Burriel, L. Dessemond, J.M. Bassat, E. Djurado, Design of interfaces in efficient Ln2NiO4 (Ln ¼ La, Pr) cathodes for SOFC applications, J. Mater. Chem. A. 4 (2016) 12451–12462. https://doi.org/10.1039/C6TA04845E.
- [28] N. Hildenbrand, P. Nammensma, D.H.A. Blank, H.J.M. Bouwmeester, B.A. Boukamp, Influence of configuration and microstructure on performance of  $La_2NiO_{4+\delta}$ intermediate-temperature solid oxide fuel cells cathodes, J. Power Sources. 238 (2013) 442–453. https://doi.org/10.1016/j.jpowsour.2013.03.192.
- [29] A. Egger, N. Schrödl, C. Gspan, W. Sitte, La<sub>2</sub>NiO<sub>4+δ</sub> as electrode material for solid oxide fuel cells and electrolyzer cells, Solid State Ion. 299 (2017) 18–25. https://doi.org/10.1016/j.ssi.2016.10.002.
- [30] S.B. Adler, J.A. Lane, B.C.H. Steele, Electrode kinetics of porous mixed- conducting oxygen electrodes, J. Electrochem. Soc. 143 (1996) 3554. https://doi.org/10.1149/1.1837252.
- [31] M. Prestat, J.-F. Koenig, L.J. Gauckler, Oxygen reduction at thin dense  $La_{0.52}Sr_{0.48}Co_{0.18}Fe_{0.82}O_{3-\delta}$  electrodes, J Electroceram. 18 (2007) 87–101. https://doi.org/10.1007/s10832-007-9012-y.
- [32] J. Laurencin, M. Hubert, K. Couturier, T.L. Bihan, P. Cloetens, F. Lefebvre-Joud, E. Siebert, Reactive Mechanisms of LSCF Single-Phase and LSCF-CGO Composite electrodes operated in anodic and cathodic polarisations, Electrochim. Acta. 174 (2015) 1299–1316. https://doi.org/10.1016/j.electacta.2015.06.080.
- M. Hubert, J. Laurencin, P. Cloetens, J.C. da Silva, F. Lefebvre-Joud, P. Bleuet, A. [33] Nakajo, E. Siebert, Role of microstructure on electrode operating mechanisms for mixed ionic electronic conductors: From synchrotron-based 3D reconstruction to State electrochemical modeling, Solid Ionics. 294 (2016)90-107. https://doi.org/10.1016/j.ssi.2016.07.001.
- [34] L. Ma, P. Priya, N.R. Aluru, A multiscale model for electrochemical reactions in lscf based solid oxide cells, J. Electrochem. Soc. 165 (2018) F1232. https://doi.org/10.1149/2.0921814jes.
- [35] E. Effori, H. Moussaoui, F. Monaco, R.K. Sharma, J. Debayle, Y. Gavet, G. Delette, G.S. Larbi, E. Siebert, J. Vulliet, L. Dessemond, J. Laurencin, Reaction mechanism and impact of microstructure on performances for the LSCF-CGO composite electrode in solid oxide cells, Fuel Cells. 19 (2019) 429–444. https://doi.org/10.1002/fuce.201800185.
- [36] F. Monaco, V. Tezyk, E. Siebert, S. Pylypko, B. Morel, J. Vulliet, T. Le Bihan, F. Lefebvre-Joud, J. Laurencin, Experimental validation of a  $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$  electrode model operated in electrolysis mode: understanding the reaction pathway under anodic polarization, Solid State Ionics. 319 (2018) 234–246. https://doi.org/10.1016/j.ssi.2018.02.012.
- [37] J.S.A. Carneiro, R.A. Brocca, M.L.R.S. Lucena, E. Nikolla, Optimizing cathode materials for intermediate-temperature solid oxide fuel cells (SOFCs): Oxygen reduction

on nanostructured lanthanum nickelate oxides, Applied Catalysis B: Environmental. 200 (2017) 106–113. https://doi.org/10.1016/j.apcatb.2016.06.073.

- [38] M.J. Escudero, A. Aguadero, J.A. Alonso, L. Daza, A kinetic study of oxygen reduction reaction on La2NiO4 cathodes by means of impedance spectroscopy, Journal of Electroanalytical Chemistry. 611 (2007) 107–116. https://doi.org/10.1016/j.jelechem.2007.08.006.
- [39] X. Tong, F. Zhou, S. Yang, S. Zhong, M. Wei, Y. Liu, Performance and stability of Ruddlesden-Popper La<sub>2</sub>NiO<sub>4+δ</sub> oxygen electrodes under solid oxide electrolysis cell operation conditions, Ceramics International. 43 (2017) 10927–10933. https://doi.org/10.1016/j.ceramint.2017.05.130.
- [40] Ph. Courty, H. Ajot, Ch. Marcilly, B. Delmon, Oxydes mixtes ou en solution solide sous forme très divisée obtenus par décomposition thermique de précurseurs amorphes, Powder Technology. 7 (1973) 21–38. https://doi.org/10.1016/0032-5910(73)80005-1.
- [41] S.B. Adler, Limitations of charge-transfer models for mixed-conducting oxygen electrodes, Solid State Ionics. 135 (2000) 603–612. https://doi.org/10.1016/S0167-2738(00)00423-9.
- [42] S.B. Adler, B.T. Henderson, M.A. Wilson, D.M. Taylor, R.E. Richards, Reference electrode placement and seals in electrochemical oxygen generators, Solid State Ionics. 134 (2000) 35–42. https://doi.org/10.1016/S0167-2738(00)00711-6.
- [43] N. Vivet, S. Chupin, E. Estrade, T. Piquero, P.L. Pommier, D. Rochais, E. Bruneton, 3D Microstructural characterization of a solid oxide fuel cell anode reconstructed by focused ion beam tomography, J. Power Sources. 196 (2011) 7541–7549. https://doi.org/10.1016/j.jpowsour.2011.03.060.
- [44] J. Villanova, J. Laurencin, P. Cloetens, P. Bleuet, G. Delette, H. Suhonen, F. Usseglio-Viretta, 3D phase mapping of solid oxide fuel cell YSZ/Ni cermet at the nanoscale by holographic X-ray nanotomography, J. Power Sources. 243 (2013) 841–849. https://doi.org/10.1016/j.jpowsour.2013.06.069.
- [45] F. Usseglio-Viretta, J. Laurencin, G. Delette, J. Villanova, P. Cloetens, D. Leguillon, Quantitative microstructure characterization of a Ni–YSZ bi-layer coupled with simulated electrode polarisation, J. Power Sources. 256 (2014) 394–403. https://doi.org/10.1016/j.jpowsour.2014.01.094.
- [46] H. Moussaoui, J. Laurencin, Y. Gavet, G. Delette, M. Hubert, P. Cloetens, T. Le Bihan, J. Debayle, Stochastic geometrical modeling of solid oxide cells electrodes validated on 3D reconstructions, Computational Materials Science. 143 (2018) 262–276. https://doi.org/10.1016/j.commatsci.2017.11.015.
- [47] J. Jochen, Microstructural Characterisation, Modelling and simulation of solid oxide fuel cell cathodes, KIT Scientific Publishing, 2017.
- [48] G.W. Coffey, L.R. Pederson, P.C. Rieke, Competition between bulk and surface pathways in mixed ionic electronic conducting oxygen electrodes, J. Electrochem. Soc. 150 (2003) A1139. https://doi.org/10.1149/1.1591758.
- [49] A.M. Svensson, S. Sunde, K. Nisşancioğlu, Mathematical modeling of oxygen exchange and transport in air- perovskite- YSZ interface regions: I. Reduction of intermediately

adsorbed oxygen, J. Electrochem. Soc. 144 (1997) 2719. https://doi.org/10.1149/1.1837887.

- [50] F. Monaco, E. Effori, M. Hubert, E. Siebert, G. Geneste, B. Morel, E. Djurado, D. Montinaro, J. Laurencin, Electrode kinetics of porous Ni-3YSZ cermet operated in fuel cell and electrolysis modes for solid oxide cell application, Electrochimica Acta. 389 (2021) 138765. https://doi.org/10.1016/j.electacta.2021.138765.
- [51] T. Nakamura, K. Yashiro, K. Sato, J. Mizusaki, Oxygen nonstoichiometry and defect equilibrium in  $La_{2-x}Sr_xNiO_{4+\delta}$ , Solid State Ionics. 180 (2009) 368–376. https://doi.org/10.1016/j.ssi.2009.01.013.
- [52] S.-Y. Jeon, M.-B. Choi, J.-H. Hwang, E.D. Wachsman, S.-J. Song, Electrical conductivity and thermoelectric power of La2NiO4+δ, J. Electrochem. Soc. 158 (2011) B476. https://doi.org/10.1149/1.3559186.
- [53] P. Kofstad, Nonstoichiometry, diffusion, and electrical conductivity in binary metal oxides., Wiley Interscience, New York, USA, 1972.
- [54] Z. Li, R. Haugsrud, Effects of surface coatings on the determination of Dchem and kchem in La2NiO4+δ by conductivity relaxation, Solid State Ionics. 206 (2012) 67–71. https://doi.org/10.1016/j.ssi.2011.11.011.
- [55] R. Tanaka, W.S. Oliveira, A. Brandão, J.C.C. Abrantes, J.R. Frade, Grain boundary conductivity of heterogeneous ceria gadolinia, Electrochimica Acta. 85 (2012) 116–121. https://doi.org/10.1016/j.electacta.2012.08.009.
- [56] B. Todd, J.B. Young, Thermodynamic and transport properties of gases for use in solid oxide fuel cell modelling, Journal of Power Sources. 110 (2002) 186–200. https://doi.org/10.1016/S0378-7753(02)00277-X.
- [57] E. Effori, J. Laurencin, E.D.R. Silva, M. Hubert, T. David, M. Petitjean, G. Geneste, L. Dessemond, E. Siebert, An elementary kinetic model for the LSCF and LSCF-CGO electrodes of solid oxide cells: impact of operating conditions and degradation on the electrode response, J. Electrochem. Soc. 168 (2021) 044520. https://doi.org/10.1149/1945-7111/abf40a.
- [58] M. Schroeder, M.-A. Dragan, Oxygen transport in La2-xSrxNiO4+δ: membrane permeation and defect chemical modelling, J Mater Sci. 42 (2007) 1972–1983. https://doi.org/10.1007/s10853-006-0739-7.
- [59] H.-S. Kim, H.-I. Yoo, Effect of acceptor size and hole degeneracy on oxygen nonstoichiometry of La2NiO4+δ, Solid State Ionics. 232 (2013) 129–137. https://doi.org/10.1016/j.ssi.2012.12.001.
- [60] T. Nakamura, R. Oike, Y. Ling, Y. Tamenori, K. Amezawa, The determining factor for interstitial oxygen formation in Ruddlesden–Popper type La2NiO4-based oxides, Phys. Chem. Chem. Phys. 18 (2016) 1564–1569. https://doi.org/10.1039/C5CP05993C.
- [61] Özden Çelikbilek, E. Siebert, D. Jauffrès, C.L. Martin, E. Djurado, Influence of sintering temperature on morphology and electrochemical performance of LSCF/GDC composite films as efficient cathode for SOFC, Electrochimica Acta. 246 (2017) 1248–1258. https://doi.org/10.1016/j.electacta.2017.06.070.

- [62] J. Fleig, R. Merkle, J. Maier, The p(O<sub>2</sub>) dependence of oxygen surface coverage and exchange current density of mixed conducting oxide electrodes: model considerations, Phys. Chem. Chem. Phys. 9 (2007) 2713–2723. https://doi.org/10.1039/B618765J.
- [63] Y. Takeda, R. Kanno, M. Noda, Y. Tomida, O. Yamamoto, Cathodic polarization phenomena of perovskite oxide electrodes with stabilized zirconia, J. Electrochem. Soc. 134 (1987) 2656. https://doi.org/10.1149/1.2100267.
- [64] T. Nakamura, Y. Takeyama, S. Watanabe, K. Yashiro, K. Sato, T. Hashida, J. Mizusaki, Oxygen nonstoichiometry, crystal structure, and mechanical properties of La2NiO4+δ, ECS Trans. 25 (2009) 2573. https://doi.org/10.1149/1.3205814.
- [65] N.Q. Minh, Solid Oxide fuel cells for power generation and hydrogen production, Journal of the Korean Ceramic Society. 47 (2010) 1–7. https://doi.org/10.4191/KCERS.2010.47.1.001.
- [66] T. Dey, D. Singdeo, M. Bose, R.N. Basu, P.C. Ghosh, Study of contact resistance at the electrode-interconnect interfaces in planar type Solid Oxide Fuel Cells, Journal of Power Sources. 233 (2013) 290–298. https://doi.org/10.1016/j.jpowsour.2013.01.111.
- [67] D. Kennouche, Q. Fang, L. Blum, D. Stolten, Analysis of the cathode electrical contact in SOFC Stacks, J. Electrochem. Soc. 165 (2018) F677. https://doi.org/10.1149/2.0761809jes.
- [68] S.P. Jiang, J.G. Love, L. Apateanu, Effect of contact between electrode and current collector on the performance of solid oxide fuel cells, Solid State Ionics. 160 (2003) 15– 26. https://doi.org/10.1016/S0167-2738(03)00127-9.
- [69] J. Sar, L. Dessemond, E. Djurado, Electrochemical properties of graded and homogeneous Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2-δ</sub>-La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> composite electrodes for intermediate-temperature solid oxide fuel cells, International Journal of Hydrogen Energy. 41 (2016) 17037–17043. https://doi.org/10.1016/j.ijhydene.2016.07.236.
- [70] S.B. Adler, Factors governing oxygen reduction in solid oxide fuel cell cathodes, Chem. Rev. 104 (2004) 4791–4844. https://doi.org/10.1021/cr0207240.
- [71] A. Egger, W. Sitte, Enhanced oxygen surface exchange of La2NiO4+δ by means of a thin surface layer of silver, Solid State Ionics. 258 (2014) 30–37. https://doi.org/10.1016/j.ssi.2014.01.038.
- [72] X. Tong, F. Zhou, S. Yang, S. Zhong, M. Wei, Y. Liu, Performance and stability of Ruddlesden-Popper La<sub>2</sub>NiO<sub>4+δ</sub> oxygen electrodes under solid oxide electrolysis cell operation conditions, Ceram. Int. 43 (2017) 10927–10933. https://doi.org/10.1016/j.ceramint.2017.05.130.
- [73] F. Monaco, V. Tezyk, E. Siebert, S. Pylypko, B. Morel, J. Vulliet, T. Le Bihan, F. Lefebvre-Joud, J. Laurencin, Experimental validation of a  $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$  electrode model operated in electrolysis mode: Understanding the reaction pathway under anodic polarization, Solid State Ion. 319 (2018) 234–246. https://doi.org/10.1016/j.ssi.2018.02.012.

## Part II

## Reaction mechanisms of of mixed ionic and electronic conductors used as oxygen electrodes in Solid Oxide Cell: focus on $La_{1-x}Sr_xCo_{y-1}Fe_yO_{3-\delta}$ and $La_2NiO_{4+\delta}$

Lydia Yefsah<sup>a,b</sup>, Giuseppe Sdanghi<sup>b,c</sup>, Giuseppe Sassone<sup>b</sup>, Jean-Marc Bassat<sup>c</sup>, Maxime Hubert<sup>b</sup>, Fabrice Mauvy<sup>c</sup>, Elisabeth Djurado<sup>a</sup>, Jérôme Laurencin<sup>b</sup>

<sup>a</sup>Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 38000 Grenoble, France <sup>b</sup>Univ. Grenoble Alpes – CEA, LITEN, DTCH, 17 rue des Martyrs, 38054, Grenoble, France <sup>c</sup>CNRS, Univ. Bordeaux, ICMCB, 87 Av. Dr. Schweitzer, 33608 Pessac, France Tel.: +33-4-76 82 65 21 <u>lydia.yefsah@lepmi.grenoble-inp.fr</u>

## Abstract

 $La_{1-x}Sr_xCo_{y-1}Fe_yO_{3-\delta}$  (LSCF), a typical oxygen electrode in Solid Oxide Cells (SOCs), is an oxygen-deficient perovskite material. Although this mixed ionic and electronic conductor (MIEC) offers good electrochemical performances, it suffers from chemical decomposition in operation at high temperature. The oxygen over-stoichiometric electrode material  $La_2NiO_{4+\delta}$  (LNO) is considered nowadays as an alternative solution to the classical perovskite-based electrodes. Indeed, LNO is chemically stable in a wide range of temperatures and oxygen partial pressures, providing high MIEC conductivity as well as fast oxygen reaction kinetics.

The deep understanding of the reaction mechanisms taking place in a SOC oxygen electrode is a prerequisite before microstructural optimization. In this work, we propose a coupled experimental and modelling approach aimed to investigate the reaction mechanisms for both under- and over-stoichiometric oxygen electrode materials. Two main reaction pathways have been considered, the oxygen incorporation/excorporation at the gas/electrode interface for the bulk path and the direct charge transfer at the TPBIs for the surface path. Polarization curves and impedance diagrams under various operating conditions (650-750°C, 0.15 - 1 atm, and  $\pm$ 100 mA cm<sup>-2</sup>) have been recorded by using a three-electrode setup. These data were used to calibrate the models based on elementary reactions. In addition, all the microstructural parameters required for the simulation have been computed on a 3D electrode reconstruction obtained by FIB-SEM tomography. A change from the bulk towards the surface path was observed for the LSCF electrode under low anodic polarization, which was explained by the progressive depletion of oxygen vacancies when increasing the anodic polarization. Conversely, a limitation of the bulk path was observed under cathodic polarization for the LNO electrode, which was due to the significant reduction of the oxygen over stoichiometry under these conditions. The impact of the temperature and the  $pO_2$  on the reaction pathways has been also investigated for both materials and is discussed in this article.

### 1. Introduction

SOCs are high-temperature electrochemical energy-conversion devices that produce efficiently clean electricity (solid oxide fuel cell, SOFC mode) or hydrogen (solid oxide electrolysis cell, SOEC mode). These technologies are composed of an assembly of two porous electrodes separated by a thin dense electrolyte in Yttria Stabilized Zirconia (YSZ). The porous hydrogen electrode is usually a Nickel and YSZ cermet while mixed ionic and electronic conductors (MIECs) are mostly developed as oxygen electrode materials. This mixed property allows extending the oxygen reaction on the whole gas/electrode interface. The classical MIECs material is the lanthanum doped strontium cobalt ferrite  $La_{1-x}Sr_xCo_{y-1}Fe_yO_{3-\delta}$  (LSCF) [1-2]. This oxygen-deficient perovskite presents a good ionic and electronic conductivity as well as a high oxygen surface exchange rate. However, LSCF suffers of large degradation rates due to chemical decomposition at high operating and reactivity with electrolyte [3-5]. These degradations induce significant loss in SOCs performances, especially when they are operated in SOEC mode. In this context, rare earth nickelates  $Ln_2NiO_{4+\delta}$  (Ln = La, Pr, Nd) are considered nowadays as alternative oxygen electrode materials. The crystal structure of this overstoichiometric material consists of LnNiO<sub>3</sub> perovskite block inter-grown between LnO rocksalt layers. The excess oxygen occupies interstitial sites within the LnO layers. Among the different component, La<sub>2</sub>NiO<sub>4+ $\delta$ </sub> (LNO) has been chosen in this study thanks to its chemical stability in a wide range of temperature [6]. The aim of this work is to analyze, by an experimental and a modelling approach, the effect of the temperature, polarization and oxygen partial pressure on the reaction pathways for LSCF and LNO electrodes.

## 2. Scientific Approach

#### 2.1 Experiments

The two electrode materials, LSCF and LNO, were deposited by screen-printing on each side of a circular and dense 8YSZ electrolyte (thickness = 260  $\mu$ m, diameter = 25 mm). In order to prevent the reactivity with YSZ that leads to the formation of insulating phases [7-8], a Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>2-8</sub> (CGO) barrier layer of 2  $\mu$ m of thickness was added in between the electrodes and the electrolyte. The symmetrical cells were then tested in a 3-electrodes setup. A platinum wire was positioned at the periphery of the electrolyte membrane and used as reference electrode (RE). Two platinum grids with a mesh of 3600 meshes cm<sup>-2</sup> and a surface equal to the electrodes were used as current collectors. It can be noticed that a thick disk in porous gold was also added between the ceramic housing and the platinum grids so that each electrode surface can be considered as equipotential. A load of 0.7 kg cm<sup>-2</sup> was applied to ensure the electric contact between the metallic grids and the electrodes. At the beginning of the test, the cells were heated up to 800 °C at a rate of 1 °C min<sup>-1</sup>. This temperature has been maintained during several hours until the stabilization of the electrochemical impedance spectra (EIS) measured at open circuit potential (OCP).

Electrochemical characterizations were then carried out at a temperature of 750, 700 and 650°C under air condition, with a gas flow rate of  $\approx 2\text{NL} \text{min}^{-1}$ . For each temperature, polarization curves have been recorded for both cells whereas EIS diagrams were acquired at OCP, in a frequency range of 10<sup>6</sup> to 10<sup>-2</sup> Hz, with an amplitude of  $\pm$  10 mA cm<sup>-2</sup>. For the temperature of 700°C, the electrochemical characterizations were complemented by EIS diagrams measured under anodic and cathodic current (with  $i_{dc} = \pm 50$  mA cm<sup>-2</sup> for LSCF electrode and  $i_{dc} = \pm 100$  mA cm<sup>-2</sup> for LNO electrode) and over a large range of oxygen partial pressure from 0.10 to 1 atm.

## 2.2 Model Description

An elementary model framework for MIEC electrodes has been developed and used to investigate the LSCF and LNO reaction mechanisms occurring under anodic and cathodic polarization. In this approach, surface and bulk species are taken into account as well as their transport in the electrodes phases. A temporal term is also added on each mass/charge balance for the EIS computations. The mass transfer in the LNO and LSCF is calculated trough the

chemical diffusivity of the oxygen interstitials or vacancies, respectively, while the electronic current density is modeled using a classical Ohm's law. Both molecular and Knudsen diffusions are taken into account for the mass transport in the gas phase. Finally, the diffusion of oxygen adatoms  $O_{ads}$ , oxygen ions  $O_{ads}^-$  and molecular oxygen  $O_{2ads}$  at the surface of both materials is computed using a classical Fick's law.

The proposed model considers two possible reaction pathways for oxygen oxidation/reduction divided in a sequence of elementary steps as represented in Figure 1 in electrolysis mode. The "bulk path" is characterized by an ionic transfer at the electrode/electrolyte interface (R1). After diffusion of the oxygen interstitials (for LNO) or oxygen vacancies (for LSCF) in the bulk of the electrode material, the oxygen is ex-corporated to produce oxygen adatoms on the electrode surface (R2). In parallel, the "surface path" considers a direct oxidation at the Triple Phase Boundary length (TPBIs) (R3) leading to the formation of oxygen ions on the electrode surface. Then, in both cases, a second reaction of charge transfer (R4) takes place on the surface to produce oxygen adatoms that can be associated (R5) and desorbed (R6) in the porosity of the electrodes.



Figure 1: Schematic description of the reaction pathway considered in the elementary model (in electrolysis mode) represented for the LNO electrode.

The kinetic constants have been estimated by calibrating the model on the LSCF and LNO polarization curves. Due to the influence of the microstructure on the electrochemical response, all the microstructural properties used as inputs in the model have been extracted from 3D reconstructions obtained for both electrodes. Thereafter, the model has been validated using the electrochemical impedance diagrams recorded at OCP and under polarization for different oxygen partial pressures. The elementary kinetic model has been already published for the LSCF electrode [9] while the one for the LNO is an adaptation of a simplified version available in [10].

## 3. Experimental Results

The experimental electrode polarization curves  $\eta$ -i at 650 °C, 700 °C and 750 °C are represented Figure 2 for the LSCF and LNO oxygen electrode.

As expected, it can be noticed that the electrode performances are thermally activated [72] [73]. With respect to the OCP, a non-symmetrical shape of the  $\eta$ -i curves is observed at 650 °C and 700 °C for both electrodes. However, it is worth mentioning that the electrode performances are better under anodic polarization (SOEC mode) for the LNO electrode, whereas the LSCF electrode exhibits lower overpotentials under cathodic current (SOFC mode). Within the narrow investigated overpotential range, a linear behavior of the  $\eta$ -i curves is observed at 750 °C. The dissymmetry of the polarization curves at lower temperature can be explained either by a change in the reaction mechanism or in the rate-determining steps. Conversely, a unique dominant mechanism with the same co-limitations could explain the linearity of  $\eta$ -i curves at 750 °C in the studied conditions.



Figure 2: Experimental (marks) and simulated (solid lines) polarization curves obtained at 650, 700, and 750 °C under air for a) LSCF[9] and b) LNO electrodes.

The EIS diagrams acquired at OCP are shown in Figure 3 for the LNO and LSCF materials. It is worth noting that the absolute values of the polarization resistances cannot be directly compared between the two electrodes since they present rather different microstructures due to the fabrication. Nevertheless, the shape of the impedance spectra can give key information about the reaction mechanisms. Indeed, for the LSCF electrode, the impedance spectra show a "Gerischer-type" element, whatever the temperature. A small contribution can be noticed at low frequencies on the EIS diagram at 750 °C that can be attributed to a limitation in the gas

conversion reaction [13]. On the contrary, the EIS diagrams at OCP of the LNO electrode shows a different evolution depending on the temperature. A "Gerisher-type" element is observed at 650 °C whereas the diagrams presents a more depressed semi-circle at 700 °C and 750 °C. This evolution suggests an influence of the temperature on the reaction mechanism at OCP for the LNO electrode. On the other hand, the non-evolution of the shape of the EIS diagrams for the LSCF electrode may suggest the presence of a unique dominant reaction mechanism in the range of the studied temperature.



Figure 3: Experimental (marks) and simulated (solid lines) EIS diagrams under air at 650 °C, 700 °C and 750 °C for LSCF [9] (a, b, c) and LNO (c, d, f) electrodes.

For both cases, the EIS diagrams recorded under dc current density at 700 °C have not revealed a change in the shape of the impedance spectra [9-10] compared to the OCP. These results suggest that, for both electrodes, there is no change in the reaction mechanism at 700 °C under polarization for the limited investigated range of dc current. The evolution of the impedance spectroscopy with the oxygen partial pressure is shown in Figure 4. As expected, the polarization resistance of both electrodes decreases with increasing pO<sub>2</sub>.



Figure 4: Impedance diagrams (Nyquist plots) recorded at 700°C for the investigated range of oxygen partial pressure for a) LSCF [9] and b) LNO electrodes.

## 4. Modelling, Results and Discussion

## 4.1 Model calibration and validation

The missing parameters for the models (i.e. the forward kinetic constants for all the reactions, the surface diffusion coefficients and surface coverages at equilibrium for  $pO_2=0.21$  atm [9-10] have been obtained by adjusting the simulations on the experimental polarization curves. The results of this fitting procedure is given in Figure 2 for the two electrodes. Once the model calibrated, the validation was carried out by simulating the impedance spectra without additional fitting. As shown in Figure 3, the model for LSCF or LNO electrode is able to simulate accurately the impedance diagrams at OCP for the three investigated temperatures. Moreover, the reaction order *n* was deduced from the experimental and simulated impedance spectra (Figure 4) according to

$$R_{nol} \propto (pO_2)^{-n}$$
 Eq. 1

These simulated reaction orders have been found to be in good agreement with the experimental ones. Indeed, the errors between the computed and experimental coefficients does not exceed 12% for LSCF [9] and less than 2% for LNO. Therefore, the model for the two electrodes can be considered validated.

## 4.2 Effect of polarization, temperature and $pO_2$ on the reaction pathways

Thanks to the model, the electrode reaction mechanism can be studied as function of the temperature, polarization and oxygen partial pressure. For this purpose, the parameter  $\xi$  is introduced to quantify the relative contribution of the surface or bulk path in the electrode operation. It is expressed as the kinetic rate ratio between (i) the oxygen ad-ions produced at the TPBIs for the surface path and (ii) to the oxygen ad-ions produced by excorporation all along the electrode thickness for the bulk path

$$\xi = v_3 / \int_{z=0}^{z=\ell} v_2 \, dz$$
 Eq. 2

Where  $v_3$  and  $v_2$  is kinetic rates for the charge transfer reactions R3 and R2, respectively. The term  $\ell$  represents the electrode thickness. According to this definition, the reaction mechanism is dominated by the "bulk path" when ratio is lower than one  $(\xi < 1)$ . At the opposite, a value higher than one  $(\xi > 1)$  indicates a mechanism controlled by the "surface path".

For the LSCF electrode, Figure 5a shows an increase of the ratio  $\xi$  when increasing the anodic polarization. A transition from the bulk path ( $\xi < 1$ ) to the surface path ( $\xi > 1$ ) is thus observed at low anodic current density for the three temperatures. This behavior can be explained by the evolution of the kinetics rates plotted in Figure 5b as function of the current density. Indeed, when the anodic polarization increases, the oxygen excorporation rate becomes bounded while the direct oxidation at TPBs remains activated. This behavior is related to the strong decrease of the oxygen vacancies concentration in the LSCF when increasing the anodic polarization [14-15]. In other words, the under-stoichiometry  $\delta$  falls to zero under anodic polarization in such a way that the material can no longer accept oxygen [16]. In parallel, the surface concentrations of the adsorbed species involved in the surface path are increased and remains unlimited (since the sum of surface coverages of all the adsorbates remains lower than the coverage of the available sites). On the other hand, the opposite trend is observed under cathodic polarization. In this case, the incorporation reaction is activated because the concentration of vacancies is increased when increasing the cathodic polarization without limitation (indeed,  $\delta$  remains lower than  $\delta^{max}$ ). Conversely, the charge transfer at TPBs becomes limited since the surface coverages decreases down to zero.

The same behavior is obtained for the three investigated temperatures (Figure 5a). Nevertheless, the influence of temperature on the reaction mechanism is not negligible. Indeed, the contribution of the surface path becomes rapidly more important at 650°C (Figure 5a). At intermediate temperatures (700°C and 750°C), the slopes of the curves are less steep. These results explains the strong dissymmetry of the experimental polarization curves at 650°C while a more linear behavior is observed at 750°C. To summarize, for LSCF oxygen electrode, the bulk path appears as the dominant pathway under fuel cell condition regardless to the temperature. For electrolysis mode, a transition from the bulk path to the surface path appears when the anodic polarization is increased. This transition occurs when the oxygen vacancy concentration tends to zero.



Figure 5: (a) Ratio of the surface to the bulk path as function of the current density plotted for the LSCF electrode at 650°C, 700°C, 750°C and 800°C. (b) Kinetics rates for the charge transfer at TPBs and the oxygen excorporation/incorporation reaction (integrated along the electrode thickness) as function of the current density at 700°C, for the LSCF electrode [9].

The same analysis has been conducted on the over-stoichiometric LNO that exhibits an opposite behavior compared to the LSCF. Indeed, as shown in Figure 6a, the surface-to-bulk path ratio decreases with increasing the overpotentials from cathodic to anodic polarization. This behavior can also be explained by the kinetics rates of the charge transfer at TPBIs and the oxygen excorporation/incorporation reaction (integrated along the electrode thickness) plotted as function of the electrode overpotential (Figure 6b). Indeed, under cathodic polarization, the charge transfer at TPBIs remains strongly activated while the oxygen incorporation reaction becomes bounded. This behavior, which is responsible for the limitation of the bulk path, is directly linked to the concentration of oxygen interstitial in the LNO. Indeed, the simulations

have revealed that the concentration of oxygen interstitial becomes very low under cathodic polarization. According to Figure 6b, the surface path is thus predominant under the investigated range of the cathodic currents. Nevertheless, the charge transfer at TPBIs should also tend towards a limitation when the surface coverage at the LNO surface falls to zero. However, it seems that this limitation is not reached even for the higher cathodic polarization achieved in this work.

Under anodic polarization, both surface and bulk paths remain activated (Figure 6b). Indeed, the concentration of oxygen interstitial is increased with increasing the polarization without reaching the maximum value of oxygen over-stoichiometry (i.e.  $\delta$  remains much lower than  $\delta_{max} = 2$  for LNO [17]). On the other hand, the direct oxidation at TPBs is still promoted since the adsorption sites are not saturated under the applied anodic polarization. These observations allow explaining the results obtained on the experimental electrode polarization curves  $\eta$ -i (Figure 2b). Indeed, the higher performances of the LNO electrode under anodic polarization are explained by the contribution of both bulk and surface paths on the reaction mechanism while only the surface path remains activated under cathodic polarization.

The impact of the temperature on the ratio is shown in Figure 6a. At OCP , the bulk path at 650°C controls the reaction mechanism ( $\xi < I$ ) while the surface path becomes predominant at higher temperature ( $\xi > I$ ). Thus, it can be stated that the temperature promotes the contribution of the charge transfer at the TPBIs for the LNO electrode.



Figure 6: (a) Ratio of the surface to the bulk path as function of the current density plotted for the LNO electrode at 650°C, 700°C, 750°C. (b) Kinetics rates for the charge transfer at TPBs and the oxygen excorporation/incorporation reaction (integrated along the electrode thickness) as function of the current density at 700°C, for the LNO electrode.

Simulations have also been carried out by changing the oxygen partial pressure from 0.10 atm to 1 atm (Figure 7). Whatever the current density, it has been found that the ratio increases with increasing  $pO_2$  for the LSCF electrode. This statement is explained because the understoichiometry is reduced at high oxygen partial pressure [16]. The opposite behavior has been obtained for the LNO electrode. Indeed, the concentration of interstitial increases with the oxygen partial pressure.



Figure 7: Ratio of the surface to bulk path as a function of the electrode overpotential at OCP and 700°C for different oxygen partial pressure for (a) LSCF [9] and (b) LNO.

From this analysis, it appears that the LNO over-stoichiometric material is especially well adapted for an operation in electrolysis mode. Indeed, it has been shown that both surface and bulk paths are promoted under anodic polarization. This result is consistent with the higher performances obtained for the material when operated in SOEC mode. Regarding the oxygen deficient LSCF material, it has been found that the bulk path is predominant for cathodic polarization whereas the surface path becomes favored under anodic current. These statements means that the material can be operated in both modes. However, its performances are slightly higher in fuel cell mode. To enhance the surface path and thus increase the electrode efficiency, it has shown for that a composite electrode made of LSCF/CGO is a relevant solution [18]. The precise role of CGO in a LNO/CGO composite electrode on its operation and performances still needs to be studied. Moreover, the stability of these electrodes for long-term operations remains also a subject of investigations for the two materials.

## 5. Conclusion

Elementary models have been developed and used to predict the electrochemical response of the classical oxygen deficient oxide  $La_{1-x}Sr_xCo_{y-1}Fe_yO_{3-\delta}$  (LSCF) and the alternative oxygen over-stoichiometric material  $La_2NiO_{4+\delta}$  (LNO). To validate the models, dedicated experiments have been performed on symmetrical cells using three-electrode configuration. For the two materials, the determination of the unknown parameters of the models have been done by fitting the experimental electrode polarization curves at three temperatures (650°C, 700°C and 750°C). For the validation, the impedance spectra at OCP and under polarization for different oxygen partial pressures have computed without additional fitting. A good agreement between the experimental and the simulations has been obtained.

Once validated, the models have been used to analyze the electrochemical response of the LSCF and LNO materials by investigating the reaction mechanisms as function of the polarization. For the LSCF, the 'bulk' path related to the oxygen exchange with the material appears as the dominant pathway under cathodic current regardless the temperature. However, the 'surface' path associated to the charge transfer at TPBIs is activated under anodic polarization. This behavior has been ascribed to the strong decrease of the oxygen vacancies concentration in the LSCF when increasing the anodic polarization.

For the LNO electrode, it has been found that both the 'bulk' and 'surface' path are favored under anodic current while only the 'surface' path remains active under cathodic polarization. In this case, the limitation of the 'bulk' path is due to the decrease of the oxygen interstitial concentration in the LNO lattice. These results have allowed explaining the better performances obtained for this material in SOEC mode.

#### Acknowledgements

This work has received funding from the French National Research Agency (ANR) project "ECOREVE" (ANR-18-CE05-0036). The work has also been supported by Genvia and the project CELCER-EHT.

## 6. References

- N.H. Menzler, D. Sebold, O. Guillon, Post-test characterization of a solid oxide fuel cell stack operated for more than 30,000 hours: The cell, J. Power Sources. 374 (2018) 69– 76. https://doi.org/10.1016/j.jpowsour.2017.11.025.
- [2] C. Endler-Schuck, A. Leonide, A. Weber, S. Uhlenbruck, F. Tietz, E. Ivers-Tiffée, Performance analysis of mixed ionic–electronic conducting cathodes in anode supported cells, J. Power Sources. 196 (2011) 7257–7262. https://doi.org/10.1016/j.jpowsour.2010.11.079.
- [3] Z. Pan, Q. Liu, L. Zhang, X. Zhang, S.H. Chan, Effect of Sr surface segregation of La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3 - δ</sub> electrode on its electrochemical performance in SOC, J. Electrochem. Soc. 162 (2015) F1316–F1323. https://doi.org/10.1149/2.0371512jes.
- [4] F. Tietz, D. Sebold, A. Brisse, J. Schefold, Degradation phenomena in a solid oxide electrolysis cell after 9000 h of operation, J. Power Sources. 223 (2013) 129–135. https://doi.org/10.1016/j.jpowsour.2012.09.061.
- [5] S. Uhlenbruck, T. Moskalewicz, N. Jordan, H.-J. Penkalla, H.P. Buchkremer, Element interdiffusion at electrolyte–cathode interfaces in ceramic high-temperature fuel cells, Solid State Ion. 180 (2009) 418–423. https://doi.org/10.1016/j.ssi.2009.01.014.
- [6] V. Vibhu, J.-M. Bassat, A. Flura, C. Nicollet, J.-C. Grenier, A. Rougier, Influence of La/Pr ratio on the ageing properties of  $La_{2-x}Pr_xNiO_{4+\delta}$  as cathodes in IT-SOFCs, ECS Trans. 68 (2015) 825.
- [7] M.D. Anderson, J.W. Stevenson, S.P. Simner, Reactivity of lanthanide ferrite SOFC cathodes with YSZ electrolyte, J. Power Sources. 129 (2004) 188–192. https://doi.org/10.1016/j.jpowsour.2003.11.039.
- [8] A. Montenegro-Hernández, A. Soldati, L. Mogni, H. Troiani, A. Schreiber, F. Soldera, A. Caneiro, Reactivity at the  $Ln_2NiO_{4+\delta}$ /electrolyte interface (Ln = La, Nd) studied by electrochemical impedance spectroscopy and transmission electron microscopy, J. Power Sources. 265 (2014) 6–13. https://doi.org/10.1016/j.jpowsour.2014.04.082.
- [9] E. Effori, J. Laurencin, E.D.R. Silva, M. Hubert, T. David, M. Petitjean, G. Geneste, L. Dessemond, E. Siebert, An elementary kinetic model for the LSCF and LSCF-CGO electrodes of solid oxide cells: impact of operating conditions and degradation on the electrode response, J. Electrochem. Soc. 168 (2021) 044520. https://doi.org/10.1149/1945-7111/abf40a.
- [10] G. Sdanghi, L. Yefsah, F. Mauvy, E. Djurado, T. David, J.-M. Bassat, J. Laurencin, Reaction mechanisms of  $La_2NiO_{4+\delta}$  oxygen electrodes operated in electrolysis and fuel cell mode, J. Electrochem. Soc. 169 (2022) 034518. https://doi.org/10.1149/1945-7111/ac58c3.
- [11] X. Tong, F. Zhou, S. Yang, S. Zhong, M. Wei, Y. Liu, Performance and stability of Ruddlesden-Popper La<sub>2</sub>NiO<sub>4+δ</sub> oxygen electrodes under solid oxide electrolysis cell operation conditions, Ceram. Int. 43 (2017) 10927–10933. https://doi.org/10.1016/j.ceramint.2017.05.130.
- [12] F. Monaco, V. Tezyk, E. Siebert, S. Pylypko, B. Morel, J. Vulliet, T. Le Bihan, F. Lefebvre-Joud, J. Laurencin, Experimental validation of a La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> electrode model operated in electrolysis mode: Understanding the reaction pathway

under anodic polarization, Solid State Ion. 319 (2018) 234–246. https://doi.org/10.1016/j.ssi.2018.02.012.

- [13] J. Nielsen, T. Jacobsen, M. Wandel, Impedance of porous IT-SOFC LSCF:CGO composite cathodes, Electrochim. Acta. 56 (2011) 7963–7974. https://doi.org/10.1016/j.electacta.2011.05.042.
- [14] J. Laurencin, M. Hubert, K. Couturier, T.L. Bihan, P. Cloetens, F. Lefebvre-Joud, E. Siebert, Reactive mechanisms of LSCF single phase and LSCF-CGO composite electrodes operated in anodic and cathodic polarisations, Electrochim. Acta. 174 (2015) 1299–1316. https://doi.org/10.1016/j.electacta.2015.06.080.
- [15] M. Hubert, J. Laurencin, P. Cloetens, J.C. da Silva, F. Lefebvre-Joud, P. Bleuet, A. Nakajo, E. Siebert, Role of microstructure on electrode operating mechanisms for mixed ionic electronic conductors: From synchrotron-based 3D reconstruction to 294 electrochemical modeling, Solid State Ion. (2016)90-107. https://doi.org/10.1016/j.ssi.2016.07.001.
- [16] S.R. Bishop, K.L. Duncan, E.D. Wachsman, Surface and bulk defect equilibria in strontium-doped lanthanum cobalt iron oxide, J. Electrochem. Soc. 156 (2009) B1242. https://doi.org/10.1149/1.3194783.
- [17] T. Nakamura, R. Oike, Y. Ling, Y. Tamenori, K. Amezawa, The determining factor for interstitial oxygen formation in Ruddlesden–Popper type La2NiO4-based oxides, Phys. Chem. Chem. Phys. 18 (2016) 1564–1569. https://doi.org/10.1039/C5CP05993C.
- [18] E. Effori, H. Moussaoui, F. Monaco, R.K. Sharma, J. Debayle, Y. Gavet, G. Delette, G.S. Larbi, E. Siebert, J. Vulliet, L. Dessemond, J. Laurencin, Reaction mechanism and impact of microstructure on performances for the LSCF-CGO composite electrode in solid oxide cells, Fuel Cells. 19 (2019) 429–444. https://doi.org/10.1002/fuce.201800185.

#### General conclusion of the chapter III

This chapter has been dedicated to the study of the reaction mechanisms that occur in the  $La_2NiO_{4+\delta}$  (LNO) oxygen electrode in fuel cell and electrolysis modes by coupling an experimental and a modelling approach. A comparative study of the reaction mechanisms was also undertaken in the classical oxygen deficient LSCF electrode.

The model developed in the first part of this work was able to reproduce and provide an explanation for the electrochemical observations measured on the LNO. Indeed, the experimental measurements carried out on a symmetrical LNO/GDC/YSZ cell showed a dependence of the operating conditions on the electrode performance. A dissymmetry of the polarization curves has been highlighted, with higher performances achieved under anodic current. Moreover, as expected, a decrease of the polarization resistance at OCP was observed with increasing the temperature. This improvement in performance is accompanied in the case of the LNO by an evolution in the shape of the impedance spectra at OCP from a "Gerishertype" diagram at 650 °C to a semi-circle at 750 °C. Finally, impedance spectra acquired at 700 °C by varying the  $pO_2$  between 0.15 to 1 atm have shown a decrease in polarization resistances with oxygen partial pressure. All these electrochemical phenomena have been explained thanks to the physical-based electrode model proposed in this work, which considers parallel pathways for the OER/ORR mechanisms, i.e.: (i) the oxygen two incorporation/excorporation at the gas/electrode interface for the bulk path and; (ii) the direct charge transfer at the TPBIs for the surface path. The plot of the evolution of the ratio between these two reaction paths has revealed a transition in the reaction mechanism from the bulk path at 650 °C to the surface path at 700 °C and 750 °C at OCP. This change explains the evolution of the shape of the observed impedance diagrams. Moreover, the evolution of this ratio as a function of temperature and current showed that

- under cathodic current (SOFC mode), the ratio surface/bulk path increases with current and with the temperature (Part I - Figure 8b). In other words, the surface path related to charge transfer at TPBs is predominant. This behaviour has been explained by the limitation of the bulk path due to the depletion of the oxygen interstitial under cathodic current (Part I - Figure 8c).
- under anodic current (SOEC mode), both bulk and surface paths remain activated. Indeed, the concentration of oxygen interstitial increases when increasing the polarization without reaching the maximum value of oxygen over-stoichiometry  $\delta_{max}=2$

for LNO. On the other hand, the direct oxidation at TPBs is still promoted since the adsorption sites are not saturated under the applied anodic polarization.

In the same way, the evolution of this ratio as a function of the oxygen partial pressure at 700 °C has shown that the bulk path becomes more and more activated while the surface path remains constant (Part I – Figure 9). This evolution explains the better performance obtained on this electrode when the  $pO_2$  is increased.

Aside from these results, even though the model is able to reproduce the experimental results, a frequency lag has been observed between the simulated and the experimental frequency diagrams. These observations were attributed to an inhomogeneity in the current distribution during electrochemical measurements. This hypothesis has been developed through a small study using the model to simulate the EIS response of a "perfect electrode" by removing the effect of the overall ohmic losses. The simulation curves which perfectly fit with the frequency diagrams confirm the influence of the contact resistance on the electrode behaviour.

The second part of this work provided a relevant comparison of the evolution of the reaction mechanisms and the rate-determining steps between under- and over- stoichiometric (i.e. LSCF versus LNO), as a function of the temperature and oxygen partial pressure. For this purpose, the LNO basic model has been extended into a full elementary kinetics, decomposed into six reactions steps. The detail of the equations is given in Appendix I. By using the same input data (i-V curves, EIS, 3D reconstruction and literature data), the number of variables included in this elementary model is more numerous. However, the conclusions remain similar to the basic model in the case of the LNO described above. Briefly, for the LNO electrode, it was found that the "bulk" and "surface" pathways are favoured under anodic current. On the other hand, under cathodic polarization, only the "surface" pathway remains active due to the limitation of the "bulk" pathway arising from the decrease of the interstitial oxygen concentration in the LNO lattice. On the contrary, for the LSCF, the "bulk" path related to the exchange of oxygen with the material appears to be the dominant path under cathodic current whatever the temperature. On the other hand, under anodic polarization, the "surface" pathway related to the charge transfer at the TPBIs is activated while the bulk path becomes more and more limited. This behaviour has been attributed to the strong decrease of the oxygen vacancies concentration in the LSCF with increasing anodic polarization.

To conclude, the evolution of these reaction mechanisms suggests that  $La_2NiO_{4+\delta}$  (LNO) seems to be more suitable as an oxygen electrode for SOEC operation than LSCF. These results

are in good agreement with the experimental measurements that have shown a better performance of LNO than LSCF under anodic current in the electrolysis mode. To conclude, it would seem that the superstoichiometric oxygen or oxygen-deficient composition plays a predominant role in the reaction mechanisms of the oxygen electrode in SOCs.

# Chapter IV

PrO<sub>1.833</sub> as a promising oxygen electrode for SOEC: electrochemical performance and durability

# Chapter IV - PrO<sub>1.833</sub> as a promising oxygen electrode for SOEC: electrochemical performance and durability

The industrial deployment of the electrolysis technology at high temperature (SOEC) is still hampered by key issues related in part to the durability of ceramic cells. It is therefore essential to study the degradation of SOECs in operation. For this, it is a question of studying the microstructural evolutions and the decompositions of the materials in SOEC conditions, according to the temperature and the polarization.

In this context, chapter IV focuses in particular on the investigation of the electrochemical performances and durability of an innovative nanostructured  $PrO_{1.833}$  oxygen electrode for SOEC. This electrode is composed of an active functional layer (AFL) fabricated by electrostatic spray deposition (ESD), topped by a current collecting layer (CCL) in LSM. The following work is based on an optimized architectured oxygen electrode. The aim of this study is to provide a better understanding of the structural, microstructural, and electrochemical properties and efficiency of this oxygen electrode in electrolysis operation. Thus, several stages have been followed to achieve this purpose:

- Electrochemical survey on complete cell (Ni-YSZ/YSZ/GDC/PrO<sub>1.833</sub>/LSM) before and after SOEC long-term test,
  - i. i-V curves (in SOEC mode at 700 °C,  $H_2O/H_2 = 90/10$ ) before and after long-term test up to 1000 h,
  - ii. EIS diagrams (OCV, 700 °C,  $H_2O/H_2 = 90/10$ ) before and after long-term tests up to 1000 h,
  - iii. Long-term test (1000 h) in SOEC mode at 700 °C and under polarization (- 0.5 A cm<sup>-2</sup>)
- Analyzis of the microstructural evolution by comparing pristine and aged cells with SEM observations
- 3) Analyzis of the structural and chemical evolutions using synchrotron-based μ-X-ray diffraction (μ-XRD) and μ-X-ray fluorescence (μ-XRF) characterizations for the initial cells and the aged ones. These characterization techniques are relevant for detecting, at the micron scale, chemical elements and phases, and their distribution in the volume of the

electrode, the electrolyte, and the interfaces.

Structural characterizations performed on two symmetrical cells with this oxygen electrode, made of  $PrO_{1.833}$  and LSM, deposited on GDC electrolyte, thermally aged at 700 °C for 1000 h and 800 °C for 700 h to complete the understanding of this durability study without any polarizations.

This study has been published in the Journal of Solid State Ionics (399 (2023) 116316).

## Electrochemical performance and stability of PrO<sub>1.833</sub> as an oxygen electrode for Solid Oxide Electrolysis Cells

Yefsah Lydia<sup>a,b</sup>, Jérôme Laurencin<sup>b</sup>, Maxime Hubert<sup>b</sup>, Dario Ferreira Sanchez<sup>c</sup>, Frédéric Charlot<sup>d</sup>, Karine Couturier<sup>b</sup>, Ozden Celikbilek<sup>b</sup> and Elisabeth Djurado<sup>a\*</sup>

<sup>a</sup>Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 38000 Grenoble, France
<sup>b</sup>Univ. Grenoble Alpes, CEA/LITEN, 17 avenue des Martyrs, F-38054 Grenoble, France
<sup>c</sup>Swiss Light Source, Paul Scherrer Institut, CH-5232, Villigen, PSI, Switzerland
<sup>d</sup>CMTC, Grenoble INP, Univ. Grenoble Alpes, F-38000, Grenoble, France

#### Abstract

Significant efforts have recently been undertaken to develop highly efficient solid oxide cells for high-temperature steam electrolysis (SOEC). Implementing new materials and microstructures that would improve the performance and durability of this technology remains a major issue. For this purpose, a nano-structured PrO<sub>1.833</sub> material coated by the electrostatic spray deposition (ESD) technique was studied as a promising active oxygen electrode for SOEC application. The study was performed considering the PrOx as the functional layer and strontium-doped lanthanum manganite (LSM) as the current collecting layer on a standard halfcell supported by a typical Ni-YSZ cermet, a YSZ electrolyte, and a gadolinium-doped ceria (GDC) barrier layer. The electrochemical characterizations showed promising initial performance at 700 °C in SOEC mode (- 1 A cm<sup>-2</sup> at 1.4 V with  $H_2O/H_2 = 90$  vol. %/10 vol. %). In addition, a reasonable degradation rate of ~ 5.8 % kh<sup>-1</sup> was obtained at 700 °C within 1000 h of SOEC operation. The structural and elemental evolutions were analyzed with micrometer size resolution all along the functional layer thickness using synchrotron µ-X-ray diffraction and fluorescence. The electrode degradation was primarily attributed to the phase transitions of PrO<sub>1,833</sub>. In particular, the structural analyses of the sample aged under applied current revealed a small quantity of  $PrO_{1.5 \le x \le 1.7}$  phase at the GDC/AFL (active functional layer) interface which is expected to be less conductive than PrO<sub>1.833</sub>, along with PrO<sub>1.714</sub> and GDC phases. Finally, additional structural characterizations were performed on samples annealed at different temperatures and dwell times: 700 °C for 1000 h and 800 °C for 700 h, respectively. The results are discussed to provide a better understanding of the stability of the praseodymium oxide.

**Keywords:** SOEC, nanostructured oxygen electrode, electrostatic spray deposition, durability study, synchrotron  $\mu$ -X-ray diffraction and  $\mu$ -X-ray fluorescence

## **1. Introduction**

Solid oxide cells (SOCs) are high-temperature electrochemical energy-conversion devices that efficiently produce clean electricity in the solid oxide fuel cell (SOFC) mode, and green hydrogen in the solid oxide electrolysis cell (SOEC) mode. The high operating temperatures (750-850°C) of the SOCs combined with the high polarizations applied on the electrodes can induce physical and chemical degradation of their components, reducing the lifetime of the cells [1,2]. One of the strategies to mitigate this issue is to reduce the operating temperatures down to 650-750°C range. However, reducing the temperature leads to a decrease in the electrochemical performance due to higher activation energy and lower reaction kinetics, especially in the oxygen electrode. Thus, a significant increase in the oxygen electrode performance is required.

One approach to improve the electrochemical performance of the oxygen electrode is to use mixed ionic and electronic conductors (MIEC) that exhibit high oxygen ion diffusion and surface exchange coefficients. Another approach is to manufacture nanostructured oxygen electrodes with a high specific surface area. Indeed, nanostructured oxygen electrodes deposited by the electrostatic spray deposition (ESD) technique have been proven to reduce substantially the polarization resistance. The ESD process consists of aerosol atomization from a solution of precursors directed to a heated substrate under high electrical voltage [3,4]. The microstructure of the coatings is controlled by the physico-chemical properties of the precursor solution as well as the ESD deposition parameters [5]. As a result, this technique is capable of depositing a variety of electrode microstructures, called dense, columnar or coral, at the nanometer length scales, with properties of high crystallinity and good adhesion to the electrolyte [6,7]. Active functional layers (AFL) made up of MIEC materials such as La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> (LSCF) and  $La_{2-x}Pr_xNiO_{4+\delta}$  ( $0 \le x \le 2$ ) have been designed by ESD and studied as oxygen electrodes for SOCs [8,9]. LSCF deposited on a gadolinia-doped ceria (Ce0.9Gd0.1O2-8, GDC) electrolyte provided an polarization resistance value as low as 0.065  $\Omega$  cm<sup>2</sup> at 600 °C, representing one of the lowest values reported in the literature [8]. This film is a bi-layer of an AFL of LSCF deposited by ESD and topped by a screen-printed (SP) current collecting layer (CCL) of the same material. The lowest polarization resistance values among the rare-earth nickelates  $La_{2-x}Pr_xNiO_{4+\delta}$  (0  $\leq x \leq 2$ ) were obtained similarly using a hierarchical double layer microstructure with highly porous coral-type ESD layer as AFL topped by a screen-printed CCL deposited on GDC electrolyte [9]. For example, a polarization resistance value of 0.42  $\Omega~\text{cm}^2$  was measured at 600°C with an AFL of La\_2NiO\_{4+\delta} (LNO, x=0) electrode with a

particle size of 150 nm. The polarization resistances were improved by increasing the active surface area at the AFL thanks to the nano-scale porosity and particle size obtained by ESD. A further reduction in  $R_{pol}$  down to 0.16  $\Omega$  cm<sup>2</sup> at 600 °C was successfully obtained for LNO when a GDC/LNO composite sub-layer was added at the electrode/electrolyte interface [10]. In comparison, Sayers et al. [11] reported a polarization resistance of 3.5  $\Omega$  cm<sup>2</sup> at 600 °C for LNO electrode, with particle size of about 1 to 2  $\mu$ m, deposited on GDC electrolyte topped by a thin compact LNO layer. A lower  $R_{pol}$  value of 0.93  $\Omega$  cm<sup>2</sup> at 600 °C was reported by Vibhu et al. [12] for screen-printed LNO electrode with particle size of 0.4 µm deposited on 8YSZ electrolyte and GDC barrier layer. Besides, the material composition also has a significant impact on the electrode performance. For La<sub>1-x</sub>Pr<sub>x</sub>NiO<sub>4+ $\delta$ </sub> ( $0 \le x \le 2$ ) deposited on GDC, it has been shown that the electrochemical performance increases with increasing Pr content [9] (i.e.  $R_{pol}$  of 0.42, 0.23, 0.12 and 0.08 Ω cm<sup>2</sup> at 600 °C for La<sub>2</sub>NiO<sub>4+δ</sub>, La<sub>1.5</sub>Pr<sub>0.5</sub>NiO<sub>4+δ</sub>, LaPrNiO<sub>4+δ</sub> and  $Pr_2NiO_{4+\delta}$  respectively). However, a higher amount of Pr in La<sub>1-x</sub>Pr<sub>x</sub>NiO<sub>4+ $\delta}$ </sub> showed a poor thermodynamic stability [13–15]. Advanced structural characterizations by synchrotron  $\mu$ -Xray diffraction showed that, under current, LaPrNiO<sub>4+ $\delta$ </sub> (LPNO, x =1) deposited by ESD on GDC electrolyte rapidly dissociated into (La,Pr)<sub>4</sub>Ni<sub>3</sub>O<sub>10-δ</sub>, (La,Pr)<sub>3</sub>Ni<sub>2</sub>O<sub>7-δ</sub> and a significant amount of Pr<sub>6</sub>O<sub>11</sub> (i.e. PrO<sub>1.833</sub>) [16].

The praseodymium oxide system is composed of polymorphs ranging from PrO<sub>2</sub> to Pr<sub>2</sub>O<sub>3</sub>. The intermediate rare earth oxides can be described by PrO<sub>x</sub> compositions, with x varying from 2 to 1.5, while the valence of the Pr cation varies from +4 to +3 when the temperature is increased and/or for a lower oxygen partial pressure. The phases are listed in Table 1 including their symmetry [17,18]. In the range  $2 \ge x \ge 1.80$ , the PrO<sub>x</sub> phases present a face-centered cubic structure (FCC) with a cell parameter, a, varying from 5.393 to 5.482 Å [18]. A rhombohedral phase can be observed for  $1.78 \ge x \ge 1.71$  while the phases with lower x are characterized by a body-centered cubic lattice (BCC) [17]. When x is ranging from 1.5 to 1.7, a BCC cubic structure with a larger cell parameter of 11.07 Å is observed. For x = 1.5, a phase transition to an A-type hexagonal structure can occur, or it can also crystallize in a cubic polymorph (C-type structure) for a specific preparation procedure [19,20]. In [21] it has been shown that the conductivity of these different PrO<sub>x</sub> phases is decreased when the oxidation degree of Pr is reduced. The transition between the various phases is controlled by the temperature and the oxygen partial pressure [17,22,23]. Hyde et al. [17] provided a detailed study on the influence of these parameters on the phase transitions. However, the formation of these various phases can also depend on other parameters such as the microstructure and the experimental deposition conditions. For instance, the processing, such as the manufacturing method, precursors, heating and cooling rate, could influence the phase transition [24–26]. Moreover, the electrode polarization or the applied current could also trigger additional decomposition.

The recent attention on the PrO<sub>x</sub> as oxygen electrode for solid oxide cells is due to its very high electrocatalytic activity at low temperatures. Indeed, a high oxygen surface exchange coefficient of  $k^* = 5.4 \times 10^{-7}$  cm s<sup>-1</sup>, was reported for PrO<sub>1.833</sub> (i.e. Pr<sub>6</sub>O<sub>11</sub>) at 600 °C [27]. Moreover, it exhibits a mixed ionic and electronic conductivity thanks to the two valence states (+3/+4) of praseodymium and the presence of oxygen vacancies in its fluorite cubic structure [28–30]. However, it should be pointed out that it has a low electrical conductivity (i.e.  $\sigma < 4$  S cm<sup>-1</sup>) for the whole range of SOEC operation temperature [21,27,30–32] compared to a state-of-the-art MIEC material such as LSCF. Nevertheless, its relatively poor conductivity does not seem to lower its electrochemical activity when used as an active layer [33,34] or as an infiltrated catalyst [27,35–37].

For example, a polarization resistance value measured as low as 0.02  $\Omega$  cm<sup>2</sup> at 600 °C was obtained for a pure PrO<sub>1.833</sub> electrode deposited on GDC by ESD and topped by a strontium-doped lanthanum manganite (LSM) [33,38]. Moreover Nicollet et al. [27] reported a low R<sub>pol</sub> value (0.028  $\Omega$  cm<sup>2</sup> at 600 °C) by infiltrating PrO<sub>1.833</sub> into GDC backbone. Several other studies also revealed a 3 to 10-fold reduction in R<sub>pol</sub> values for different electrodes infiltrated by PrO<sub>x</sub> [35,36,39]. Additionally, complete cells manufactured with PrO<sub>x</sub> as oxygen electrode exhibited high electrochemical performance. Most of the works are using PrO<sub>x</sub> as an oxygen electrode in the SOFC mode [27,34,37,40]. For instance, Dogdibegovic et al. [37] performed measurements on metal supported solid oxide cells using different oxygen electrode materials such as perovskite, nickelate or praseodymium oxide. The authors reported the highest power density (1.56 W cm<sup>-2</sup> at 700 °C) when they used the infiltrated PrO<sub>x</sub> catalyst in the AFL. In SOEC mode, Wang et al. [41] reported a very high efficiency (- 1.5 A cm<sup>-2</sup> at 1.4 V with 50 vol.% steam on hydrogen electrode side at 700 °C).

Despite the good performances obtained with  $PrO_x$  as oxygen electrode material, the average oxidation state of Pr in operating conditions remains a fundamental question for SOC applications. Indeed, preliminary XRD studies on  $PrO_x$  electrode deposited by ESD on GDC showed the presence of  $PrO_{1.5}$  as well as a low quantity of another unknown phase after thermal aging at 900 °C for 10 days in air [18].

In this work, it is proposed to study the performance and the stability of  $PrO_x$  electrode deposited by ESD onto standard half-cell. A columnar-type AFL deposited by ESD and a screen-printed CCL made of  $La_{0.7}Sr_{0.3}MnO_{3-\delta}$  (LSM) on top were prepared following our previous microstructural optimization [33,38]. The electrochemical measurements have been

investigated before and after a long-term test (at 700 °C for 1000 h) under electrolysis mode (-0.5 A cm<sup>-2</sup>, with ratio H<sub>2</sub>O/H<sub>2</sub>=90/10 and steam conversion (SC) of 25%). The microstructure of the electrodes was characterized by scanning electron microscopy (SEM). The structural and chemical stability of PrO<sub>x</sub> was assessed by synchrotron  $\mu$ -X ray diffraction and fluorescence with a micrometer scale resolution. Moreover, a thermal aging study was conducted at 700 °C for 1000 h and at 800 °C for 700 h to investigate the thermal stability of the electrode without applied current. Finally, the electrochemical results were discussed in light of the structural and microstructural evolution of the oxygen electrode.

Formula	x in PrOx	Symbol of the	Oxidation	Symmetry, Bravais lattice	Lattice parameters (Å)	Ref
		phase	Pr	Di avais lattice	purumeters (Ay	
PrO <sub>2</sub>	2	α	4.000	Cubic, FCC	a = 5.393	[18]
$Pr_6O_{11}$	1.833	β	3.667	Cubic, FCC	a = 5.469	[18]
$Pr_{11}O_{20}$	1.818	δ	3.636	Cubic, FCC	a = 5.478	[18]
Pr₅O <sub>9</sub>	1.8	ε	3.600	Cubic, FCC	a = 5.482	[18]
Pr <sub>7</sub> O <sub>12</sub>	1.714	ι	3.428	Rhombohedral,	a = b =10.295	
				$R\overline{3}$	c = 9.598	
	1.5 < x < 1.7	σ		Cubic, BCC		[17]
$Pr_2O_3$	1.5	ф	3.000	Cubic, BCC	a = 11.14	[18]
				Hexagonal, A-	a = 3.85, c = 6.008	
				type		

Table 1: Non-exhaustive list of homologous series of the praseodymium oxides.

### 2. Experimental

#### 2.1. Cell preparation

The oxygen electrode is composed of  $PrO_x$  as AFL deposited by ESD and topped by LSM  $(La_{0.7}Sr_{0.3}MnO_{3-\delta})$  as CCL deposited by screen-printing in a double-layer architecture. ESD works with a heated substrate that moves in X-Y to ensure uniform deposition of the oxide layer on the entire area while the needle is fixed. A metallic circle-shaped screen of 14 mm or 34 mm in diameter is fixed on the substrate to form a circle-shaped deposited layer. For the ESD deposition of  $PrO_{1.833}$  praseodymium nitrate hexahydrate powder ( $Pr(NO_3)_3 \cdot 6H_2O$ , Aldrich, 99 %) was dissolved in a 0.02 M of solvent mixture of ethanol (EtOH,  $CH_3CH_2OH$ , 99 %, Fisher) and butyl carbitol (BC, diethylene glycol monobutyl ether  $CH_3(CH_2)_3(OC_2H_4)_2OH$ ), i.e.

(EtOH:BC, 1:2). The deposition parameters, which were already optimized in previous works [33,38], are briefly summarized hereafter. A columnar-type microstructure was obtained using a needle-to-substrate distance of 20 mm, a flow rate of 1.5 mL h<sup>-1</sup>, a substrate temperature of 300 °C. The deposition time was 3 h and 8 h for respectively, for an electrode diameter of 14 mm and 34 mm. A sintering at 600 °C for 2 h in air was required to obtain the crystalline PrO<sub>1.833</sub> single phase. A CCL of LSM is added by the screen-printing technique on the top of PrO<sub>1.833</sub>. The ink for the screen-printing is composed of a mixture of a commercial powder of LSM (La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3-δ</sub>, SSC Inc.) with an organic solvent (KD2921, Zschimmer, and Schwarz). A 1 wt.% of polyvinyl butyral ((C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>)n, Aldrich) was added as a binder. The ink was then mixed in a three-roll mill to promote a good homogeneity. To remove the binders and the solvents, the film was first dried at 450 °C for 2 h in air with a ramp of 0.5 °C min<sup>-1</sup> and then sintered at 600 °C for 2 h in air with a ramp of 2 °C min<sup>-1</sup>. This oxygen electrode in a double-layer architecture was deposited on two different types of cell.

Cell 1 consisted of a gadolinium-doped ceria (Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2-δ</sub>, GDC) electrolyte as support and was used in the thermal aging study. The GDC was 1.1 mm thick and 19.6 mm in diameter. After the electrode deposition, cell 1 was annealed at 700 °C for 1000 h in air at a 1 °C min<sup>-1</sup> heating and cooling rate to avoid mechanical stress. For cell 2, the thermal aging was performed at 800 °C for 700 h in air with the same heating and cooling rate. The pristine cell and cell 3 refer to complete cells using hydrogen electrode-supported half-cells provided by Forschungszentrum Jülich (FZJ), Germany. The cells were based on tape-cast NiO-YSZ supports of ~300 µm thickness, and screen-printed NiO-YSZ anodes were obtained from CeramTec GmbH (Marktredwitz, Germany). The 1.5 µm thin YSZ electrolyte was prepared by the sequential deposition of YSZ nano-dispersion and polymeric sol, followed by co-sintering of the half-cell at 1400 °C [42]. Subsequently,  $a \sim 0.5 \mu m$  thin  $Gd_{0.2}Ce_{0.8}O_{1.9}$  diffusion barrier layer was deposited via Magnetron Sputtering. The diameter of the half-cells was 50 mm while that of the oxygen electrode was 34 mm. The pristine cell used as a reference was only sintered at 600 °C for 2h in air. The cell 3 was aged at 700 °C for 1000 h under electrolysis conditions (with  $H_2O/H_2 = 90/10$  at i = -0.5 A cm<sup>-2</sup> and SC = 25%). A summary of the cells and the composition of the oxygen electrode characterized by synchrotron µ-X-ray diffraction are presented in Table 2.

Table 2: Summary of the samples reporting the praseodymium phases detected by the synchrotron  $\mu$ -X-ray diffraction.

		Without aging	Therma	ally-aged	Long-term test in	
					SOEC mode	
Notation		Pristine cell	cell 1	cell 2	cell 3	
Composition		PrO <sub>1.833</sub> + LSM deposited on FZJ half-cell (GDC/YSZ/NiO- YSZ)	PrO <sub>1.833</sub> + LSM deposited on GDC	PrO <sub>1.833</sub> + LSM deposited on GDC	PrO <sub>1.833</sub> + LSM deposited on FZJ half-cell (GDC/YSZ/NiO- YSZ)	
Treatment		Sintered at 600 °C/2 h/air	700 °C during 1000 h	800 °C during 700 h	700 °C, 1000 h with H <sub>2</sub> O/H <sub>2</sub> =90/10 at - 0.5 A cm <sup>-2</sup>	
μ-XRD	GDC/PrO <sub>x</sub> interface	PrO <sub>1.80</sub> + Pr(OH) <sub>3</sub>	PrO <sub>1.714</sub> + Pr(OH) <sub>3</sub> + unknown peaks	PrO <sub>1.5<x<1.7< sub=""></x<1.7<></sub>	PrO <sub>1.714</sub> + PrO <sub>1.5<x<1.7< sub=""></x<1.7<></sub>	
	LSM/PrO <sub>x</sub> interface	PrO <sub>1.80</sub>	PrO <sub>1.714</sub> + Pr(OH) <sub>3</sub> + unknown peaks	PrO <sub>1.5<x<1.7< sub=""></x<1.7<></sub>	PrO <sub>1.714</sub> + unknown peaks	

## 2.2. Electrochemical characterization of cell 3

The complete cell (cell 3) was tested in an in-house test bench depicted in Figure 1. A nickel grid (50 mm in diameter with a mesh density of 100 mesh cm<sup>-2</sup>) was used to collect the current at the hydrogen side. For the oxygen electrode, a gold grid of 100 mesh cm<sup>-2</sup> was combined with a fine platinum grid of 3600 mesh cm<sup>-2</sup> to optimize the current collection. Besides, a load of 600 g cm<sup>-2</sup> was applied to further minimize the electric contact resistances between the metallic grids and the electrodes. The gas tightness of the hydrogen electrode compartment was achieved by a ceramic glass sealing located on the cell periphery. The glass formation was obtained after a treatment at temperature higher than 800°C. The NiO reduction into Ni for the cermet was carried out at 800 °C. The procedure started by sweeping the hydrogen electrode with pure N<sub>2</sub> at a total flow rate of 4 Nl h<sup>-1</sup>. Nitrogen was then progressively replaced by H<sub>2</sub>. After reduction, the open circuit voltage (OCV) was measured in different humidified
atmospheres and compared to the theoretical Nernst voltage to verify the gas tightness. Steam was produced by mixing controlled flow rates of hydrogen and oxygen in a combustion chamber within the hot zone. The cell initial performances were then acquired in the SOEC mode, at 700 °C, with 90 vol.% H<sub>2</sub>O and 10 vol.% H<sub>2</sub> at the hydrogen side with a total flow rate of 15.5 Nml min<sup>-1</sup> cm<sup>-2</sup> and air at the oxygen side. The i-V curves were measured under galvanostatic mode from 0 to 1.6 V. The electrochemical impedance spectra (EIS) were acquire d at OCV, in a frequency range of  $10^6$  to  $10^{-2}$  Hz, with an amplitude of  $\pm 10$  mA cm<sup>-2</sup> using a potentiostat/galvanostat (Autolab PGSTAT-302N) equipped with a Frequency Response Analyzer module (FRA) and coupled with a 10 A booster. The EIS diagrams were normalized by the electrode surface area (S =  $9.08 \text{ cm}^2$ ). The polarization resistance R<sub>pol</sub> was deduced from the impedance diagram as the difference between the intercepts with the real axis at low frequency (LF) and high frequency (HF). Both polarization curves and EIS measurements were carried out before and after the durability test. The long-term SOEC test was conducted in galvanostatic mode at - 0.5 A cm<sup>-2</sup> and 700 °C, with H<sub>2</sub>O/H<sub>2</sub> ratio of 90/10 and a SC of 25 %. After the long-term test and the final characterizations, the cell was cooled down to room temperature by supplying the hydrogen electrode with a mixture of nitrogen and hydrogen to maintain the cermet in its reduced state. It is worth noting that all the samples have been cooled down in the same conditions at 1 °C min<sup>-1</sup>. Therefore, the differences in phase transitions observed at room temperature with post-test characterizations are due to operation at high temperatures and/or applied polarization.



Figure 1: Schematic representation of the experimental test bench for complete cell measurements.

#### 2.3 Structural and microstructural characterizations

#### 2.3.1 SEM observations

Scanning electron microscopy (SEM, ZEISS Ultra 55 instrument) with a field emission gun (FEG) and an energy-dispersive X-ray spectroscopy (EDX) analyzer, using an acceleration voltage of 20 keV, were used for the electrode microstructure observations and the composition analyses, respectively. The particle size and the electrode thickness were then estimated from SEM cross-sections using an image analysis tool (Image J software).

#### 2.3.2 $\mu$ -XRD and $\mu$ -XRF characterization

A thin lamella was extracted from each studied sample using a plasma-focused ion beam (p-FIB) Vion (FEI<sup>TM</sup>) using Xe<sup>+</sup> ion source. For the preparation, a cell fragment was placed on a 5-axial motorized stage in the p-FIB vacuum chamber. Adjustments of the height and the inclination of the sample were done to determine the position of the eucentric point. Afterwards, a protective layer in platinum (Pt), with a thickness of 10  $\mu$ m, was deposited on the top of the electrode using a current of 59 nA. The areas surrounding the sample were milled with a current of 470 nA. It is worth noting that a lower current of 180 nA was used in the final stage of the milling procedure to refine the lamella surfaces in order to prevent any damage to the material. The isolated lamella was then cut from the cell fragment with a micromanipulator using a low ion current of 180 nA. The detached sample was then fixed on an aluminum pin with a platinum deposit. As shown in Figure 2a, the lamella dimensions are approximately 80  $\mu$ m, 50  $\mu$ m and 20  $\mu$ m for the width, height and thickness, respectively.

The prepared lamella was used for synchrotron X-ray characterizations at microXAS beamline on the Swiss Light Source (SLS), Paul Scherrer Institut (PSI), Switzerland. The procedure has been already detailed in previous works [16,43] and only a brief description is reported hereafter.

A schematic representation of the microXAS beamline setup is shown in Figure 2b. The lamella was illuminated by an X-ray incident beam with a high energy of 17.995 keV, focused by a Kirkpatrick-Baez (KB) mirror system to a spot size of  $1 \times 1 \mu m^2$  (horizontal by vertical dimension). The sample was positioned in the focal plane of the X-ray beam and 2D raster scans on horizontal (X) and vertical (Y) directions were performed all over the lamella using a step

size of 500 nm. Thanks to the specific beam energy (relatively high, and just below the Zr Kedge resonance) and the thin lamella, the X-ray beam was able to pass through the overall thickness of the samples. Therefore, a 2D diffraction detector was positioned behind the samples to record the XRD patterns in transmission mode. In addition, four silicon drift detectors (SDD; Ketek GmbH, Germany) were positioned at 50° of the incoming beam to collect the fluorescence spectrum [44].

Classical 1D diffractograms were obtained by azimuthal integration of the 2D diffraction rings measured in each point using pyFAI library [45]. The XRD data were then integrated over the horizontal direction (X-direction) for each vertical position of the sample. XRDUA [46] and FullProf softwares [47] were used to identify the phases and the structure of the resulting diffraction patterns. LeBail method was applied to refine the diffraction patterns [48]. International Centre for Diffraction Data (ICDD) database was used as reference for phase identification.

The fluorescence spectra have been fitted using PyMCA [49]. Thus, 2D images of each detected element were generated and post-processed using Image J software.



Figure 2: a) View of the lamella extracted from cell 3 by plasma-focused ion beam using Xe<sup>+</sup> ion source b) Schematic representation of  $\mu$ -XRF and  $\mu$ -XRD characterization at microXAS beamline, SLS, PSI, Switzerland.

## 3. Results and Discussion

#### 3.1. Performances and durability study of cell 3

3.1.1 Initial performance

The polarization curve of cell 3 was recorded at 700 °C under electrolysis mode, using air at the oxygen electrode side and a gas composition of 90 vol.% H<sub>2</sub>O and 10 vol.% H<sub>2</sub> at the hydrogen electrode side (with a total flow rate of 15.5 Nml min<sup>-1</sup> cm<sup>-2</sup>) (Figure 3a). First, it can be noticed that the experimental OCV of 0.875 V is in good agreement with the theoretical Nernst value of 0.881 V in the testing conditions (less than 1% difference). Thus, the gas tightness between the anodic and cathodic chambers is considered to be ensured. Secondly, a current density of -1 A cm<sup>-2</sup> was reached for a cell voltage of 1.4 V and a SC of 50 %. This level of performance is consistent with expected values in these operating conditions [50,51]. Nevertheless, the cell performance is lower than those reported by Wang et al [41] who obtained initial performances of - 1.5 A cm<sup>-2</sup> at 1.4 V for a  $PrO_{1.833}$  electrode and -2.64 A cm<sup>-2</sup> at 1.4 V for a composite PrO<sub>1.833</sub>-SDC (samarium-doped ceria) electrode. The lower performance in this study could be ascribed to the relative strong activation overpotentials, which can be observed in the polarization curve at low current densities (Figure 3a in black). They are consistent with the relatively high polarization resistance determined on the impedance diagram measured at OCV ( $R_p = 0.78 \ \Omega \ cm^2$ , Figure 3b in black). The spectrum presents a small arc at high frequencies usually assigned to the hydrogen electrode together with the ionic transfer between the GDC barrier layer and the oxygen electrode [52-54]. A second contribution arises at intermediate and low frequencies. This contribution is generally associated to the oxygen incorporation in the O<sub>2</sub> electrode material convoluted with the gas diffusion and conversion [52,53]. As it represents a large part of the polarization resistance, there might still be room for the optimization of the micro- and nano-structure of the oxygen electrode. Besides, even if the electrochemical activity of PrOx is very high [27,38], its electrical conductivity remains limited (i.e. 3.7 S cm<sup>-1</sup> at 800 °C for x=1.833 [27]). In this condition, the ESD layer in pure PrO<sub>1.833</sub> could add a supplementary resistance. Nevertheless, the cell performances are not far from the state-of-the-art values for typical SOCs.



Figure 3: a) i-V curves of cell 3 at 700 °C, at t = 0 h and t = 1000 h under H<sub>2</sub>O/H<sub>2</sub>=90/10 on the hydrogen electrode side with an inlet flow of 15.5 NmL min<sup>-1</sup> cm<sup>-2</sup> (SC=50 %) and air on the O<sub>2</sub> electrode side. Electrochemical impedance spectra of cell 3, at OCV, and at 700 °C before and after aging for 1000 h in electrolysis mode represented in b) Nyquist plot and c) Bode plot.

#### 3.1.2 Long-term SOEC test

The durability study of cell 3 was conducted at 700 °C in SOEC mode at a current density of  $-0.5 \text{ A cm}^{-2}$  (SC=25 %) for 1000 h under H<sub>2</sub>O/H<sub>2</sub>=90/10. The evolution of the cell voltage is plotted as a function of the elapsed time in the Figure 4. At the beginning, the curve exhibited a rapid increase of the cell voltage from 1.16 V at t = 0 h (t<sub>0</sub>) to 1.2 V at t = 100 h. Similar initial degradation was observed in the literature for other electrodes with the same hydrogen electrode supported cells [55] and it is usually ascribed to a microstructural evolution in the cermet [53,56]. After 100 h, the degradation tended to stabilize towards a steady-state regime so that the cell voltage versus time exhibited a linear evolution. According to equation 1, a degradation

$$\frac{\Delta U \times 100}{\Delta t \times U(i,t_0)}$$
Eq. 1

rate of  $\sim 5.8$  % kh<sup>-1</sup> (correspondingly 69 mV kh<sup>-1</sup>) was estimated from this linear region. It is worth noting that the degradation rate reported in this work cannot be directly compared to the

literature values since the operating conditions are different. Nevertheless, it can be stated that the measured degradations are in the average of what can be observed currently [55,57–59]. Among the lowest reported values for single cells, The et al. [56] observed a degradation of 0.98 % kh<sup>-1</sup> and 3.8 % kh<sup>-1</sup> using H<sub>2</sub>O/H<sub>2</sub>=80/20 at -0.75 A cm<sup>-2</sup> for 6100 h and -1 A cm<sup>-2</sup> for 9000 h with classical LSCF electrode at 780°C. The measured degradation (Figure 4) can originate from the reactivity between the different components (air electrode, barrier layer, electrolyte ...). A reactivity between GDC and PrO<sub>1.833</sub> was already observed for powders calcined at 600°C leading to the formation of Ce<sub>1-x</sub>Pr<sub>x</sub>O<sub>2-6</sub> (CPO) [35] but it is reported in the literature that this phase usually enhances the performance of SOC electrodes [60,61]. Another investigation of the reactivity between 8YSZ and PrO<sub>1.833</sub> at 900 °C led to the formation of the insulating Pr<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> [34]. On the other hand, Sharma et al. [38], reported a good stability between the ESD deposited PrO<sub>1.833</sub> and GDC electrolyte up to 800°C for 10 days in air. However, they observed a partial decomposition of PrO<sub>1.833</sub> into PrO<sub>1.5</sub> (i.e. Pr<sub>2</sub>O<sub>3</sub>), and another unknown phase in similar conditions but at 900°C. In the following, the main causes of the observed degradations in cell 3 are investigated.



Figure 4: Evolution of the cell voltage versus time in electrolysis mode at 700 °C, under  $H_2O/H_2=90/10$ , at a current density of - 0.5 A cm<sup>-2</sup> (SC = 25%) for cell 3.

An i-V curve and an impedance diagram were recorded after the long-term test in similar conditions as the ones of the initial characterization (Figure 3a and 3b in red). A significant performance loss is observed in Figure 3a. Indeed, the current density of -1 A cm<sup>-2</sup> at 1.4 V measured at t = 0 h falls down to -0.65 A cm<sup>-2</sup> after 1000 h of operation. It can be noticed that

this loss of cell performances is consistent with the degradation rates measured on the durability curve.

The evolution of the impedance spectrum at OCV is displayed in Figure 3b before and after the durability test. An increase of the series resistance and the high frequency contribution is clearly observed. Both changes could be explained by a Ni migration away from the electrolyte interface when the cell was operated in SOEC mode and/or a reactivity at the interface between the barrier layer and the oxygen electrode hindering the ionic transfer [52,53]. However, from these measurements, it is difficult to dissociate the contributions of the two electrodes (anode or cathode). Therefore, in order to better identify the origin of these degradations, several posttest characterizations, including SEM observations and synchrotron  $\mu$ -X-ray diffraction and fluorescence were carried out.

#### 3.2. Post-mortem microstructural characterization

#### 3.2.1 Microstructural characterization of the hydrogen electrode

SEM micrographs of polished cross-sections are displayed in Figure 5 for the pristine sample and cell 3 (after aging at 700 °C for 1000 h under current). The comparison of the two images reveals a loss of Ni at the interface between the electrolyte and the cermet, Ni coarsening as well. Indeed, it is well established that Ni migration away from the electrolyte interface occurs in the hydrogen electrode in the SOEC mode [52,53]. This microstructural evolution is in good agreement with the increase of the series resistance and the high frequency arc observed in the impedance spectra and the Bode plots (Figure 3b and 3c). Indeed, the Ni loss induces some depleted zones at the vicinity of the electrolyte interface resulting in an increase of the cell ohmic resistance. On the other hand, the decrease of the active triple phase boundary lengths (TPBIs) limits the charge transfer reactions and thus increases the high frequency contribution in the impedance spectrum [62].



Figure 5: SEM image of the polished cross-section of hydrogen electrode/electrolyte interface a) pristine cell after cermet reduction (dark: pores, bright grey: Ni, dark grey: YSZ). b) aged cell 3: the arrows show the Ni depletion zone (presence of larger pores in black) after aging in the SOEC mode (dark: pores, bright grey: YSZ, dark grey: Ni), (back-scattered electrons imaging mode for an accelerating voltage of 2 kV).

# 3.2.2 Microstructural characterization of the oxygen electrode: comparison of cell 3 with the pristine cell

The oxygen electrodes were observed by SEM before and after long-term operation. Several SEM micrographs in Figure 6 show the electrolyte, the barrier layer and the double-layered oxygen electrode for pristine cell and cell 3.

First, for the pristine electrode (Figure 6a and b), the columnar microstructure of the ESD deposited  $PrO_x$  AFL appears uniform, with a quite good reproducibility to the previous work [38]. Moreover, the contact area between  $PrO_x$  and LSM remains rather poor and could be further improved to facilitate the current conduction. This remark could thus explain the relatively high activation overpotentials observed in the polarization curves along with the resistance of the intermediate and low frequency contribution in the impedance spectra.

The comparison of the microstructure of the AFL in the pristine cell (Figure 6a and b) and the one in the cell 3 (Figure 6c and d) reveals a noticeable grain growth of the  $PrO_x$  particles. Indeed, the grain size was found to be around 3-fold larger for the cell 3 than for the pristine cell (respectively, around 120 nm in average (Figure 6d) against around 40 nm (Figure 6b)). The grain growth with long-term operation could reduce the performance of the oxygen electrode by deteriorating the nano-scale microstructure. Consequently the kinetic rate for the reaction of oxygen exchange at the  $PrO_x/LSM$  interface is expected to be lowered [63]. This evolution is expected to affect the intermediate frequency contribution in the impedance diagram [54]. However, as shown in Figure 3b, before and after aging, there is no difference in the impedance response in the medium frequency band. Therefore, despite the grain growth, the cell

performance loss cannot be attributed to the oxygen electrode's microstructural degradation over time.

The evolution of the ohmic resistance and the high frequency contribution in the impedance spectra could be explained by a delamination at the electrode/electrolyte interface after long-term tests [64]. However, in this work, a good adhesion between the different layers seems to be preserved after operation (Figure 6c and d).



Figure 6: SEM micrographs of double layer oxygen electrode (PrOx-ESD topped by LSM-SP) in pristine cell and cell 3. Pristine cell: (a) cross-section of the oxygen electrode, (b) zoomed cross-section of  $PrO_x$  AFL. Cell 3: (c) cross-section of the oxygen electrode, (d) zoomed cross-section of  $PrO_x$ . For clarity, a yellow dashed line was added to show the ESD layer.

## 3.3. Post-mortem structural and elemental characterizations

#### 3.3.1 Pristine oxygen electrode

The characterization of the pristine cell allows assessing the initial state of the oxygen electrode. For this purpose, local  $\mu$ -XRF and  $\mu$ -XRD data were acquired on the oxygen electrode as well as the barrier layer and a part of the electrolyte. Interdiffusion of elements and possible reactivity between the layers can thus be revealed by plotting the distributions of elements and material phases across the cell layers.

The elements map extracted from the  $\mu$ -XRF data is shown in Figure 7 for the pristine cell. For the sake of clarity, only some of the elements, namely zirconium (Zr), cerium (Ce),

praseodymium (Pr) and lanthanum (La), are plotted on an area including a part of the 8YSZ electrolyte and the  $PrO_x/LSM$  electrode. As expected, no noticeable interdiffusion of elements is observed after the electrode sintering performed at low temperature (i.e. 600 °C, cf. section 2.1).



Figure 7: The 2D elemental map of pristine cell cross-section obtained by µ-XRF.

Regarding the  $\mu$ -XRD patterns, the 8YSZ electrolyte was indexed with a cubic fluorite structure with  $Fm\overline{3}m$  space group (No. 225). Similarly, the GDC barrier layer was identified as a cubic unit cell (ICDD 04-011-7336) with  $Fm\overline{3}m$  space group (No. 225). It was refined to a lattice parameter of 5.424 Å, corresponding well with Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>2- $\delta$ </sub> reported in the literature [65].

Concerning the PrO<sub>x</sub> ESD layer, a cubic crystal structure (ICDD 04-016-6186) crystallizing in the  $Fm\overline{3}m$  space group (No. 225) was found, with a lattice parameter of 5.493 Å at the GDC/PrO<sub>x</sub> interface (Figure 8a) and 5.496 Å at the LSM/PrO<sub>x</sub> interface (Figure 8b). This average lattice parameter would correspond to a PrO<sub>x</sub> composition of PrO<sub>1.80</sub> or Pr<sub>5</sub>O<sub>9</sub>, (Tables 1 and 2). Therefore, the  $PrO_x$  phase in the pristine sample is slightly reduced compared to the expected PrO<sub>1.833</sub> (i.e. Pr<sub>6</sub>O<sub>11</sub>). This phase evolution should be ascribed to the electrode sintering treatment at 600 °C for 2 h in air. Indeed, as already mentioned, PrO<sub>x</sub> tends to be reduced when exposed to high temperatures [17,66]. When passing from GDC/PrOx interface to the LSM/PrOx one, peaks associated to the GDC, YSZ and NiO phases were found to considerably decrease while an increase of the intensity of the LSM peaks has been detected. A low quantity of LSM close to the GDC/PrO<sub>x</sub> interface can be explained by the shape of the ESD layer (cf. Figure 6) and by the rather porous ESD  $PrO_x$  layer. The LSM layer has been indexed with a rhombohedral crystal structure (ICDD 00-064-0177) with  $R\overline{3}c$  space group (No. 167), with lattice parameters of a = b = 5.5059 Å and c = 13.3741 Å. These values are also consistent with the available data in the literature [67]. In addition to  $PrO_{1.80}$  and GDC, a praseodymium hydroxide Pr(OH)<sub>3</sub> phase was detected but only at the GDC/PrO<sub>x</sub> interface as shown in Figure 8a and Table 2. This hydroxide phase appears during the cell manufacturing and is consistent with previous observations. Indeed, some studies highlighted the formation of  $Pr(OH)_3$  nanoparticles during the preparation of the  $PrO_x$  phase starting from  $Pr(NO_3)_3.6H_2O$  precursor, as similarly used in this work [68,69]. Furthermore, YSZ is detected at the GDC interface since the barrier layer is very thin (~ 600 nm). Finally, some traces of NiO from the hydrogen electrode have been detected (that should come from the sample preparation).



Figure 8: XRD lattice parameter refinement of pristine cell focused at the (a) GDC/  $PrO_x$  interface and (b) LSM/  $PrO_x$  interface.

In the following, samples thermally aged at 700 and 800 °C (cell 1 and cell 2) and the complete cell aged in the SOEC mode (cell 3) at 700 °C were compared to differentiate the influence of temperature and current on the electrode stability.

#### 3.3.2 Thermally aged cells: cell 1 and cell 2

As for the pristine cell, no specific interdiffusion of elements between the cell layers has been found with the  $\mu$ XRF characterizations for cell 1 and cell 2. However, the  $\mu$ -XRD analyses of both cells revealed phase transitions into other secondary phases belonging to the praseodymium oxide system.

*Cell 1* – The local  $\mu$ -XRD pattern acquired at the GDC/PrO<sub>x</sub> interface is shown in Figure 9a. In this case, a rhombohedral crystal structure with space group  $R\overline{3}$  (No 148) has been identified for the PrO<sub>x</sub> phase. Lattice parameter of a = b = 10.245 Å, and c = 9.574 Å have been calculated for PrO<sub>x</sub>. This structure corresponds to the composition PrO<sub>1.714</sub> (i.e. to Pr<sub>7</sub>O<sub>12</sub>, Tables 1 and 2)-It can be noted that this structure exhibits some characteristic peaks appearing at  $2\theta = 6.04^{\circ}$ , 7.68°, 9.34°, 9.78°. Consequently, as already observed in the literature [23,66], the thermal ageing at 700°C has induced a further reduction of the praseodymium oxide. However, the PrO<sub>1.714</sub> formation at around 700 °C should not be detrimental for the electrode performance as PrO<sub>1.714</sub> remains a mixed ionic-electronic conductor which is expected to be electrochemically active [27]. Besides, Pr(OH)<sub>3</sub> phase is still visible in the vicinity of the GDC/PrO<sub>x</sub> interface, as similarly observed in the pristine cell. Therefore, Pr(OH)<sub>3</sub> did not totally disappear after annealing at 700 °C under atmospheric condition. This could be due to some traces of humidity in air [70]. Finally, three peaks at angles  $2\theta = 5.89^{\circ}$ , 12.94° and 13.11° were not fitted and correspond to may be more than one minority phases.

The diffractogram recorded at the LSM/PrO<sub>x</sub> interface for the cell 1 is shown in Figure 9b. Similarly to the GDC/PrO<sub>x</sub> interface,  $PrO_{1.714}$  and  $Pr(OH)_3$  phases are detected. By comparing both diffractograms in Figure 9a and 9b, the peak intensity of  $Pr(OH)_3$  appears clearly lower at the LSM/PrO<sub>x</sub> interface, while the one for  $PrO_{1.714}$  remains roughly the same as the one at the GDC interface. Finally, the same unidentified minority peaks are still visible in the bulk of the electrode, but at lower intensity.



Figure 9: XRD lattice parameter refinement of cell 1 (thermally aged cell at 700 °C for 1000 h) focused on (a) the GDC/  $PrO_x$  interface and (b) the LSM/ $PrO_x$  interface.

*Cell 2* – The local  $\mu$ -XRD patterns are plotted for cell 2 at the GDC/PrO<sub>x</sub> and LSM/ PrO<sub>x</sub> interfaces in Figure 10a and 10b, respectively. In both cases, the peaks identified for the PrO<sub>x</sub> structure correspond to a BCC cubic structure (*Ia* $\overline{3}$ , No 206). Indeed, the characteristic peaks of this phase can be seen at 20 = 7.08°, 8.67°, 10.02° and 15.06°. The lattice parameter has been estimated to 11.156 Å. This value corresponds to a PrO<sub>x</sub> with x=1.52 lying in the range

of 1.5 to 1.7 [17,71] (Tables 1 and 2). Therefore, increasing the annealing temperature from 700°C to 800 °C has reduced  $PrO_{1.714}$  into  $PrO_x$  (1.5 < x < 1.7) in the whole electrode. This evolution driven by the temperature at 800°C is quite unexpected, as it should occur at higher temperature under air [17]. In our case, this transition at relatively low temperature could be explained by the nanometer grain size of the ESD layer that would promote the phase transition. In other words, the very small crystal grains, which are typical of the ESD layer, are very reactive in such way that the  $PrO_x$  reduction should arise at lower temperatures compared to more standard microstructures.



Figure 10: XRD lattice parameter refinement of cell 2 (thermally aged cell at 800 °C for 700 h) focused on (a) the GDC/PrO<sub>x</sub> interface and (b) the LSM/PrO<sub>x</sub> interface.

#### 3.3.3 Long-term durability test of cell 3 in SOEC mode

Cell 3 operated at 700 °C under anodic current (-  $0.5 \text{ A cm}^{-2}$ ) was characterized by  $\mu$ -XRF and  $\mu$ -XRD. Even under polarization, no significant interdiffusion has been detected by the fluorescence analyses (Figure S1). A similar conclusion was reached by energy dispersive X-ray spectroscopy (EDX) analyses (Figure S2). However, as for the cell aged at 700 °C without current, structural transitions of PrO<sub>x</sub> have been highlighted thanks to the  $\mu$ -XRD analyses (Figure 11). The diffractograms obtained at GDC/PrO<sub>x</sub> and LSM/ PrO<sub>x</sub> interfaces are plotted in Figures 11a and 11b, respectively.

The phase refinement at the barrier layer interface (Figure 11a) indicates the presence of two crystalline phases. First, as expected for this operating temperature and in good agreement with the thermally aged sample, the main peaks of the diffractogram are related to  $PrO_{1.714}$  ( $R\overline{3}$ , No. 148) (i.e.  $Pr_7O_{12}$ , Tables 1 and 2). More surprisingly, typical peaks associated to cubic crystal structure ( $Ia\overline{3}$ , No 206) can be also noticed in the diffractogram. A lattice parameter of 11.147 Å has been obtained by Lebail refinement. This phase could thus correspond to a  $PrO_x$  in the range of 1.5 < x < 1.7 for the BCC structure.

On the other hand, at the current collector interface (Figure 11b), only the phase  $PrO_{1.714}$  has been observed refined with a = b = 10.275 Å and c = 9.584 Å. These values are in good agreement with the lattice parameters obtained for the pristine cell and the thermally aged sample at 700 °C (cell 1). Additionally, the same unknown peaks observed in the cell 1 are also present in the bulk of this sample ( $2\theta = 5.89^\circ$ ,  $12.94^\circ$  and  $13.11^\circ$ ,  $25.89^\circ$ ) as shown in Figure 11b. It can be mentioned that some studies reported a reactivity between GDC and PrO<sub>x</sub> leading to the formation of Ce<sub>1-x</sub>Pr<sub>x</sub>O<sub>2- $\delta$ </sub> (CPO) [35]. However, the characteristic peaks for CPO were not detected in our case. From this analysis, it appears that the main phases detected in the bulk of the ESD layer after a long-term operation under current (cell 3) are similar to the ones detected in the thermally aged sample at 700 °C for 1000 h (cell 1) except for Pr(OH)<sub>3</sub>. Finally, a small amount of Ni was observed in the bulk of cell 3, which could be due to a contamination during the preparation of the lamellae.



Figure 11: XRD lattice parameter refinement of cell 3 (700 °C for 1000 h under current of - 0.5 A cm<sup>-2</sup>) (a) at the GDC/ PrO<sub>x</sub> interface and (b) at LSM/ PrO<sub>x</sub> interface.

From an electrochemical point of view, even though  $PrO_{1.714}$  has a slightly lower electrical conductivity than  $PrO_{1.833}$  [21,31,72] (i.e. total conductivity:  $\sigma = 8.4 \times 10^{-2}$  S cm<sup>-1</sup> for  $PrO_{1.833}$  and  $\sigma = 1.7 \times 10^{-2}$  S cm<sup>-1</sup> for  $PrO_{1.714}$  and at 600 °C in the pO<sub>2</sub> range from 2 to 15 mm Hg [31]), the detection of this phase can be considered as not limiting since  $PrO_{1.714}$  remains electrochemically active. However, as mentioned in the introduction, the electrical conductivity of the  $PrO_{1.5 \le x \le 1.7}$  phase detected at the interface with the barrier layer is even lower than the one of  $PrO_{1.714}$ . The presence of this phase is not expected to affect the electrochemical reaction of oxygen incorporation/excorporation taking place at the top surface of the ESD layer (cf. section 3.2.2). However, it could add a supplementary ohmic resistance that could be consistent with the series resistance increase observed in the impedance spectra (Figure 3b).

In our case, the presence of  $PrO_{1.714}$  at the electrochemical interface suggests that the oxidizing condition due to the electrolysis operation is not sufficient to trigger a phase transition towards a more oxidized phase. However, the origin of the  $PrO_{1.5<x<1.7}$  BCC structure identified at the barrier layer interface is more challenging to interpret. Indeed, the oxidizing condition should prevent a further reduction of  $PrO_{1.714}$  at 700°C. In our case, it could be proposed that the  $PrO_{1.5<x<1.7}$  BCC structure could be a result of the decomposition of  $Pr(OH)_3$  which was present at the interface as identified on the pristine cell (Figure 8). Indeed, a transformation from  $Pr(OH)_3$  to c- $Pr_2O_3$  at high-temperature (> 770 K) has been already reported by Gasnier et al [20]. It could be also suggested that a slight inter-diffusion, which was not detected by the  $\mu$ XRF and EDX analyses, could arise at the interface. Indeed, the diffusion of Gd into  $PrO_x$  could lead to  $Pr_{1-x}Gd_xO_2$  phase that also exhibits a BCC structure [73]. However, the lattice parameter of this compound is not consistent with the one identified in this work. Finally, a small dissolution of Pr into the GDC barrier layer cannot be excluded. Therefore, further investigations are still required to explain the small quantity of  $PrO_{1.5<x<1.7}$  detected at the barrier layer interface.

Finally, all the results are summarized in Table 3 with the typical  $PrO_x$  phases, expected versus temperature and  $pO_2$  with their crystallographic data. It is worth to note that these phases are characterized by micron grain sizes. In addition to  $PrO_x$  phases, we have also reported  $Pr(OH)_3$  which has been detected in some samples. As a general matter from this study, it has been found that the transition of  $PrO_{1.833}$  towards more reduced phases is mainly driven by the temperature without a huge impact of polarization.

Temperature (°C)		1300				700	500		450	
PO <sub>2</sub> evolution										-
PrOx formula	Pr(OH)₃	Pr <sub>2</sub> O <sub>3</sub>				Pr <sub>7</sub> O <sub>12</sub>	Pr <sub>5</sub> O <sub>9</sub>	Pr <sub>11</sub> O <sub>20</sub>	Pr <sub>6</sub> O <sub>11</sub>	PrO <sub>2</sub>
n for Pr+n	3	3		3.2	3.4	3.43	3.60	3.62	3.66	4
<u>x</u> for <u>PrOx</u>		1.50	1.50	1.60	1.70	1.71	1.80	1.81	1.83	2.00
Symmetry	Hexagonal	Hexagonal	BCC			Rhombohedral	FCC			
Space group	Р6 <sub>3</sub> /т	P3m	<u>la</u> 3			R3	Fm3m			
Cell parameters	a = b = 6.49	*a = b = 3.859	*a = 11.14	0	*a = 11.07	*a = b = 10.295	*a = 5.482	*a = 5.478	*a = 5.469	*a = 5.393
(Å)	c = 377	*c = 6.008				*c = 9.598				
*[18]	[19]									
Pristine										
LSM/PrOx							<u>a</u> = 5.496			
PrOx/GDC	x						<u>a</u> = 5.493			
Cell 1						a = b = 10.259				
LSM/PrOx	х					c = 9.567				
PrOx/GDC	x					a = b = 10.245				
						c = 9.574				
Cell 2										
LSM/PrOx			<u>a</u> = 11.156							
PrOx/GDC			<u>a</u> = 11	.156						
Cell 3						a = b = 10.275				
LSM/PrOx						c = 9.585				
PrOx/GDC			<u>a</u> = 11	.147		a = b = 10.311				
						c = 9.635				

Table 3: Summary of the praseodymium oxide phases with crystallographic data from  $Pr_2O_3$  to  $PrO_2$  versus temperature and  $pO_2$ .  $Pr(OH)_3$  is also given since it has been observed experimentally. Transition temperatures are given for micron grain sizes.

#### 4. Conclusion

In this work, we reported the performance and stability of nanostructured PrO<sub>1,833</sub> used as an AFL of the oxygen electrode for SOECs. For this purpose,  $PrO_{1.833}$  was deposited by ESD on GDC pellets that were thermally aged at 700 °C for 1000 h and 800 °C for 700 h, respectively. For the long-term stability tests under current, screen-printed CCL made of LSM was deposited on top of PrO<sub>1.833</sub> on a standard half-cell composed of a Ni-YSZ support, a thin YSZ electrolyte and a GDC barrier layer. The complete cell was operated in electrolysis mode at 700 °C and -0.5 A cm<sup>-2</sup> for 1000 h. Rather good initial performance and reasonable degradation rate of 5.8 % kh<sup>-1</sup> were measured. Impedance spectra recorded before and after the long-term test revealed an increase in the pure ohmic resistance and the contribution at high frequencies. On the other hand, the durability test had no effect on the medium and low frequencies in the impedance spectra. SEM observations have shown that a Ni particle coarsening and migration away from the hydrogen electrode/electrolyte interface occurred in operation. This microstructural evolution could explain a significant portion of the evolution of the impedance spectra. Additionally, the phase and chemical stability of the oxygen electrode was thoroughly investigated by SEM-EDX and synchrotron µ-XRD and µ-XRF measurements with micrometer size resolution. A substantial grain growth in the ESD layer was observed after thermal aging

and cell operation. However, it seems that this evolution does not affect the performances as the intermediate frequencies related to the oxygen electrode remain stable upon operation. Besides, SEM-EDX and µ-XRF analyses did not reveal a noticeable elemental interdiffusion between the different layers. On the other hand, the µ-XRD characterizations at the interface and the bulk of the oxygen electrode shed light onto the phase transitions of PrOx depending on the operational conditions. Indeed, structural transitions of PrO<sub>1.833</sub> towards more reduced phases has been observed in all the samples. As expected, the pristine electrode sintering at 600°C leads to the formation of the cubic PrO<sub>1.80</sub>. Moreover, the thermal aging at 700°C has induced a phase transition into the rhombohedral PrO<sub>1.714</sub>. In our case, it has been found that the thermal aging at 800°C has led to a phase transition into a more reduced PrO<sub>1.5<x<1.7</sub> phase with a BCC structure. For the cell operated in electrolysis mode, PrO<sub>1.714</sub>, which is still electrochemically active, has been mainly detected in the ESD layer despite the anodic polarization. Therefore, the polarization under oxidizing condition seems to not affect the oxidation state of Pr. In other words, the phase transition seems to be only driven by the temperature. Finally, a slight amount of PrO<sub>1.5<x<1.7</sub> with a BCC structure has been identified at the barrier layer interface. Although the origin of this phase transition is still unclear, it could participate into the increase in the ohmic resistance since its electrical conductivity is expected to be lower than the one of oxidized  $PrO_x$ .

#### **CRediT** author statement

Lydia Yefsah: Resources, Formal analysis, Investigation, Writing Jérôme Laurencin: Conceptualization, Methodology, Supervision, Writing-review editing, Funding acquisition, Project administration Maxime Hubert: Formal analysis, Writing Dario Ferreira Sanchez: Investigation, Funding acquisition Frédéric Charlot: Investigation Karine Couturier: Investigation Ozden Celikbilek: Formal analysis Elisabeth Djurado: Conceptualization, Supervision, Writing-review editing, Project administration, Funding acquisition.

#### Acknowledgments

This work has received funding from the French National Research Agency (ANR) project "ECOREVE" (ANR-18-CE05-0036). The experiments performed on the micro-XAS beamline at SLS (Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland) are based on the proposal ID 20210398. The authors would like to thank CMTC platform in Grenoble for the

SEM images and EDX analyses. The authors also acknowledge Christian Lenser and Norbert H. Menzler from the Forschungszentrum Jülich (FZJ), Germany for the supplied half-cells.

#### 5. References

- I. Sreedhar, B. Agarwal, P. Goyal, A. Agarwal, An overview of degradation in solid oxide fuel cells-potential clean power sources, J Solid State Electrochem. 24 (2020) 1239–1270. https://doi.org/10.1007/s10008-020-04584-4.
- [2] K. Chen, S.P. Jiang, Review—Materials degradation of solid oxide electrolysis cells, j. electrochem. Soc. 163 (2016) F3070. https://doi.org/10.1149/2.0101611jes.
- [3] D. Marinha, C. Rossignol, E. Djurado, Influence of electrospraying parameters on the microstructure of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> films for SOFCs, J. Solid State Chem. 182 (2009) 1742– 1748. https://doi.org/10.1016/j.jssc.2009.04.018.
- [4] C.H. Chen, M.H.J. Emond, E.M. Kelder, B. Meester, J. Schoonman, Electrostatic sol–spray deposition of nanostructured ceramic thin films, Journal of Aerosol Science. 30 (1999) 959–967. https://doi.org/10.1016/S0021-8502(98)00075-5.
- [5] R. Neagu, D. Perednis, A. Princivalle, E. Djurado, Zirconia coatings deposited by electrostatic spray deposition. Influence of the process parameters, Surf. Coat. Technol. 200 (2006) 6815– 6820. https://doi.org/10.1016/j.surfcoat.2005.10.014.
- [6] E. Djurado, A. Salaün, G. Mignardi, A. Rolle, M. Burriel, S. Daviero-Minaud, R.N. Vannier, Electrostatic spray deposition of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9+δ</sub> layers to be used as cathode materials for IT-SOFC, Solid State Ionics. 286 (2016) 102–110. https://doi.org/10.1016/j.ssi.2016.01.021.
- [7] O. Celikbilek, D. Jauffrès, E. Siebert, L. Dessemond, M. Burriel, C.L. Martin, E. Djurado, Rational design of hierarchically nanostructured electrodes for solid oxide fuel cells, J. Power Sources. 333 (2016) 72–82. https://doi.org/10.1016/j.jpowsour.2016.09.156.
- [8] O. Celikbilek, L. Dessemond, E. Djurado, State-of-the-Art La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-δ</sub> Cathode for SOFC: Microstructural and electrochemical properties, ECS Trans. 78 (2017) 747–758. https://doi.org/10.1149/07801.0747ecst.
- [9] R.K. Sharma, S.-K. Cheah, M. Burriel, L. Dessemond, J.-M. Bassat, E. Djurado, Design of La<sub>2-x</sub>Pr<sub>x</sub>NiO<sub>4+δ</sub> SOFC cathodes: a compromise between electrochemical performance and thermodynamic stability, J. Mater. Chem. A. 5 (2017) 1120–1132.
- [10] R. K. Sharma, M. Burriel, L. Dessemond, J. M. Bassat, E. Djurado, Design of interfaces in efficient Ln<sub>2</sub>NiO<sub>4+δ</sub> (Ln = La, Pr) cathodes for SOFC applications, J. Mater. Chem. A. 4 (2016) 12451–12462. https://doi.org/10.1039/C6TA04845E.
- [11] R. Sayers, M. Rieu, P. Lenormand, F. Ansart, J.A. Kilner, S.J. Skinner, Development of lanthanum nickelate as a cathode for use in intermediate temperature solid oxide fuel cells, Solid State Ionics. 192 (2011) 531–534. https://doi.org/10.1016/j.ssi.2010.02.014.

- [12] V. Vibhu, A. Rougier, C. Nicollet, A. Flura, J.-C. Grenier, J.-M. Bassat, La<sub>2-x</sub>Pr<sub>x</sub>NiO<sub>4+δ</sub> as suitable cathodes for metal supported SOFCs, Solid State Ionics. 278 (2015) 32–37. https://doi.org/10.1016/j.ssi.2015.05.005.
- [13] P. Odier, Ch. Allançon, J.M. Bassat, Oxygen exchange in Pr<sub>2</sub>NiO<sub>4+δ</sub> at High temperature and direct formation of Pr<sub>4</sub>Ni<sub>3</sub>O<sub>10-x</sub>, J. Solid State Chem. 153 (2000) 381–385. https://doi.org/10.1006/jssc.2000.8786.
- [14] A.V. Kovalevsky, V.V. Kharton, A.A. Yaremchenko, Y.V. Pivak, E.N. Naumovich, J.R. Frade, Stability and oxygen transport properties of Pr<sub>2</sub>NiO<sub>4+δ</sub> ceramics, J. Eur. Ceram. 27 (2007) 4269– 4272. https://doi.org/10.1016/j.jeurceramsoc.2007.02.136.
- [15] V. Vibhu, J.-M. Bassat, A. Flura, C. Nicollet, J.-C. Grenier, A. Rougier, Influence of La/Pr Ratio on the Ageing Properties of La<sub>2-X</sub> Pr x NiO<sub>4+δ</sub> as Cathodes in IT-SOFCs, ECS Trans. 68 (2015) 825. https://doi.org/10.1149/06801.0825ecst.
- [16] N.I. Khamidy, J. Laurencin, D. Ferreira Sanchez, F. Monaco, F. Charlot, E. Djurado, Durability of nanostructured LaPrNiO<sub>4+ $\delta$ </sub> electrode for solid oxide cells: Electrochemical, microstructural, and structural investigation, J. Power Sources. 450 (2020) 227724. https://doi.org/10.1016/j.jpowsour.2020.227724.
- B.G. Hyde, D.J.M. Bevan, L. Eyring, On the Praseodymium+Oxygen System, Phil. Trans. R. Soc. Lond. A. 259 (1966) 583–614. https://doi.org/10.1098/rsta.1966.0025.
- [18] L. Eyring, N.C. Baenziger, On the structure and related properties of the oxides of praseodymium, J. Appl. Phys. 33 (1962) 428–433. https://doi.org/10.1063/1.1777136.
- [19] R.L.N. Sastry, P.N. Mehrotra, C.N.R. Rao, Phase transformation, oxidation and hydration of praseodymium sesquioxide, Trans. Faraday Soc. 62 (1966) 1632. https://doi.org/10.1039/tf9666201632.
- [20] M. Gasnier, G. Schiffmacher, L. Albert, P.E. Caro, H. Dexpert, J.M. Esteva, C. Blancard, R.C. Karnatak, Preparation, crystalline properties and x-ray absorption spectra of rare earth oxides R6, (R = Ce, Pr and Tb; 1.5 d x d 2), 156 (1989) 59–73. https://doi.org/10.1016/0022-5088(89)90407-4.
- [21] V. Thangadurai, R.A. Huggins, W. Weppner, Mixed ionic-electronic conductivity in phases in the praseodymium oxide system, J Solid State Electrochem. 5 (2001) 531–537.
- [22] D.A. Burnham, L. Eyring, Phase transformations in the praseodymium oxide-oxygen system: high-temperature x-ray diffraction studies, J. Phys. Chem. 72 (1968) 4415–4424. https://doi.org/10.1021/j100859a010.
- [23] A. Abrutis, M. Lukosius, Z. Saltyte, R. Galvelis, P.K. Baumann, M. Schumacher, J. Lindner, Chemical vapour deposition of praseodymium oxide films on silicon: influence of temperature and oxygen pressure, Thin Solid Films. 516 (2008) 4758–4764. https://doi.org/10.1016/j.tsf.2007.08.097.

- [24] B.L. Treu, W.G. Fahrenholtz, M.J. O'Keefe, Thermal decomposition behavior of praseodymium oxides, hydroxides, and carbonates, Inorg Mater. 47 (2011) 974–978. https://doi.org/10.1134/S0020168511090214.
- [25] M.F. Gazulla, M.J. Ventura, C. Andreu, J. Gilabert, M. Orduña, M. Rodrigo, Praseodymium oxides. Complete characterization by determining oxygen content, Microchem. J. 148 (2019) 291–298. https://doi.org/10.1016/j.microc.2019.05.013.
- [26] G.A.M. Hussein, Formation of praseodymium oxide from the thermal decomposition of hydrated praseodymium acetate and oxalate, J Anal Appl Pyrolysis. 29 (1994) 89–102. https://doi.org/10.1016/0165-2370(93)00782-I.
- [27] C. Nicollet, A. Flura, V. Vibhu, A. Rougier, J.-M. Bassat, J.-C. Grenier, An innovative efficient oxygen electrode for SOFC: Pr<sub>6</sub>O<sub>11</sub> infiltrated into Gd-doped ceria backbone, Int. J. Hydrog. Energy. 41 (2016) 15538–15544. https://doi.org/10.1016/j.ijhydene.2016.04.024.
- [28] Y. Borchert, P. Sonström, M. Wilhelm, H. Borchert, M. Bäumer, Nanostructured praseodymium oxide: preparation, structure, and catalytic properties, J. Phys. Chem. C. 112 (2008) 3054–3063. https://doi.org/10.1021/jp0768524.
- [29] P. Sonström, J. Birkenstock, Y. Borchert, L. Schilinsky, P. Behrend, K. Gries, K. Müller, A. Rosenauer, M. Bäumer, Nanostructured praseodymium oxide: correlation between phase transitions and catalytic activity, ChemCatChem. 2 (2010) 694–704. https://doi.org/10.1002/cctc.200900311.
- [30] B.M. Abu-Zied, Y.A. Mohamed, A.M. Asiri, Fabrication, characterization, and electrical conductivity properties of Pr6O11 nanoparticles, J. Rare Earths. 31 (2013) 701–708. https://doi.org/10.1016/S1002-0721(12)60345-7.
- [31] G.V.S. Rao, S. Ramdas, P.N. Mehrotra, C.N.R. Rao, Electrical transport in rare-earth oxides, J. Solid State Chem. 2 (1970) 377–384. https://doi.org/10.1016/0022-4596(70)90095-2.
- [32] M. Shamshi Hassan, M. Shaheer Akhtar, K.-B. Shim, O.-B. Yang, Morphological and electrochemical properties of crystalline praseodymium oxide nanorods, Nanoscale Res Lett. 5 (2010) 735–740. https://doi.org/10.1007/s11671-010-9547-8.
- [33] R.K. Sharma, E. Djurado, An efficient hierarchical nanostructured Pr 6 O 11 electrode for solid oxide fuel cells, J. Mater. Chem. A. 6 (2018) 10787–10802. https://doi.org/10.1039/C8TA00190A.
- [34] H. Taguchi, R. Chiba, T. Komatsu, H. Orui, K. Watanabe, K. Hayashi, LNF SOFC cathodes with active layer using Pr<sub>6</sub>O<sub>11</sub> or Pr-doped CeO<sub>2</sub>, J. Power Sources. 241 (2013) 768–775. https://doi.org/10.1016/j.jpowsour.2013.04.141.
- [35] M. Khoshkalam, M.A. Faghihi-Sani, X. Tong, M. Chen, P.V. Hendriksen, Enhanced activity of Pr<sub>6</sub>O<sub>11</sub>and CuO Infiltrated Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2</sub> based composite oxygen electrodes, J. Electrochem. Soc. 167 (2020) 024505. https://doi.org/10.1149/1945-7111/ab6821.

- [36] R. Chiba, H. Aono, K. Kato, An SOFC cathode infiltrated with Pr6O11, ECS Trans. 57 (2013) 1831–1840. https://doi.org/DOI 10.1149/05701.1831ecst.
- [37] E. Dogdibegovic, R. Wang, G.Y. Lau, M.C. Tucker, High performance metal-supported solid oxide fuel cells with infiltrated electrodes, J. Power Sources. 410–411 (2019) 91–98. https://doi.org/10.1016/j.jpowsour.2018.11.004.
- [38] R.K. Sharma, N.I. Khamidy, L. Rapenne, F. Charlot, H. Moussaoui, J. Laurencin, E. Djurado, Highly efficient architectured Pr<sub>6</sub>O<sub>11</sub> oxygen electrode for solid oxide fuel cell, J. Power Sources. 419 (2019) 171–180.
- [39] X. Ding, W. Zhu, G. Hua, J. Li, Z. Wu, Enhanced oxygen reduction activity on surface-decorated perovskite La<sub>0.6</sub>Ni<sub>0.4</sub>FeO<sub>3</sub> cathode for solid oxide fuel cells, Electrochimica Acta. 163 (2015) 204–212. https://doi.org/10.1016/j.electacta.2015.02.084.
- [40] B. Kamecki, J. Karczewski, P. Jasiński, S. Molin, Improvement of oxygen electrode performance of intermediate temperature solid oxide cells by spray pyrolysis deposited active layers, Advanced Materials Interfaces. 8 (2021) 2002227. https://doi.org/10.1002/admi.202002227.
- [41] R. Wang, E. Dogdibegovic, G.Y. Lau, M.C. Tucker, Metal-supported solid oxide electrolysis cell with significantly enhanced catalysis, Energy Technol. 7 (2019) 1801154. https://doi.org/10.1002/ente.201801154.
- [42] N.H. Menzler, J. Malzbender, P. Schoderböck, R. Kauert, H.P. Buchkremer, Sequential tape casting of anode-supported solid oxide fuel Cells, Fuel Cells. 14 (2014) 96–106. https://doi.org/10.1002/fuce.201300153.
- [43] F. Monaco, D. Ferreira-Sanchez, M. Hubert, B. Morel, D. Montinaro, D. Grolimund, J. Laurencin, Oxygen electrode degradation in solid oxide cells operating in electrolysis and fuel cell modes: LSCF destabilization and interdiffusion at the electrode/electrolyte interface, Int. J. Hydrog. Energy. 46 (2021) 31533–31549. https://doi.org/10.1016/j.ijhydene.2021.07.054.
- [44] D.F. Sanchez, D. Grolimund, M. Hubert, P. Bleuet, J. Laurencin, A 2D and 3D X-ray μdiffraction and μ-fluorescence study of a mixed ionic electronic conductor, Int. J. Hydrog. Energy. 42 (2017) 1203–1211. https://doi.org/10.1016/j.ijhydene.2016.11.094.
- [45] G. Ashiotis, A. Deschildre, Z. Nawaz, J.P. Wright, D. Karkoulis, F.E. Picca, J. Kieffer, The fast azimuthal integration Python library: pyFAI, J Appl Cryst. 48 (2015) 510–519. https://doi.org/10.1107/S1600576715004306.
- [46] W. De Nolf, F. Vanmeert, K. Janssens, XRDUA: crystalline phase distribution maps by twodimensional scanning and tomographic (micro) X-ray powder diffraction, J Appl Cryst. 47 (2014) 1107–1117. https://doi.org/10.1107/S1600576714008218.
- [47] J. Rodriguez-Carvajal, Recent developments of the program FULLPROF, Comm. Powder Diffr. (2001) 12–19.

- [48] A. Le Bail, Extracting structure factors from powder diffraction data by iterating, full pattern profile fitting, NIST Special Publication. (1992) 846.
- [49] W. De Nolf, K. Janssens, Micro X-ray diffraction and fluorescence tomography for the study of multilayered automotive paints, Surf Interface Anal. 42 (2010) 411–418. https://doi.org/10.1002/sia.3125.
- [50] X. Tong, S. Ovtar, K. Brodersen, P.V. Hendriksen, M. Chen, A 4 × 4 cm<sup>2</sup> Nanoengineered solid oxide electrolysis cell for efficient and durable hydrogen production, ACS Appl. Mater. Interfaces. 11 (2019) 25996–26004. https://doi.org/10.1021/acsami.9b07749.
- [51] S.J. Kim, K.J. Kim, A.M. Dayaghi, G.M. Choi, Polarization and stability of La2NiO4+δ in comparison with La0.6Sr0.4Co0.2Fe0.8O3-δ as air electrode of solid oxide electrolysis cell, Int. J. Hydrog. Energy. 41 (2016) 14498–14506. https://doi.org/10.1016/j.ijhydene.2016.05.284.
- [52] R. Knibbe, M.L. Traulsen, A. Hauch, S.D. Ebbesen, M. Mogensen, Solid oxide electrolysis cells: degradation at high current densities, J. Electrochem. Soc. 157 (2010) B1209. https://doi.org/10.1149/1.3447752.
- [53] X. Sun, P.V. Hendriksen, M.B. Mogensen, M. Chen, Degradation in solid oxide electrolysis cells during long term testing, Fuel Cells. 19 (2019) 740–747. https://doi.org/10.1002/fuce.201900081.
- [54] G. Sassone, E.D.R. Silva, M. Prioux, M. Hubert, B. Morel, A. Léon, J. Laurencin, Multiscale modelling of solid oxide cells validated on electrochemical impedance spectra and polarization curves, ECS Trans. 111 (2023) 649. https://doi.org/10.1149/11106.0649ecst.
- [55] V. Vibhu, I.C. Vinke, R.-A. Eichel, L.G.J. de Haart, Cobalt substituted Pr2Ni1-xCoxO4+δ (x = 0, 0.1, 0.2) oxygen electrodes: Impact on electrochemical performance and durability of solid oxide electrolysis cells, J. Power Sources. 482 (2021) 228909. https://doi.org/10.1016/j.jpowsour.2020.228909.
- [56] D. The, S. Grieshammer, M. Schroeder, M. Martin, M. Al Daroukh, F. Tietz, J. Schefold, A. Brisse, Microstructural comparison of solid oxide electrolyser cells operated for 6100 h and 9000 h, J. Power Sources. 275 (2015) 901–911. https://doi.org/10.1016/j.jpowsour.2014.10.188.
- [57] F. Tietz, D. Sebold, A. Brisse, J. Schefold, Degradation phenomena in a solid oxide electrolysis cell after 9000 h of operation, J. Power Sources. 223 (2013) 129–135. https://doi.org/10.1016/j.jpowsour.2012.09.061.
- [58] X. Sun, M. Chen, Y.-L. Liu, P.V. Hendriksen, Life Time Performance characterization of solid oxide electrolysis cells for hydrogen production, ECS Trans. 68 (2015) 3359. https://doi.org/10.1149/06801.3359ecst.
- [59] M. Al Daroukh, F. Tietz, D. Sebold, H.P. Buchkremer, Post-test analysis of electrode-supported solid oxide electrolyser cells, Ionics. 21 (2015) 1039–1043. https://doi.org/10.1007/s11581-014-1273-2.

- [60] A. Flura, C. Nicollet, V. Vibhu, A. Rougier, J.-M. Bassat, J.-C. Grenier, Ceria doped with praseodymium instead of gadolinium as efficient interlayer for lanthanum nickelate SOFC oxygen electrode, Electrochimica Acta. 231 (2017) 103–114. https://doi.org/10.1016/j.electacta.2017.02.019.
- [61] M. A. Laguna-Bercero, H. Monzón, A. Larrea, V. M. Orera, Improved stability of reversible solid oxide cells with a nickelate-based oxygen electrode, Journal of Materials Chemistry A. 4 (2016) 1446–1453. https://doi.org/10.1039/C5TA08531D.
- [62] F. Monaco, M. Hubert, J. Vulliet, J.P. Ouweltjes, D. Montinaro, P. Cloetens, P. Piccardo, F. Lefebvre-Joud, J. Laurencin, Degradation of Ni-YSZ Electrodes in solid oxide cells: impact of polarization and initial microstructure on the Ni evolution, J. Electrochem. Soc. 166 (2019) F1229. https://doi.org/10.1149/2.1261915jes.
- [63] O. Celikbilek, C.-A. Thieu, F. Agnese, E. Calì, C. Lenser, N.H. Menzler, J.-W. Son, S.J. Skinner,
  E. Djurado, Enhanced catalytic activity of nanostructured, A-site deficient (La0.7Sr0.3)0.95(Co0.2Fe0.8)O3-δ for SOFC cathodes, J. Mater. Chem. A. 7 (2019) 25102–25111. https://doi.org/10.1039/C9TA07697B.
- [64] A. Nechache, M. Cassir, A. Ringuedé, Solid oxide electrolysis cell analysis by means of electrochemical impedance spectroscopy: A review, J. Power Sources. 258 (2014) 164–181. https://doi.org/10.1016/j.jpowsour.2014.01.110.
- [65] V.V. Kharton, F.M. Figueiredo, L. Navarro, E.N. Naumovich, A.V. Kovalevsky, A.A. Yaremchenko, A.P. Viskup, A. Carneiro, F.M.B. Marques, J.R. Frade, Ceria-based materials for solid oxide fuel cells, J. Mater. Sci. 36 (2001) 1105–1117. https://doi.org/10.1023/A:1004817506146.
- [66] A. Netz, W.F. Chu, V. Thangadurai, R.A. Huggins, W. Weppner, Investigations of praseodymium oxide electrodes in lithium concentration cells, Ionics. 5 (1999) 426–433. https://doi.org/10.1007/BF02376009.
- [67] T.L. Pham, J.H. Yu, J.-S. Lee, Conductivity transitions of  $La_{0.7}Sr_{0.3}MnO_{3\pm\delta}$  and  $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$  in  $Ce_{0.9}Gd_{0.1}O_{2-\delta}$  Matrix for dual-phase oxygen transport membranes, Crystals. 11 (2021) 712. https://doi.org/10.3390/cryst11060712.
- S. Shrestha, C.M.Y. Yeung, C. Nunnerley, S.C. Tsang, Comparison of morphology and electrical conductivity of various thin films containing nano-crystalline praseodymium oxide particles, Sensors and Actuators A: Physical. 136 (2007) 191–198. https://doi.org/10.1016/j.sna.2006.11.019.
- [69] N. Krishna Chandar, R. Jayavel, Structural, morphological and optical properties of solvothermally synthesized Pr(OH)<sub>3</sub> nanoparticles and calcined Pr<sub>6</sub>O<sub>11</sub> nanorods, Mater. Res. Bull. 50 (2014) 417–420. https://doi.org/10.1016/j.materresbull.2013.11.006.

- [70] J.M. Haschke, L. Eyring, Hydrothermal equilibria and crystal growth of rare earth oxides, hydroxides, hydroxynitrates, and hydroxy carbonates, Inorg. Chem. 10 (1971) 2267–2274. https://doi.org/10.1021/ic50104a036.
- [71] R.P. Turcotte, J.M. Warmkessel, R.J.D. Tilley, L. Eyring, On the phase interval PrO<sub>1.50</sub> to PrO<sub>1.71</sub> in the praseodymium oxide-oxygen system, Journal of Solid State Chemistry. 3 (1971) 265–272. https://doi.org/10.1016/0022-4596(71)90039-9.
- [72] G.V. Chandrashekhar, P.N. Mehrotra, G.V.S. Rao, E.C. Subbarao, C.N.R. Rao, Semiconduction in non-stoichiometric rare earth oxides, Trans. Faraday Soc. 63 (1967) 1295. https://doi.org/10.1039/tf9676301295.
- [73] K. Endo, S. Yamauchi, K. Fueki, T. Mukaibo, An X-Ray study of non-stoichiometric  $Pr_{0.6}Gd_{0.4}O_{1.5+\delta}$ , Bulletin of the Chemical Society of Japan. 49 (1976) 1191–1193.

### **Supporting information**

# Electrochemical performance and stability of PrO<sub>1.833</sub> as an oxygen electrode for Solid Oxide Electrolysis Cells

Yefsah Lydia<sup>a,b</sup>, Jérôme Laurencin<sup>b</sup>, Maxime Hubert<sup>b</sup>, Dario Ferreira Sanchez<sup>c</sup>, Frédéric Charlot<sup>d</sup>, Karine Couturier<sup>b</sup>,Ozden Celikbilek<sup>b</sup> and Elisabeth Djurado<sup>a</sup>

<sup>a</sup>Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 38000 Grenoble, France <sup>b</sup>Univ. Grenoble Alpes, CEA/LITEN, 17 avenue des Martyrs, F-38054 Grenoble, France <sup>c</sup>Swiss Light Source, Paul Scherrer Institut, CH-5232, Villigen, PSI, Switzerland <sup>d</sup>CMTC, Grenoble INP, Univ. Grenoble Alpes, F-38000, Grenoble, France

\**Corresponding author*: Elisabeth Djurado E-mail: elisabeth.djurado@lepmi.grenoble-inp.fr, Tel: +33-476826684;



Figure S1: Elementary distribution map by  $\mu$ -XRF in the thickness of the lamella of cell 3 after aging at 700 °C for 1000 h under current (- 0.5 A cm<sup>-2</sup>).



Figure S2: EDX maps of cell 3 after aging at 700 °C for 1000 h under current (-0.5 A cm<sup>-2</sup>).

#### General conclusion of the chapter IV

From survey the literature,  $PrO_{1.833}$  (i.e.  $Pr_6O_{11}$ ) appears as a suitable oxygen electrode for SOEC operation at intermediate temperature (IT) compared to a state-of-the-art MIEC material such as LSCF. Indeed, it presents a high oxygen surface exchange coefficient despite a low electrical conductivity and high electrocatalytic activity at low temperatures. Thus, it has inspired several researchers who have incorporated  $PrO_x$  nanoparticles to boost the performance of conventional electrodes or by infiltration into electrolyte materials to produce composite electrodes.

This work has been guided by a previous thesis in LEPMI, where an optimum polarization resistance has been obtained at 600 °C in symmetrical cell measurement at OCP when a hierarchical columnar-type  $PrO_{1.833}$  (AFL) topped with LSM (CCL) was employed as an oxygen electrode in SOFC mode. Moreover, the laboratory XRD analysis of the thermal aged sample during 10 days did not show any reactivity or decomposition of this material. However, according to the literature, the stability of this phase is apparently dependent on many factors, including temperature and oxygen partial pressure. For several decades in LEPMI, electrostatic spray deposition has been used for the elaboration of electrode with controlled microstructure and composition, with micro- to nano- particle size. Basically, it has been evidenced that the nanostructured particle size obtained by ESD facilitates the oxygen surface exchange and ion diffusion. The ion transfer is also favored at the electrode/electrolyte interface thanks to a good adhesion at this interface.

However, today, the stability of  $PrO_{1,833}$  as a function of temperature and polarization remains an open question. As already discussed,  $PrO_{1,833}$  is a member of the praseodymium oxide series  $PrO_x$  ranged from  $PrO_2$  to  $PrO_{1,5}$  (i.e.  $Pr_2O_3$ ). These prasodymium oxides undergo controlled phase transitions whose composition is dependent on temperature and oxygen partial pressure. Thus, in this work, we have investigated the electrochemical performance of nanostructured  $PrO_{1.833}$ , and for the first time, we propose an in-depth study of the durability of nanostructured material used as the AFL of the oxygen electrode in actual electrolysis operation.

For that purpose, long-term test up to 1000 h has been carried out on a complete SOEC (Ni-YSZ/YSZ/GDC/PrO<sub>1.833</sub>/LSM) composed with this nanostructured double-layered architectured  $PrO_{1.833}$  electrode. Then, microstructural and structural characterizations have been used to analyze pristine and operated cells to highlight the modifications induced by the aging. From the electrochemical measurements, rather good initial performance (-1 A cm<sup>-2</sup> at 1.4 V with  $H_2O/H_2 = 90$  vol. %/10 vol. % at 700 °C) has been reported. However, it seems to be limited by a strong activation overpotential observed in the i-V polarization curves. On the other hand, a reasonable degradation rate of 5.8 % kh<sup>-1</sup> has been measured for the long-term test performed at 700 °C under polarization of - 0.5 A cm<sup>-2</sup> during 1000 h. Moreover, an increase of the series resistance and the high frequency contribution after the long-term test have been observed. This evolution in the impedance spectra have been attributed to the Ni migration observed at the hydrogen electrode/electrolyte interface. On the other hand, no delamination or cracks have been detected in the oxygen electrode. The microstructural analyses showed only an increase of nearly 3 fold of the ESD particle size compared to the pristine cell. This particle growth which should affect the intermediate and low frequency contributions in the impedance diagrams. However, this behavior does not appear in the observations of the impedance spectra. Thus, a large proportion of the measured degradation can be attributed to Ni evolution at the hydrogen electrode. However, phase transitions of the PrO<sub>1.833</sub> also seem to have impacted the overall cell degradations. Indeed, the lamellas extracted from the pristine and aged cells characterized by synchrotron X-ray reported phase transformations of PrO<sub>1.833</sub> into more reduced PrO<sub>x</sub> phases. In the context of this work on nanostructured electrodes, in these operating conditions, it appears that this phase transition is driven by the temperature. To the point, structural characterization revealed the presence of a slightly reduced PrO<sub>1.8</sub> phase instead of the expected PrO<sub>1.833</sub> phase for the pristine cell sintered at 600°C for two hours in air. This evolution is pursued for the thermally aged cells. A transition into the phase  $PrO_{1.714}$  (i.e. Pr<sub>7</sub>O<sub>12</sub>) is predominating for the sample aged at 700 °C for 1000 h. Finally, peaks corresponding to a body-centered cubic (BCC) structure attributed to  $PrO_x$  with x in the range of 1.5 to 1.7 have been identified in the whole electrode diffractograms for the sample aged at 800 °C for 700 h. In the particular case of the sample aged at 700 °C under polarization of - 0.5 A cm<sup>-2</sup> for 1000 h, the phase refinement has yielded some interesting results. As expected at this operating temperature, the analysis of the diffractograms indicates main peaks attributed to the phase PrO<sub>1.714</sub> through the entire ESD electrode thickness. However, a more in-depth view in the diffractogram revealed some additional peaks at the GDC/PrOx interface. These peaks have been identified with BCC crystal structure that could correspond to the more reduced phase  $PrO_{1.5 \le x \le 1.7}$ . The reduction into  $PrO_{1.714}$  would be due to a thermal effect since this phase also appeared on the sample thermally aged at 700°C. This phase transformation should not affect the electrode and cell performances as PrO<sub>1.714</sub> is expected to remain electrochemically active unlike the presence of the more reduced phase PrO<sub>1.5<x<1.7</sub> phase which appears to be less

conductive. Indeed, according to the literature (c.f. chapter I and article in the chapter IV), the conductivity of these praseodymium oxides phases  $PrO_x$  is decreased towards the more reduced phases. Therefore, the presence of this  $PrO_{1.5 \le x \le 1.7}$  phase at the GDC/PrO<sub>x</sub> interface could add an additional ohmic resistance. This observation is consistent with the increase in series resistance observed in the impedance spectra after the long-term test. The origin of this phase transformation is not yet fully understood. Several hypotheses have been put forward to explain this transition. Firstly, it could be the result of the decomposition of  $Pr(OH)_3$  which was present at the identified interface on the pristine cell as reported in some literature studies. Nor does it explains why it would not show up on the cell thermally aged at 700 °C. The other hypothesis suggests that this phase would not be  $PrO_{1.5 \le x \le 1.7}$  but rather a phase with the same crystalline structure resulting either from (i) an inter-diffusion at the barrier layer or (ii) small dissolution of Pr into the GDC. Preliminary research has been unable to find a phase with lattice parameters that would allow the indexation of the identified peaks. Thus, the understanding this phenomenon requires further investigation.

To conclude this study, one could say that  $PrO_{1.833}$  (i.e.  $Pr_6O_{11}$ ) seems to be an interesting material for SOCs application. Indeed, moderate degradation rate (i.e.  $\sim$  of 5.8 % kh<sup>-1</sup>) have been measured for the operating conditions used in this work. On the other hand, the O<sub>2</sub> electrode does not seem to suffer from major delamination. Moreover, the structural analyses did not reveal any element diffusion or significant reactivity with the other materials of the cell, which is one of the major causes of degradation on the classical materials. This being said, the phase transformations undergone by  $PrO_{1.833}$  could be limiting for future applications. It is therefore necessary to better understand (i) the effective impact of these phases on the performance of the electrode (ii) the origin of these decompositions and (iii) evolution of these phases under more severe operating conditions such as higher current density. Besides, the activation overpotentials measured on the i-V curves seem to limit the performance of this electrode. Indeed, polarization curves have been measured, under the same conditions, on other cells composed of this PrO<sub>1.833</sub> ESD electrode by modifying either the current collector or the half-cell support. The results, provided in Appendix II, reported these activation overpotentials for all the cells, suggesting that it is related to the functional layer. It would be thus interesting to study other electrode architectures to overcome this phenomenon.

# General conclusion

# **General conclusion**

In the context of improving the durability of SOECs, one solution consists to lower the operating temperature to around 650-700 °C. A detrimental consequence of this strategy is that the oxygen electrode performances become relatively insufficient. This Ph.D. thesis aimed to deeply investigate some oxygen electrode materials that would be able to reach high electrochemical efficiency with limited degradation at an intermediate temperature (700 °C) for SOEC operation. The origins of the degradation are diverse including physical-chemical decompositions, inter-diffusion, delamination, etc. Thus, the choice of the oxygen electrode material needs to fulfill a set of criteria regarding the intrinsic properties (oxygen surface exchange coefficient, oxygen diffusion coefficient, ...) as well as the compatibility with the other materials composing the cell (thermal expansion coefficient (TEC), ...). Besides, the microstructure of the electrode, interfaces, and composition also play a key role in the electrochemical performances. Following the literature survey, two materials have been selected for this study, namely rare earth nickelates  $La_2NiO_{4+\delta}$  and praseodymium oxide  $PrO_{1.833}$ , which are the subject of chapters III and IV, respectively.

The La<sub>2</sub>NiO<sub>4+ $\delta$ </sub> phase has been selected thanks to its good chemical stability in a wide range of temperatures and oxygen partial pressure associated with acceptable performances. However, despite its interest for an operation at intermediate temperature, the underlying mechanisms controlling its electrochemical performances remained unknown. For this reason, an electrochemical model has been proposed for this over-stoichiometric electrode material. Thanks to this micro-scale model, it is possible to provide a better understanding of the reaction mechanisms and define the rate-determining step of this LNO electrode as a function of the operating conditions. For this purpose, experimental polarization resistances and electrochemical impedance diagrams have been measured at OCP and at different temperatures (650, 700, and 750 °C). At the targeted operating temperature of 700 °C, the EIS spectra have been also recorded under anodic and cathodic polarizations and at OCP. It has been observed for this over-stoichiometric material that the LNO electrode is more performant under anodic polarization in the electrolysis mode than in cathodic polarization in the fuel mode. Moreover, as expected, it has been found that the performance of the LNO electrode improved when increasing the temperature. Indeed, the polarization resistance decreased from 0.78  $\Omega~\text{cm}^2$  at 650 °C to 0.20  $\Omega$  cm<sup>2</sup> at 750 °C at OCP. That being said, it has to be noted that a change in the shape of the EIS diagrams has been observed when increasing the temperature. The obtained
EIS diagrams has evolved from a Gerischer-type element at 650 °C to a more depressed semicircle at higher temperatures (700 and 750 °C). This evolution suggests a change in the reaction mechanism, which will be discussed afterwards through the model. Finally, the effect of the oxygen partial pressure on the LNO electrode response has been also investigated. The EIS diagrams recorded at 700 °C and OCP for  $pO_2$  range of 0.15 - 1 atm have shown a decrease in polarization resistance when increasing the oxygen partial pressure has been recorded. This electrochemical measurement have been used for model calibration and validation. In addition, all the microstructural parameters required for the simulation have been computed on a 3D electrode reconstruction obtained by FIB-SEM tomography. Yet, the validation of the model allowed us to provide an explanation of the reaction mechanisms involved in the electrolysis and fuel cells modes. The model is based on two considered pathways i.e. (i) the bulk path related to the oxygen incorporation/excorporation at the gas/electrode interface and; (ii) the surface path related to the direct charge transfer at the TPBIs. The plot of the ratio of the surface to the bulk path as function of the current density for the three investigated temperatures have shown that the charge transfer at TPBIs (surface pathway) is the dominant reaction pathway under cathodic polarization. Indeed, in this operating mode, the rate of the oxygen incorporation (bulk pathway) becomes bounded due to the depletion of interstitial oxygen in the LNO material. On the other hand, both pathways remain activated under anodic polarization (in the electrolysis mode), thus explaining the higher performance achieved in this SOEC condition. Moreover, the evolution of the slope of the EIS diagrams as a function of the temperature has been attributed to a transition from the bulk path to the surface path. Indeed, at OCP and 650 °C, the reaction mechanism is controlled by the bulk path. Then, when increasing the operating temperature, the contribution of the surface path increases. Finally, whatever the current density, the bulk path seems to be more and more favored when increasing the pO2. This behavior is attributed to an increase in the concentration of the oxygen ions in interstitial sites with the oxygen partial pressure. The reaction mechanism for this over-stoichiometric material has been compared and deeply discussed with the classical under- stoichiometric LSCF electrode. From this study, it has been shown that LNO is a very promising material for SOEC operation. Besides, its performances can be still improved by microstructural optimization.

To date SOECs are known to suffer from long-term durability issues. In chapter IV, we undertook a durability study of an oxygen electrode material made of  $PrO_{1.833}$ , characterized by excellent catalytic properties. Indeed, in a previous study, we found that  $PrO_{1.833}$ , which is a decomposition product of LPNO after aging, is an electrochemically active oxygen electrode

material. In this work, long-term electrochemical measurements of a nanostructured PrO<sub>1.833</sub>, were carried out using a complete cell configuration and compared to thermal aging using symmetrical cells. For that purpose, ESD has been used as a promising process to design innovative architecture and nanostructure. From previous work at LEPMI, we have selected the optimal ESD processing conditions for depositing a columnar-type PrO<sub>1.833</sub>, functional layer that presents the best electrochemical performances. In this work, this active porous layer was deposited on typical half-cell support, and then topped with LSM CCL. The electrochemical characterizations on this complete cell showed promising initial performance at 700 °C in SOEC mode (- 1 A cm<sup>2</sup> at 1.4 V with  $H_2O/H_2 = 90$  vol. %/10 vol. %). However, relative high activation overpotentials were observed in the polarization curve. This may be due to the low electrical conductivity values reported for  $PrO_{1.833}$ . The other assumption is that it can be attributed to the contact area between PrO<sub>1.833</sub> and LSM that could be further improved to facilitate the current conduction. In addition, a reasonable degradation rate of  $\sim 5.8$  % kh<sup>-1</sup> has been obtained at 700 °C within 1000 h of operation. No delamination or cracks have been detected after ageing. On the other hand, SEM observations performed on the hydrogen electrode have shown a Ni particle migration away from the fuel electrode/electrolyte interface which has partly contributed to cell degradation. Nevertheless, even though some microstructural evolution has been observed, the phase transformation that occurred by the PrO<sub>1.833</sub> phase under the operating conditions used in this work also seems to be involved in the cell degradation. Indeed, lamellas extracted by PFIB from the aged and pristine cells have been characterized through synchrotron µ-XRD and µ-XRF to investigate the physicochemical evolutions as a function of the operating conditions. These fine characterization techniques have been very helpful to highlight the various decompositions all along the electrode thickness. For a reminder, four samples listed below have been analyzed in order to understand the impact of operating conditions such as temperature or current:

- Pristine cell (as prepared complete cell, sintered at 600 °C for 2 h in air)

- Aged cell under SOEC operation (700 °C, - 0.5 A cm<sup>-2</sup> for 1000 h,  $H_2O/H_2 = 90/10$  with SC = 25 %)

Two thermally aged cells: (i) 700 °C for 1000 h and (ii) 800 °C for 700 h.

The analyses showed phase transitions of  $PrO_x$  towards more reduced phases, which would be driven by a thermal effect for this ESD electrode under these operating conditions. The pristine cell sintered at 600 °C results to the formation of the phase  $PrO_{1.80}$ . Thermal aging at temperature of 700 °C has led to a phase transition into the  $PrO_{1.714}$  phase in the whole electrode. Finally, increasing temperature to 800 °C induced a phase transition into even more reduced

 $PrO_x$  (1.5 < x < 1.7) phase with a BCC structure. For the sample aged at 700 °C under current at - 0.5 A cm<sup>-2</sup> for 1000 h, the  $PrO_x$  ESD layer is mainly composed of the phase  $PrO_{1.714}$ , in good agreement with the thermally aged cell at the same temperature. However, some peaks corresponding to a BCC cubic structure have been also identified in the diffractograms at the electrode/electrolyte interface. Rightly so, this phase could thus correspond to the phase  $PrO_x$ in the range of 1.5 < x < 1.7 with the BCC structure. From an electrochemical point of view, PrO<sub>1.714</sub> is expected to remain electrochemically active. Therefore, the detection of this phase could be considered as not limiting. On the other hand,  $PrO_{1.5 \le x \le 1.7}$  exhibits a smaller electrical conductivity than the one of  $PrO_{1.714}$ . This behavior could explain the loss in cell performance. Besides, the detection of this phase at the interface was correlated with the increase of the contact resistance in the impedance spectra. The phase transition into  $PrO_{1.5 < x < 1.7}$  is not yet fully understood. Several hypotheses have been proposed. The first one stipulates that the transition into  $PrO_{1.5 \le x \le 1.7}$  would be accelerated by the polarization. Indeed, this phase has not been observed for the sample thermally aged at 700 °C. However, in electrolysis mode, the oxidizing conditions should promote the phase transformation towards more oxidized phases than  $PrO_{1.714}$ . The second hypothesis is that  $PrO_{1.5 \le x \le 1.7}$  could be the result of the decomposition of Pr(OH)<sub>3</sub> which has been identified at the interface on the pristine cell. The last assumption is that this phase could be induced by a reactivity between the PrO<sub>x</sub> and the CGO (e.g. interdiffusion) that could lead to the formation of phases with BCC structure. In other words, that this phase won't be  $PrO_{1.5 \le x \le 1.7}$ , but another phase with the same crystalline structure. However, to date, the structural analyses did not reveal any element diffusion which could suggest a reactivity with the electrolyte, the barrier layer. On the other hand, it should be specified that some small peaks in XRD patterns have not been identified yet. Thus, their impacts in the evolution of cell performances are still not established. In summary, based on the electrochemical measurement, it can be said that this nanostructured PrO<sub>1.833</sub> (i.e. Pr<sub>6</sub>O<sub>11</sub>) remains to be an interesting material for SOECs application. Thanks to the microstructural and structural analyses, it has been possible to define the limitations of this electrode and to provide guidelines for the improvement of this electrode.

# Perspectives

This work has allowed us to better understand the behavior of the two MIEC oxygen electrodes, LNO and  $PrO_{1.833}$  under the studied conditions (either in a fuel cell or in electrolysis mode) and to define several possibilities for improving the performances and/or stability.

Thanks to the kinetic model developed for the LNO oxygen electrode, it has been shown that the surface path play a key role on the electrode efficiency in both SOEC and SOFC operating modes. From this result, it can be proposed to design a LNO/CGO composite electrode in order to promote the surface path by increasing the density of active TPBIs. Indeed, a previous student E. Effori has investigated the evolution of the reaction mechanism on composite LSCF-CGO. Her study confirmed that from 700 °C, the reaction mechanism for the LSCF-CGO electrode is dominated by the surface path whatever the polarization. The optimum in term of electrode composition (LNO/CGO ratio), porosity, particle size distribution, etc. could be identified using the model. The numerical study should thus provide valuable guidelines for the electrode fabrication. Moreover, to mitigate the well-established reactivity between LNO and CGO which can lead to the formation of insulating phases (i.e. NiO), and the diffusion of lanthanum into CGO, it can be proposed to produce this LNO/CGO composite electrode combining the SP and ESD techniques. Indeed, the chemical reactivity is expected to be exacerbated by electrospraying simultaneously LNO and CGO on YSZ electrolyte topped by a thin CGO dense barrier layer. In fact ESD allows to get crystallization at low annealing temperatures, and the obtention of very reactive nanostructured particles. Our proposal based on Sharma's Ph. D. thesis is to avoid this reactivity by designing the oxygen electrode as a triple layer. The procedure consists of first depositing large grains of CGO by SP forming a porous layer and then in a second step, to infiltrate by ESD nanostructured LNO in the porous CGO layer. The expected oxygen electrode is finally topped by the CCL.

Once the microstructural optimization for best electrochemical performance is obtained, a longterm test on the complete cell should be performed to study the stability of this electrode for SOEC and SOFC operation. In parallel, the model previously developed for the LNO single phase can be adjusted in order to investigate the reaction mechanisms involved in this composite electrode stability. This work reported rather good initial performance and reasonable degradation of nanostructured PrO<sub>x</sub> used as an AFL of the oxygen electrode for SOECs. Post-mortem structural characterizations by X-ray µ-diffraction and µ-fluorescence performed at the PSI synchrotron revealed a material evolution that would contribute to the loss of the cell performances during operation under SOEC mode. More precisely, typical peaks associated to the BCC structure, assigned to PrO<sub>1.5<x<1.7</sub> have been observed at the barrier layer interface. Therefore, it would be interesting to understand the origin of this phase and its precise effect on cell efficiency. The first proposed hypothesis is that the current has an impact on this decomposition. Thus, it would be relevant to conduct long-term study by applying a much higher current with PrO<sub>x</sub> deposited by ESD on a CGO electrolyte. The other hypothesis suggests that this phase would not be PrO<sub>1.5<x<1.7</sub> but rather a phase with the same crystalline structure, resulting from a reactivity between PrO<sub>x</sub> and CGO. A first approach would be to mix PrO<sub>x</sub> and CGO powders. However, it should be noted that grain size and study conditions are not representative of what can be achieved in complete cell, under SOEC conditions. On the other hand, assuming that no reactivity with the CGO has been evidenced from the structural analysis performed on PrO<sub>x</sub>. a study of a composite electrode PrOx/CGO, with various microstructures, could be also interesting in order to improve the cell performances.

# APPENDICES

## **Appendix I**

# Development of the elementary kinetic model for the LNO electrode

An elementary model has been developed and used to investigate the LNO reaction mechanisms occurring under anodic and cathodic polarization. The full description of the governing equations is given hereafter.

#### **Model description:**

The model considers an isothermal electrode slice of LNO porous electrode including a CGO barrier layer for which the computed microstructural parameters are obtained from 3D reconstruction (already published in [1]).

**Reaction mechanisms** - The proposed model considers two possible reaction pathways for oxygen oxidation/reduction divided into a sequence of elementary steps as represented in Figure 1 in the electrolysis mode. The "bulk path" is characterized by an ionic transfer at the electrode/electrolyte interface (R1). After diffusion of the oxygen in the bulk of the electrode material, the oxygen is ex-corporated to produce oxygen adatoms on the electrode surface (R2). In parallel, the "surface path" considers direct oxidation at the Triple Phase Boundary length (TPBI) (R3) leading to the formation of oxygen ions on the electrode surface. Then, in both cases, a second reaction of charge transfer (R4) takes place on the surface to produce oxygen adatoms that can be associated (R5) and desorbed (R6) in the porosity of the electrodes.



Figure 1 from Chapter III - Part II - Schematic description of the reaction pathway considered in the elementary model (in electrolysis mode) represented for the LNO electrode.

The equations of the considered reactions and the corresponding kinetic rates for LNO are listed in the Table 1 using the Kröger-Vink notation.

*Kinetic rates* - The kinetic rates are expressed as a difference between the forward and backward reactions for the anodic and cathodic polarizations (Table 1). In this frame, the forward and backward kinetic constants are linked together through the thermodynamic constant (Table 2). A classical Butler-Volmer formalism was used in the expression of the kinetic rates of ionic transfer reaction (R1) at the CGO/LNO interface (Eq. 1 – Table 1), the charge transfer at TPBIs (R3) (Eq. 3 – Table 1), and the oxidation/reduction reactions (R2 and R4) (Eqs. 2 and 4 – Table 1). Indeed, in addition to the direct oxidation at the TPBIs (R3), the charge transfers that take place at the LNO surface (R2 and R4) are classical electrochemical reactions for which the classical Butler-Volmer can be used. On the other hand, even if there is no change in the oxidation state between the reactant and the product for the ionic transfer reaction (R1), it is assumed that the reaction is affected by the electrical field between the electrode and the electrolyte. Thus, the kinetic rate is dependent on the local electrode potential E(Z)

$$E(z) = \varphi_{LNO}(z) - \varphi_{CGO}(z) = -\frac{\tilde{\mu}_{e,LNO}}{F} - \frac{\tilde{\mu}_{V_{O,CGO}}}{2F}$$
Eq. 13

where  $\tilde{\mu}_{V_{O,CGO}^{\bullet}}$  and  $\tilde{\mu}_{e,LNO}$  are the electrochemical potentials for the oxygen vacancies in CGO and for the electrons in LNO, respectively.

Besides, for the charge transfers that take place at the surface of the electrode (R2 and R4), the kinetics rates of the reactions are affected by the surface electrostatic potential step  $\chi$  [2]. Indeed, because of the accumulation of oxygen ions on the surface of the electrode, a double layer can arise at the LNO/gas interface. This behaviour leads to a surface electrostatic potential step  $\chi$  expressed as follows

$$\chi(z) = \chi_{LNO}^{bulk} - \chi_{LNO}^{surf} = \frac{\Gamma F \theta_{O_{\overline{s}_{LNO}}}(z)}{C_{dl}^{surface}}$$
Eq. 14

Finally, the kinetic rates of the association and desorption steps, respectively (R5) and (R6) (Eqs. 5 and 6 – Table 1), are expressed by a classical expression of a pure chemical reaction. The surface species are assumed to be adsorbed on the same sites at the surface of the electrode. Thus, the Langmuir hypothesis considering a monolayer of adsorbates without interaction can be used

$$\theta_{s,LNO} + \theta_{O_{s,LNO}} + \theta_{O_{s,LNO}} + \theta_{O_{2s,LNO}} = 1$$
 Eq. 15

where  $\theta_i$  is the surface coverage of respectively the free site and the adsorbates (oxygen adions, neutral ad-atoms and ad-molecules).

Furthermore, the kinetic rates also depend on the corresponding microstructural properties of the material. The ionic transfer R1 is linked to the CGO/LNO specific surface area  $(S_p^{CGO/LNO})$  while the direct oxidation/reduction at TPBs (R3) is dependent on the density of active phase at TPBIs ( $\xi_{TPBs}$ ). For the reactions that take place at the surface of the LNO electrode, the kinetic rates are proportional to the LNO/gas specific surface area  $(S_p^{LNO/gas})$ .

Moreover, all the reactions are assumed to be thermally activated. Thus, the kinetic constant k<sub>i</sub> is expressed according to an Arrhenius law

$$k_i = k_{o,i} \exp\left(-\frac{E_{act,i}}{RT}\right)$$
 Eq. 16

where  $E_{act,i}$  is the activation energy.

*Transport phenomena and conservation equations* – The equations related to the mass and charge transport are expressed in Table 3. The ionic current in CGO (Eq. 17 – Table 3) and electronic current in LNO (Eq. 23 – Table 3) have been expressed using the classical Ohm's law. It should be noted that in this model, the evolution of electronic conductivity with temperature is considered to be negligible. On the other hand, the dependency with the oxygen partial pressure is assumed. Thus, the electronic conductivity has been calculated following the power law equation

$$\sigma_{e^-} = \sigma_0(p_{O_2})^k$$
 Eq. 33

On the other hand, the ionic conductivity in the CGO is thermally activated. Thus, the values have been expressed using Arrhenius law according to the activation energy ( $E_a = 65 \text{ kJ mol}^{-1}$ ) provided by Kim et al. [3].

The fluxes of the adsorbed oxygen species and the solid-state diffusion of the interstitial oxygens in the LNO follow a classical Fick's law. The diffusivity of the oxygen adsorbed on the LNO surface is supposed to be thermally activated. However, there is limited available information about the values of these diffusion coefficients. Therefore, these parameters have been implemented in the model as unknown data and have been fitted through the polarization curves.

The gas transport in the electrode porosities is described by the Dusty Gas Model (DGM) that combines a molecular and Knudsen diffusion (Eq 21). The molecular diffusivity ( $D_{O_2,N_2}$ ) coefficient can be expressed according to the Fuller theory

$$D_{O_2,N_2} = \frac{0.00143}{P_{tot} \cdot \left( \left( V_{O_2} \right)^{1/3} + \left( V_{N_2} \right)^{1/3} \right)^2 \cdot \sqrt{\frac{2}{\frac{1}{M_{O_2}} + \frac{1}{M_{N_2}}}} \cdot T^{1.75}$$
Eq. 34

where  $M_i$  is the to the molecular weight and  $V_i$  the Fuller diffusion volume for the i-species ( $V_i$  found from [4]).

The Knudsen coefficient  $(D_{k,O_2})$  is expressed by

$$D_{k,O_2} = \bar{r}_{pores} \cdot \frac{2}{3} \sqrt{\frac{8 \cdot RT}{\pi M_i}}$$
 Eq. 35

where  $\bar{r}_{pores}$  is the mean pore radius.

*Thermodynamic description* – The equations of the thermodynamic equilibrium constants are expressed in the Table 2. According to Eq. 14 defined above, the surface potential step at equilibrium is expressed as following  $\chi(z) = \Gamma F \theta_{O_{sLNO}}^{eq}(z) / C_{dl}^{surface}$ . It is worth noting that the surface coverage of adsorbed species at equilibrium  $(\theta_{O_{sLNO}}^{eq}, \theta_{O_{sLNO}}^{eq})$  and  $\theta_{O_{2sLNO}}^{eq})$  are considered as input parameters in the model at pO<sub>2</sub> = 0.21 atm., and thus, obtained by fitting the experimental polarization curves. Furthermore, once the  $\theta_i^{eq}$  are fitted at pO<sub>2</sub> = 0.21 atm, and assuming that they are independent to the temperature, it is possible to determine the thermodynamic constants for the surface reactions  $K_e^{(4)}, K_e^{(5)}$  and  $K_e^{(6)}$ . Indeed, the last assumption can be made as long as the surface site. Hence, the evolution of the  $\theta_i^{eq}$  with the oxygen partial pressure can be deduced from the Eq. 12 in Table 2.

Finally, the equilibrium constants  $K_e^{(1)}$  and  $K_e^{(2)}$  are calculated with Eqs. 7 and 8. The concentration of interstitial oxygens  $c_{O_i'}^{eq}$  is dependent on the temperature. It is expressed as following as a function of the oxygen over stoichiometry ( $\delta^{eq}$ ) and the volume of the lattice unit-cell where (a,b,c) are the lattice parameter of the LNO:

$$c_{O_i'}{}^{eq} = \frac{4 \times \delta^{eq}}{(a \times b \times c) \times N_a}$$
 Eq. 36

*Model calibration* – The set of equations listed above have been implemented in COMSOL Multiphysics software. The reaction rate (Eq 1-6 in Table 1), charge and mass balances (Eqs. 25-32 in Table 3) and the corresponding fluxes (Eqs. 17-24 in Table 3) constitute a set of Partial Differential Equations (PDEs) which have been solved in the time domain by the Finite Element Method (FEM). The boundary conditions for the LNO electrode model are given in Table 4. The microstructural parameters extracted from the 3D reconstruction have been implemented as input data in the model (already published in [1]). The effective transport parameters have been expressed with these microstructural properties. Regarding the other parameters, the

chemical diffusivity  $D_{chem}$  has been fitted from the i-V curve for the three investigated temperatures. It has to be specified that, the estimation of the D<sub>chem</sub> is around one order of magnitude higher than the ones reported in the literature [5-8]. The reason of this discrepancy is not fully understood. The diffusivity of the adsorbed species at the surface of the electrode are unknown parameters and thus, fitted in the experimental i-V curves. The electronic conductivity in LNO have been estimated through the Eq. 33 for the investigated oxygen partial pressure by considering the  $\sigma_0 \approx 86$  S cm<sup>-1</sup> and an exponent k of 0.07 provided by Jeon et al. [9]. The evolution of the ionic conductivity of the CGO with the temperature has been calculated by following an activation energy  $E_a \approx 65$  kJ mol<sup>-1</sup> [10]. The concentration of interstitial oxygen at equilibrium  $c_{O''}^{eq}$  has been evaluated with the equation 36. For the calculation, the LNO oxygen over stoichiometry values ( $\delta^{eq}$ ) as a function of the temperature at  $pO_2 = 0.21$  atm were deduced from Nakamura et al. [11] and the lattice parameters were taken from Flura et al. [12]. On the other hand, the maximum concentration  $c_{0''}^{max}$  has been calculated by assuming that the LNO saturation in interstitial oxygen is reached for  $\delta_{max} \approx 2$ . The double layer capacitance, C<sub>dl</sub> has been fixed at 10 F m<sup>-2</sup> for the LNO electrode. Finally, two assumptions have been considered in the kinetics parameters for model calibration. First, the ionic transfer reaction at the CGO/LNO interface (R1) has been considered as not limiting (k+ >> 0). Second, the associative reaction on the LNO surface (R5) has been considered to be very fast. In summary, the kinetic constants for the reactions (R2), (R3), (R4) and (R6) as well as the surface coverages and the surface diffusivities, remain unknown.

# Tables

Table 2: Reactions a	and	expressions	of the	kinetics	rates
----------------------	-----	-------------	--------	----------	-------

-	Reactions	Kinetic rates	
R1	$O_0^{X}(CGO) + V_i^{X}(LNO) \stackrel{k_+}{\leftrightarrow} V_0^{\bullet}(CGO) + O_i^{\prime\prime}(LNO)$ $k$	$\begin{split} \nu_{(1)} &= S_p^{CGO/LNO} \left\{ k_+ \exp\left(\frac{2\alpha_{(1)}^{ox}FE}{RT}\right) \left(1 - \frac{c_{o_i'}}{c_{o_i'}^{max}}\right) \\ &- k \exp\left(\frac{-2\alpha_{(1)}^{red}FE}{RT}\right) \left(\frac{c_{o_i'}}{c_{o_i'}^{max}}\right) \right\} \end{split}$	Eq. 1
R2	$O_i''(LNO) + s_{LNO} \qquad \begin{array}{c} k_{ox} & ^{LNO/gas} \\ \leftrightarrow \\ k_{red} & ^{LNO/gas} \end{array} V_i^X(LNO) + 1e^- + O_{s,LNO}^- \\ \end{array}$	$\begin{split} \nu_{(2)} &= S_p^{LNO/gas} \left\{ k_{ox}^{LNO/gas} \Gamma \theta_{S_{LNO}} \frac{c_{o_l''}}{c_{o_l''}^{max}} exp\left(\frac{\alpha_{o2}^{o2} F \chi}{RT}\right) \\ &- k_{red}^{LNO/gas} \Gamma \theta_{o_{5-LNO}} \left(1 - \frac{c_{o_l''}}{c_{o_l''}^{max}}\right) exp\left(\frac{-\alpha_{(2)}^{red} F \chi}{RT}\right) \right\} \end{split}$	Eq. 2
R3	$O_{O}^{X}(CGO) + s_{LNO} \overset{k_{OX}^{TPB}}{\underset{k_{red}}{\leftrightarrow}} V_{O}^{\bullet\bullet}(CGO) + 1e^{-} + O_{s,LNO}^{-}$	$\nu_{(3)} = \xi_{TPBs} \left\{ k_{ox}^{TPB} \exp\left(\frac{\alpha_{(3)}^{xs}FE}{RT}\right) \Gamma \theta_{s_{LNO}} - k_{red}^{TPB} \exp\left(\frac{-\alpha_{(3)}^{red}FE}{RT}\right) \Gamma \theta_{o_{s_{LNO}}^-} \right\}$	Eq. 3
R4	$\begin{array}{ccc} & k_{deion} \\ O^{s,LNO} & \leftrightarrow & O_{s_{LNO}} + 1e^- \\ & k_{ion} \end{array}$	$\begin{split} v_{(4)} &= S_p^{LNO/gas} \left\{ k_{deion} \Gamma \theta_{O_{s,LNO}} exp\left(\frac{\alpha_{(4)}^{deion} F \chi}{RT}\right) \\ &- k_{ion} \Gamma \theta_{O_{s_{LNO}}} exp\left(\frac{-\alpha_{(4)}^{ion} F \chi}{RT}\right) \right\} \end{split}$	Eq. 4
R5	$2O_{s_{LNO}} \stackrel{k_{ass}}{\underset{k_{diss}}{\leftrightarrow}} O_{2s_{LNO}} + s_{LNO}$	$v_{(5)} = S_p^{LNO/gas} \left\{ k_{ass} \Gamma^2 \theta_{O_{s_{LNO}}}^2 - k_{diss} \Gamma^2 \theta_{O_{2s_{LNO}}} \theta_{s_{LNO}} \right\}$	Eq. 5
R6	$ \begin{array}{ccc}                                   $	$v_{(6)} = S_p^{LNO/gas} \left\{ k_{des} \Gamma \theta_{O_{2s_{LNO}}} - k_{ads} \Gamma \theta_{s_{LNO}} P_{O_2} \right\}$	Eq. 6

Table 3: Equations for the thermodynamic equilibrium constants

Therm	Thermodynamic equilibrium constants		
R1	$K_{e}^{(1)} = \frac{k_{+}}{k_{-}} = \frac{c_{O_{i'}}e^{eq}}{\left(c_{O_{i'}}max, eq - c_{O_{i'}}e^{q}\right)} exp\left(\frac{-2FE^{eq}}{RT}\right)$	Eq. 7	
R2	$K_e^{(2)} = \frac{k_{ox}^{LNO/gas}}{k_{red}^{LNO/gas}} = \frac{\theta_{O_{s,LNO}^-}^{eq} \left(c_{O_i^{\prime\prime}}^{max,eq} - c_{O_i^{\prime\prime}}^{eq}\right)}{c_{O_i^{\prime\prime}}^{eq}} exp\left(\frac{-F\chi^{eq}}{RT}\right)$	Eq. 8	
R3	$K_e^{(3)} = \frac{k_{ox}^{TPB}}{k_{red}^{TPB}} = \frac{\theta_{o_{s,LNO}}^{-eq}}{\theta_{s,LNO}^{eq}} exp\left(\frac{-FE^{eq}}{RT}\right)$	Eq. 9	
R4	$K_e^{(4)} = \frac{k_{deion}}{k_{ion}} = \frac{\theta_{O_{s,LNO}}^{eq}}{\theta_{O_{s,LNO}}^{-eq}} exp\left(\frac{-F\chi^{eq}}{RT}\right)$	Eq. 10	
R5	$K_{e}^{(5)} = \frac{k_{ass}}{k_{diss}} = \frac{\theta_{O_{2s,LNO}}^{eq} \theta_{s,LNO}^{eq}}{\left(\theta_{O_{s,LNO}}^{eq}\right)^{2}}$	Eq. 11	

R6	$K_e^{(6)} = \frac{k_{des}}{k_{ads}} = \frac{\theta_{s,LNO} e^{eq} P_{O_2} e^{eq}}{\theta_{O_{2s,LNO}} e^{eq}}$		Eq. 12
----	---	--	--------

Table 4: Equations of charge and mass conservations associated with the current and fluxes taken into account in the physically-based model

Electrode					
Transport phenomena		Conservation equations			
$\vec{i}_{io} = -\sigma_{io,CGO} \times \vec{\nabla} \varphi_{CGO}$	Eq. 17	$\vec{\nabla} \cdot \vec{t}_{io} = 0$	Eq. 25		
$\vec{N}_{O_i''} = -\frac{\varepsilon_{LNO}}{\tau_{LNO}} \widetilde{D}_{chem} \times \widetilde{V} c_{O_i''}$	Eq. 18	$\vec{\nabla} \cdot \vec{N}_{O_i''} = -\nu_{(2)} - \varepsilon_{LNO} \frac{\partial c_{O_i''(z,t)}}{\partial t}$	Eq. 26		
$\vec{N}_{O_{\vec{s}_{LNO}}} = -S_p^{LNO/gas} \cdot D_{O_{\vec{s}_{LNO}}} \cdot \Gamma \cdot \vec{\nabla} \theta_{O_{\vec{s}_{LNO}}}$	Eq. 19	$\vec{\nabla} \cdot \vec{N}_{O_{s_{LNO}}} = \left(\nu_{(2)} - \nu_{(4)}\right) - S_p^{LNO/gas} \Gamma \frac{\partial \theta_{O_{s_{LNO}}}(z, t)}{\partial t}$	Eq. 27		
$\vec{N}_{O_{S_{LNO}}} = -S_p^{LNO/gas} \cdot D_{O_{S_{LNO}}} \cdot \Gamma \cdot \vec{\nabla} \theta_{O_{S_{LNO}}}$	Eq. 20	$\vec{\nabla} \cdot \vec{N}_{O_{S_{LNO}}} = \left(\nu_{(4)} - 2\nu_{(5)}\right) - S_p^{LNO/gas} \Gamma \frac{\partial \theta_{O_{S_{LNO}}}(z,t)}{\partial t}$	Eq. 28		
$\vec{N}_{O_{2s_{LNO}}} = -S_p^{LNO/gas} \cdot D_{O_{2s_{LNO}}} \cdot \Gamma \cdot \vec{\nabla} \theta_{O_{2s_{LNO}}}$	Eq. 21	$\vec{\nabla} \cdot \vec{N}_{O_{2s_{LNO}}} = \left(\nu_{(5)} - \nu_{(6)}\right) - S_p^{LNO/gas} \Gamma \frac{\partial \theta_{O_{2s_{LNO}}}(z, t)}{\partial t}$	Eq. 29		
$\vec{\nabla}y_{O_2} = -\frac{RT}{P_t} \left( \frac{N_{O_2}}{\frac{\varepsilon_{pores}}{\tau_{pores}}} D_{k,O_2} + \frac{N_{O_2}y_{N_2}}{\frac{\varepsilon_{pores}}{\tau_{pores}}} D_{O_2,N_2} \right)$	Eq. 22	$\vec{\nabla} \cdot \vec{N}_{O_2} = \nu_{(6)} - \frac{\varepsilon_{pores}}{RT} P_t \frac{\partial y_{O_2}(z,t)}{\partial t}$	Eq. 30		
$\vec{\iota}_{e^-} = -\frac{\varepsilon_{LNO}}{\tau_{LNO}} \sigma_{e^-} \times \vec{\nabla} \varphi_{LNO}$	Eq. 23	$\vec{\nabla} \cdot \vec{\iota}_{e^-} = -F(\nu_{(2)} + \nu_{(4)}) + S_p^{LNO/gas} C_{dl} \frac{\partial \chi}{\partial t}$	Eq. 31		
Electrolyte					
$\vec{i}_{io} = -\sigma_{io,CGO} \times \vec{\nabla} \varphi_{CGO}$	Eq. 24	$\vec{\nabla} \cdot \vec{\iota}_{io} = 0$	Eq. 32		

Species	Boundary Conditions				
	z = 0	$z = \ell_{CGO}$		$z = \ell_{LNO}$	
	0		1		r
<i>O</i> ''	n.a.*	$N_{O_i''} = v_{(1)}$	Eq. 37	$N_{O_i'' z=L} = 0$	Eq. 44
$O_{S_{LNO}}^{-}$	n.a.	$N_{O_{\tilde{s}_{LNO}},local} = \nu_{(3)}$	Eq. 38	$N_{O_{s_{LNO}}^- z=L}=0$	Eq. 45
O <sub>SLNO</sub>	n.a.	$N_{O_{S_{LNO}},local} = 0$	Eq. 39	$N_{O_{S_{LNO}} z=L} = 0$	Eq. 46
O <sub>2SLNO</sub>	n.a.	$N_{O_{2S_{LNO}},local} = 0$	Eq. 40	$N_{O_{2s_{LNO}} z=L} = 0$	Eq. 47
02	n.a.	$N_{O_2,local} = 0$	Eq. 41	$C_{O_2 z=L} = \frac{P_{O_2}}{RT}$	Eq. 48
Electronic current in LNO, e <sup>-</sup>	n.a.	$i_{e^{-},local} = -2Fv_{(3)} + S_p^{CGO/LNO}C_{dl}\frac{\partial E}{\partial t}$	Eq. 42	$\varphi_{e^- z=L}=0$	Eq. 49
Ionic current in CGO, $i_0$	imp osed	$i_{io,local} = +2F(v_{(1)} + v_{(3)})$ $- S_p^{CGO/LNO}C_{dl}\frac{\partial E}{\partial t}$	Eq. 43	$i_{io z=L} = 0$	Eq. 50

Table 5: Boundary conditions

\*n.a. = Not applicable

## Reference

- [1] G. Sdanghi, L. Yefsah, F. Mauvy, E. Djurado, T. David, J.-M. Bassat, J. Laurencin, Reaction mechanisms of La2NiO4+δ oxygen electrodes operated in electrolysis and fuel cell mode, J. Electrochem. Soc. 169 (2022) 034518. https://doi.org/10.1149/1945-7111/ac58c3.
- [2] J. Fleig, On the current-voltage characteristics of charge transfer reactions at mixed conducting electrodes on solid electrolytes, Phys. Chem. Chem. Phys. 7 (2005) 2027– 2037. https://doi.org/10.1039/B501086A.
- [3] H.-S. Kim, H.-I. Yoo, Effect of acceptor size and hole degeneracy on oxygen nonstoichiometry of La2NiO4+δ, Solid State Ion. 232 (2013) 129–137. https://doi.org/10.1016/j.ssi.2012.12.001.
- [4] B. Todd, J.B. Young, Thermodynamic and transport properties of gases for use in solid oxide fuel cell modelling, J. Power Sources. (2002) 186.
- [5] Z. Li, R. Haugsrud, Effects of the surface coatings on the determination of Dchem and kchem in La2NiO4 by conductivity relaxation, Solid State Ion. (2012) 67–71.

- [6] E. Boehm, J.-M. Bassat, P. Dordor, F. Mauvy, J.-C. Grenier, Ph. Stevens, Oxygen diffusion and transport properties in non-stoichiometric Ln2–xNiO4+δ oxides, Solid State Ion. 176 (2005) 2717–2725. https://doi.org/10.1016/j.ssi.2005.06.033.
- [7] J.A. Kilner, C.K.M. Shaw, Mass transport in La2Ni1-xCoxO4+δ oxides with the K2NiF4 structure, Solid State Ion. 154–155 (2002) 523–527. https://doi.org/10.1016/S0167-2738(02)00506-4.
- [8] G. Amow, S.J. Skinner, Recent developments in Ruddlesden–Popper nickelate systems for solid oxide fuel cell cathodes, J Solid State Electrochem. 10 (2006) 538–546. https://doi.org/10.1007/s10008-006-0127-x.
- [9] S.-Y. Jeon, M.-B. Choi, J.-H. Hwang, E.D. Wachsman, S.-J. Song, Electrical Conductivity and Thermoelectric Power of La2NiO4+δ, J. Electrochem. Soc. 158 (2011) B476. https://doi.org/10.1149/1.3559186.
- [10] R. Tanaka, W.S. Oliveira, A. Brandao, J.C.C. Abrantes, J.R. Frade, Grain boundary conductivity of heterogeneous ceria gadolinia., Electrochim. Acta. (2012) 116.
- [11] T. Nakamura, R. Oike, Y. Ling, Y. Tamenori, K. Amezawa, The determining factor for interstitial oxygen formation in Ruddlesden–Popper type La2NiO4-based oxides, Phys. Chem. Chem. Phys. 18 (2016) 1564–1569. https://doi.org/10.1039/C5CP05993C.
- [12] A. Flura, S. Dru, C. Nicollet, V. Vibhu, S. Fourcade, E. Lebraud, A. Rougier, J.-M. Bassat, J.-C. Grenier, Chemical and structural changes in Ln2NiO4 (Ln=La, Pr or Nd) lanthanide nickelates as a function of oxygen partial pressure at high temperature, J. Solid State Chem. 228 (2015) 189–198. https://doi.org/10.1016/j.jssc.2015.04.029.

# **Appendix II**

## Complementary results on Pr<sub>6</sub>O<sub>11</sub> electrode

This appendix aims to provide additional information concerning the study of the efficiency of the nanostructured  $Pr_6O_{11}$  (i.e.  $PrO_{1.833}$ ) oxygen electrode used as an active functional layer for SOEC operation.

Several electrochemical characterizations have been carried out in order to study the impact of the electrode manufacturing, type of cells and testing conditions on the performances (e.g. the current collector, anode support, sintering temperature ...). For that purpose, i-V curves and EIS impedance spectra have been recorded at 700 °C, under the same SOEC operating conditions. Each time, a component has been changed in order to analyze its influence on the cell performance.

Three different cells have been elaborated in this work. For all the studied cells, the fabrication of the Pr<sub>6</sub>O<sub>11</sub> layer by ESD has followed the same protocol already described in the Chapter II and sintering was performed at 600 °C. All oxygen electrodes have been deposited on half cells composed with a NiO-YSZ cermet and a 8 mol% yttria-stabilized zirconia (8YSZ) electrolyte topped by a thin GDC barrier layer. The contribution of the substrate on the electrode performances has been investigated using two different Ni-YSZ substrates, provided either by Forschungszentrum Jülich GmbH institute (referred to as FZJ) or by CEA Le-Ripault (referred to as CEA). A detailed description of the studied cells as well as a summary table are given below:

- (i) The first cell named  $FZJ/Pr_6O_{11}/LSM$  correspond to the cell, which has been fully detailed in the Chapter IV.
- (ii) The second cell named CEA/ $Pr_6O_{11}$ /LSM which fsollowed the same process for the deposition of the both  $Pr_6O_{11}$  and LSM
- (iii) For the third cell, the LSM pure electronic conductor has been replaced by the MIEC LSCF. Indeed, the current collector should not play a fundamental role in the electrocatalytic activity of the electrode, however, the use of a MIEC would allow to extend the oxygen evolution reaction zones. Moreover, it is also known that optimization of the sintering temperature is a key point that should be carefully considered. Indeed, if the temperature is too low, the sintering will not be sufficient thus resulting in a fragmentation of the layer. If the temperature is too high, inter-

diffusion problems can arise. Moreover, in this work, the increase of the temperature could lead to a decrease of the specific surface of the elaborated  $Pr_6O_{11}$  active electrodes with nanometric grain size. Thus, the screen-printing LSCF deposition has been sintered first at 450 °C for 2 h in air with a ramp of 0.5 °C.min<sup>-1</sup> to remove the binders and ink solvents and then, at 900 °C for 1 h in air with a ramp of 2 °C.min<sup>-1</sup>.

Name	Half-cell support	Functional layer	Current layer
FZJ/Pr <sub>6</sub> O <sub>11</sub> /LSM	FZJ	Pr <sub>6</sub> O <sub>11</sub>	LSM deposited by
			SP and sintered at
			600 °C/2h/air
CEA/Pr <sub>6</sub> O <sub>11</sub> /LSM	CEA	Pr <sub>6</sub> O <sub>11</sub>	LSM deposited by
			SP and sintered at
			600 °C/1h/air
FZJ/Pr <sub>6</sub> O <sub>11</sub> /LSCF	FZJ	Pr <sub>6</sub> O <sub>11</sub>	LSCF deposited by
			SP and sintered at
			900 °C/2h/air

Moreover, in order to assess the performance of this architecture  $Pr_6O_{11}$  electrode, the Forschungszentrum Jülich GmbH institute (FZJ) provided a classical complete cell composed with pure LSCF electrode. This cell has been also tested in our test bench, with the same conditions, in order to have a relevant comparison.

## (i) Electrochemical measurements

For all the investigated cells, the polarization curves have been measured at 700 °C under electrolysis mode, with 90 vol.%  $H_2O + 10$  vol.%  $H_2$  in the hydrogen side with a total gas flow of 15.5 Nml min<sup>-1</sup> cm<sup>-2</sup> and air in oxygen side with SC = 50% at i = -1 A cm<sup>-2</sup>.



Figure 1: Comparison of the initial polarizations curves of different complete cells (with  $Pr_6O_{11}$  electrode) to a reference cell (LSCF electrode) under SOEC conditions (H<sub>2</sub>O/H<sub>2</sub> 90/10 SC = 50% 700 °C).

As can be observed in Figure 1, the polarization curves of the FZJ/Pr<sub>6</sub>O<sub>11</sub>/LSM and FZJ/Pr<sub>6</sub>O<sub>11</sub>/LSCF cells are quite similar. Moreover, the initial performances are close to the reference cell with the LSCF oxygen electrode. For instance, a current density of - 1.1 A cm<sup>2</sup> has been achieved at 1.4 V for the FZJ/Pr<sub>6</sub>O<sub>11</sub>/LSM and - 1.15 A cm<sup>2</sup> has been obtained for the reference cell. On the other hand, the current density of - 0.82 A/cm<sup>2</sup> at 1.4 V achieved by the CEA/Pr<sub>6</sub>O<sub>11</sub>/LSM cell is lower than the one of FZJ cells, suggesting a limitation from the half-cell support. In any case, this measurement shows that for all the Pr<sub>6</sub>O<sub>11</sub> cells, the slope of the curve is higher at low current density. In another words, activation overpotentials have been assessed for all the cells composed with the Pr<sub>6</sub>O<sub>11</sub> electrode, whatever the half-cell support and whatever the current collecting layer. This result confirms the poor electrochemical kinetics using Pr<sub>6</sub>O<sub>11</sub> as a single solid phase electrode.

# **Appendix III**

# Scientific production

#### List of peer-review publications

– <u>Sdanghi G.</u>, **Yefsah L.**, Mauvy F., Djurado E., David T., Bassat J-M., Laurencin J. Reaction mechanisms of  $La_2NiO_{4+\delta}$  oxygen electrodes operated in electrolysis and fuel cell mode. Journal of The Electrochemical Society, 169 (2022) 034518. 10.1149/1945-7111/ac58c3

– <u>Yefsah L.</u>, Laurencin J., Hubert M., Sanchez D. –F., Charlot F., Couturier K., Celikbilek O., Djurado E.

Electrochemical performance and stability of PrO<sub>1.833</sub> as an oxygen electrode for Solid Oxide Electrolysis Cells. Journal of Solid State Ionics, 399 (2023) 116316. 10.1016/j.ssi.2023.116316

## Oral international communication with proceeding

- <u>Yefsah L.</u>, Sdanghi G., Sassone G., Bassat J.-M., Hubert M., Mauvy F., Djurado E., Laurencin J.

Reaction mechanisms of mixed ionic and electronic conductors used as oxygen electrodes in Solid Oxide Cell: focus on  $La_{1-x}Sr_xCo_{y-1}Fe_yO_{3-\delta}$  and  $La_2NiO_{4+\delta}$ .

15th European SOFC & SOE Forum 2022, Lucerne, Suisse, 05-08/07/2022

Actes du congrès, Edited by J. Mougin and J. Laurencin, European Fuel Cell Forum, Suisse, 2022

-Djurado E., Sharma R., Celikbilek O., Khamidy Nur I., Yefsah L., Laurencin J.

Innovative architectural oxygen electrodes for solid oxide cells using electrostatic spray deposition.

15th European SOFC & SOE Forum 2022, Lucerne, Suisse, 05-08/07/2022

Actes du congrès, Edited by J. Mougin and J. Laurencin, European Fuel Cell Forum, Oberrohrdorf, Suisse, 2022

#### Conferences

1. Oral presentation given by L. Yefsah

– <u>Yefsah L.</u>, Khamidy N.I., Laurencin J., Djurado E.

 $Pr_6O_{11}$ , électrode à oxygène prometteuse pour les électrolyseurs à haute température (EHT). Journées Nationales de la Recherche sur la production, la conversion et le stockage de l'hydrogène (JNRH2), 31/05-04/06/2021 (Virtual). 2. Oral presentations given by another co-author

– Celikbilek O., Sharma R., Khamidy N.I., Yefsah L., Djurado E.

Innovative nanostructured and architectured oxygen electrodes for solid oxide fuel cells using electrostatic spray deposition.

GSENN2022, 2nd Global Summit and Expo on Nanotechnology and Nanomaterials, Copenhagen, Danemark, 13-15/06/2022

- <u>Djurado E.</u>, Sharma R., Çelikbilek Ö., Khamidy N.I., **Yefsah L**., Laurencin J. Innovative architectural oxygen electrodes for solid oxide cells using electrostatic spray deposition

ECerS XVII, ICC9 and Electroceramics XVIII Conferences, Krakow, Poland - 10-14/07/2022

-<u>Spann M</u>., **Yefsah L.**, Steil C., Dessemond L., Laurencin J., Djurado E. Designed lanthanum nickelates as oxygen electrodes for solid oxide cells by electrostatic spray deposition ECerS XIX, Lyon, France - 02-06/07/2023

## 3. Poster presentations

- <u>Yefsah L.</u>, Khamidy N.I., Laurencin J., Djurado E. La<sub>2-x</sub>Pr<sub>x</sub>NiO<sub>4+ $\delta$ </sub> (x = 0, 0.5, 1): innovative architectured oxygen electrodes designed by ESD and SP for SOCs. GDR HySPac, Le Croisic, France, 11-13/06/2019

- Yefsah L., Khamidy N.I., Sanchez D.F., Monaco F., Laurencin J., Djurado E.

Etude de vieillissement et analyses post-mortem par  $\mu$ -diffraction et  $\mu$ -fluorescence par rayonnement X synchrotron de LaPrNiO<sub>4+δ</sub>, électrode à oxygène innovante pour les cellules à oxydes solides.

AFC2021, Congrès de l'Association Française de Cristallographie 2021, Grenoble, France, « cristallographie en science des matériaux », 29/06-02/07/2021