

# Films nanométriques poreux élaborés par DLI-CVD comme catalyseurs de mu-PEMFC: une alternative au tout platine?

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## **UNIVERSITE BOURGOGNE FRANCHE-COMTE**

U.F.R Sciences & Techniques Laboratoire Interdisciplinaire Carnot de Bourgogne Ecole doctorale Carnot-Pasteur

# THESE DE DOCTORAT

Pour obtenir le grade de Docteur de l'Université Bourgogne Franche-Comté Discipline : Chimie-Physique

> par **M. Zanfoni Nicolas**

# Films nanométriques poreux élaborés par DLI-CVD comme catalyseurs de μ-PEMFC : une alternative au tout platine ?

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### Résumé

Ce travail porte sur le développement de protocoles de croissance par CVD à injection directe de liquide (DLI-CVD) de films catalytiques poreux potentiellement utilisables dans les piles à combustible de type PEMFC. Les objectifs étaient de contrôler et de réduire au maximum la charge en platine, d'obtenir des matériaux à grande surface spécifique, c'est-à-dire très poreux, mais aussi d'utiliser des précurseurs à bas coût.

Dans un premier temps, le platine a été promu par de l'oxyde de cérium, matériau qui possède luimême des propriétés catalytiques. L'optimisation des paramètres de croissance a montré le rôle majeur de la température de dépôt mais aussi du flux des précurseurs sur la morphologie finale des films. Un dopage contrôlé en platine de la surface de l'oxyde de cérium a ainsi pu être mis au point à partir du dépôt simultané de cérine et de platine. Le flux de précurseur du platine a alors permis d'ajuster la charge et l'état d'oxydation de cet élément au sein des films sans pour autant modifier leur porosité. Il est, par exemple, possible d'élaborer des films minces d'oxyde de cérium composés de particules nanométriques dopées en extrême surface avec 5 % de platine à l'état +II. L'effet du flux de précurseur sur l'état d'oxydation du platine a été confirmé pour le système Pt/TiO<sub>2</sub>.

Dans un second temps, des oxycarbures de tungstène ont été synthétisés de façon à éliminer totalement le platine du catalyseur. Un procédé en deux étapes a été mis au point permettant d'obtenir des dépôts d'oxycarbure de tungstène possédant de grandes surfaces spécifiques en déposant un film utra-mince et conforme d'oxycarbure sur une couche poreuse d'oxyde de tungstène.

Mots-clés : DLI-CVD, XPS, piles à combustible, catalyseur, PEMFC, films poreux

### Abstract

This work is focused on development of growth protocols by direct liquid injection chemical vapor deposition (DLI-CVD) of catalytic porous films which could be used in proton exchange membrane fuel cells (PEMFC). The aim of this work was to reduce or even proscribe platinum in catalysts having large specific surface area i.e. being very porous. Besides, the aim is also to use mainly low cost precursors.

Cerium oxide, which is a material widely used as catalyst, has been chosen to partially substitute platinum. Porous  $CeO_2$  layers were obtained by the optimization of processing parameters such as deposition temperature or precursors flow rates. Controlled platinum doping of cerium oxide surface has been obtained from deposition of ceria and platinum at the same time. The platinum precursor flow rate has allowed adjusting the load and the oxidation state of Pt in films without changing their porosity. For example, it was possible to synthesize thin cerium oxide films composed of surface Pt doped nanoparticles. In such a case, the Pt content is 5% in top most layers and its oxidation state is +II. The effect of precursor flow rate on the platinum oxidation state was confirmed from the study of the Pt / TiO<sub>2</sub> system.

Finally, platinum has been fully replaced by tungsten oxycarbide. A two steps process has been developed to obtain porous oxycarbide layers by depositing a conformed tungsten oxycarbide ultrathin film on a porous tungsten oxide layer.

Keywords : DLI-CVD, XPS, Fuel Cell, PEMFC, catalyst, porous layer

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### Introduction

Depuis plusieurs années, le lithium est utilisé comme élément principal dans la conception d'unités de stockage de l'énergie électrique. L'explosion des ventes d'appareils mobiles et un marché des véhicules électriques grandissant ont obligé, en 10 ans, à doubler l'utilisation du lithium. Cette surconsommation entraîne un problème écologique dans les zones où il est extrait ainsi qu'une augmentation des prix.

Afin de répondre aux demandes croissantes de sources d'énergie à haute densité de puissance, plusieurs alternatives sont développées. L'une d'elles consiste à remplacer les batteries au lithium par des piles à combustible (PAC). Il existe différents types de piles à combustible qui se différencient en fonction de leurs caractéristiques (cf. chapitre 1). L'utilisation de PAC dans les appareils mobiles nécessite un fonctionnement à basse température. C'est pour cela que le choix se porte actuellement, essentiellement, sur les piles à combustibles à membranes à échanges de protons (PEMFC). Pour obtenir la même densité d'énergie que les piles au lithium actuelles, il est nécessaire de développer de nouveaux matériaux permettant une miniaturisation des technologies tout en améliorant la densité de puissance des dispositifs.

Pour améliorer la puissance des piles à combustible, un catalyseur est utilisé afin d'accélérer les cinétiques de réactions au sein de la pile. Ces réactions sont de deux types : l'oxydation d'un combustible réducteur tel que le dihydrogène ou le méthanol à l'anode et la réduction d'un oxydant tel que le dioxygène de l'air à la cathode. Couplées, ces réactions produisent de l'électricité, de l'eau et de la chaleur. Le rôle du catalyseur est donc d'accélérer ces deux réactions afin d'augmenter la production d'électricité. Le platine est le matériau le plus répandu en catalyse mais il est reste très onéreux et, tout comme le lithium, se raréfie. Un défi consiste à remplacer en partie ou en totalité la charge en platine des catalyseurs par un autre matériau sans pour autant diminuer leurs propriétés catalytiques. Par ailleurs, afin d'optimiser l'activité des matériaux retenus, il est nécessaire d'obtenir des dépôts très poreux de façon à augmenter la surface spécifique offerte à la réaction catalytique.

Cette thèse de doctorat s'intègre dans un projet européen, chipCAT, qui a pour objectif de développer des micro-piles à combustibles sur puces. Le présent travail s'intègre dans ce vaste projet en se concentrant sur le développement de protocoles d'élaboration de catalyseur innovants s'intégrant dans de tels dispositifs et permettant de limiter l'utilisation du platine voire de s'en affranchir.

Ce travail se subdivise en plusieurs étapes. Aussi, dans un premier temps, s'est-il agi d'élaborer un matériau avec une charge en platine contrôlée permettant d'obtenir un rapport masse de platine accessible et actif sur masse de platine total le plus proche de un. Pour cela, l'oxyde de cérium a été retenu comme matériau support puisqu'il est déjà largement utilisé comme catalyseur depuis plusieurs années. L'avantage de ce matériau est sa grande capacité à stocker l'oxygène du fait de la coexistence possible de deux états d'oxydation qui permet un échange rapide de l'oxygène. En outre, il a été montré que l'utilisation combinée de l'oxyde de cérium et d'un métal noble améliore les propriétés catalytiques.

Dans une seconde étape, une alternative au platine a été proposée permettant de limiter les coûts de production et d'éviter une trop forte consommation de métaux nobles. L'oxycarbure de tungstène a alors été retenu pour ces propriétés catalytiques proches du platine. Celles-ci

sont liées aux lacunes de carbone dans le réseau de WC. L'ajout d'oxygène permet aux sites vacants d'être occupés par des atomes d'oxygène modifiant les interactions de surface entre le catalyseur et l'électrolyte ce qui a pour effet de créer des liaisons W-O.

Ce mémoire est divisé en six chapitres. Le premier présente l'état de l'art des piles à combustible et des matériaux utilisés pour la catalyse. La technique d'élaboration des films par dépôt chimique en phase vapeur avec injection directe de liquide (DLI-CVD) ainsi que les techniques de caractérisation utilisées lors de cette étude sont présentées dans le chapitre 2. Le troisième chapitre se concentre sur la synthèse et la caractérisation de films minces d'oxyde de cérium non dopé, dans le but de trouver les paramètres optimaux permettant d'obtenir des couches couvrantes, homogènes et poreuses. Les dépôts ont été réalisés sur des substrats en silicium et en carbone dans le but d'obtenir la surface spécifique la plus importante. Le quatrième chapitre est consacré à l'étude de la croissance et de la caractérisation de couches minces d'oxyde de cérium dopé avec une charge en platine limitée et contrôlée. La cinquième partie étudie le comportement du platine lorsqu'il est utilisé comme dopant dans un autre oxyde, le dioxyde de titane. Enfin, le dernier chapitre propose une alternative au platine au travers de la synthèse d'oxycarbure de tungstène de grande porosité.

### 1 Etat de l'art

### **1.1 Bref historique de la pile à combustible**

L'histoire de la pile à combustible (PAC) commence en 1839 quand Sir William Robert Grove découvre son principe, mais c'est en 1845 qu'il présente la première pile à combustible oxygène/hydrogène à partir d'électrodes en platine poreux, l'acide sulfurique jouant le rôle de l'électrolyte<sup>1</sup>. Ses travaux s'inspirent de ceux de Christian Friedrich Schönbein qui, en 1838, lors d'une expérience sur l'électrolyse de l'eau, observe que lorsque l'alimentation électrique est coupée, il apparaît un courant dans le sens inverse de celui imposé lors de l'électrolyse<sup>2</sup>.

Le 19<sup>ème</sup> siècle étant celui de l'invention de la pile Volta et du moteur à explosion, la découverte de la pile à combustible reste pendant un siècle au stade de l'anecdote malgré quelques améliorations au début du 20<sup>ème</sup> siècle. C'est dans les années 1930, que l'anglais Francis Thomas Bacon réussit à améliorer cette technologie en remplaçant l'acide sulfurique par un électrolyte alcalin et en utilisant des électrodes poreuses à base de nickel et d'oxyde de nickel<sup>3</sup>. En 1959, il réalise un prototype de pile à combustible alcaline (AFC, alcaline fuel cell) de 5 kW et démontre l'intérêt de cette source d'énergie<sup>4</sup>. Peu après, Harry Karl Ihrig fit fonctionner un tracteur avec une PAC de 15 kW s'inspirant du modèle de Bacon<sup>5</sup>. S'en suivit la fabrication de multiples véhicules alimentées par des PAC mais des coûts de production importants et l'utilisation massive du pétrole ne permirent pas un développement à grande échelle.

A partir des années 1960, la NASA trouva un grand intérêt à la pile à combustible qui constitue un générateur électrique mais qui peut aussi remplir d'autres fonctions vitales puisque l'oxygène embarquée peut être parallèlement utilisé pour la génération de l'air au sein

<sup>&</sup>lt;sup>1</sup> G. Hoogers, Fuel Cell Technology Handbook, CRC Press (2002) 2-3.

<sup>&</sup>lt;sup>2</sup> U. Bossel, The Birth of the Fuel Cell, 1835-1845, European Fuel Cells Forum (2000).

<sup>&</sup>lt;sup>3</sup> F. T. Bacon, Beama Journal, 6 (1954) 61.

<sup>&</sup>lt;sup>4</sup> F. T. Bacon, Electrochimica Acta, 14 (1969) 569-585.

<sup>&</sup>lt;sup>5</sup> M. Boudellal, La pile à combustible, l'hydrogène et ses applications, DUNOD (2012) 17.

de l'habitacle tandis que la chaleur dégagée peut servir à chauffer le module. Enfin, le produit de réaction étant de l'eau, cette dernière peut être utilisée par les astronautes. C'est lors de la mission Gemini (1963) que la première pile à combustible à membrane échangeuse de protons (PEMFC, proton exchange membrane fuel cell) fût utilisée à partir d'un modèle développé par Willard Thomas Grubb et Leonard Niedrach de General Electric<sup>6</sup>.

Avec le choc pétrolier des années 1970, les recherches autour de la PAC s'accélérèrent en Europe, au Japon et aux Etats-Unis pour limiter l'utilisation du pétrole. Des véhicules électriques à pile à combustible sont alors produits du fait de l'amélioration de la puissance des PAC et du développement des systèmes de stockage de l'hydrogène. Mais les coûts de production toujours trop élevés, une durée de vie trop courte et une autonomie trop faible firent perdre l'intérêt des constructeurs pour cette technologie.

Toutefois, le début des années 1990 est marqué par une prise de conscience générale sur la quantité limitée des ressources naturelles et par le souhait de moins polluer. Les gouvernements développent les transports en commun non polluant et plusieurs villes s'équipent de bus « zéro émission ». Etant encore trop chère, la technologie n'intéresse pas le grand public.

Néanmoins, depuis le début du 21<sup>ème</sup> siècle, la prise de conscience sur l'état du climat s'accentue et préoccupe les gouvernements mais aussi les entreprises et les consommateurs. L'attention se tourne à nouveau vers la pile à combustible qui peut être une alternative efficace et non polluante. Les gouvernements et des fonds privés investissent de façon accrue dans la recherche et les premiers modèles domestiques ainsi que pour le transport sont commercialisés. Au milieu des années 2000 débute le projet HyFleet/CUTE (2006-2009) financé en partie par le sixième programme-cadre européen (FP6) et commun à l'Europe, la Chine et l'Australie. Ce projet permet de financer 47 bus dans 10 villes sur 3 continents<sup>7</sup>. Les

<sup>&</sup>lt;sup>6</sup> M. Warshay, P. R. Prokopius, NASA Technical Memorandum 102366 (1989) 2.

<sup>&</sup>lt;sup>7</sup> http://www.global-hydrogen-bus-platform.com

premiers modèles à usage domestique pour l'habitation sont commercialisés dès 2009 par Panasonic sous le nom Ene-Farm<sup>8</sup>. Par ailleurs, de grandes marques automobiles telles que Honda et Toyota commercialisent des modèles fonctionnant au dihydrogène et dioxygène de l'air.

### **1.2** Les principales technologies de piles à combustibles

Parmi les différentes technologies de piles à combustible, l'AFC, déjà citée, fonctionne au dihydrogène et au dioxygène avec échange d'ions hydroxydes (OH<sup>-</sup>). Cette PAC a été développée au début des années 1930 par F. T. Bacon<sup>3</sup>. Ce dernier observa qu'en utilisant de l'hydroxyde de potassium (KOH) comme électrolyte à la place de l'acide sulfurique et des électrodes en nickel et en oxyde de nickel dans la PAC inventée par Sir W. R. Grove cela améliorait la puissance et limitait la corrosion des électrodes. De plus, il pressurisa les gaz afin de limiter la présence de KOH dans les pores des électrodes. Actuellement ce type de PAC fonctionne à une température comprise entre 50 °C et 200 °C avec une puissance produite comprise entre 10 kW et 150 kW<sup>9</sup>. Elle est principalement utilisée dans le domaine spatial et le transport.

La pile à combustible à carbonate fondu (MCFC) a commencé à être développée au milieu du 20<sup>ème</sup> siècle. Elle fonctionne au dihydrogène, au méthane ou au gaz de synthèse à l'anode et au dioxygène à la cathode. Son principe repose sur l'échange d'ions carbonates. La température de fonctionnement est d'environ 650 °C et sa puissance peut atteindre plusieurs centaines de kW<sup>10</sup>. Elle est principalement utilisée dans les générateurs électriques stationnaires.

La pile à combustible à acide phosphorique (PAFC) fonctionne au dihydrogène et au dioxygène de l'air avec de l'acide phosphorique liquide pour électrolyte. Les électrodes sont

<sup>&</sup>lt;sup>8</sup> http://panasonic.co.jp/ap/FC/en\_history\_01.html

<sup>&</sup>lt;sup>9</sup> L. Carrette, K. A Friedrich and U. Stimming, Fuel Cells 1 (2001) 5 - 39.

 $<sup>^{10}</sup>$  A. Dicks, A. Siddle, Journal of Power Sources 86 (2000) 316 – 323.

principalement composées d'une couche de carbone sur laquelle des particules de platine ont été dispersées. D'une puissance pouvant atteindre 10 MW, elle fonctionne à environ 200 °C et est utilisée dans les transports et les générateurs électriques stationnaires.

La pile à combustible à méthanol (éthanol) direct (DMFC/DEFC) fonctionne avec un alcool sans étape de reformage et du dioxygène. L'électrolyte est une membrane polymère perméable aux protons. La température de fonctionnement est comprise entre 50 °C et 100 °C. Du fait de sa faible puissance (de quelques mW jusqu'à 5 kW<sup>9</sup>), cette PAC est principalement utilisée dans les appareils électroniques portables.

La pile à combustible à oxyde solide (SOFC) dérive de la MCFC puisque leurs combustibles sont communs. La pile SOFC se différencie par l'électrolyte : une céramique perméable aux ions O<sup>2-</sup>. La température de fonctionnement est comprise entre 450 °C et 1000 °C et la puissance développée peut atteindre 250 kW<sup>9</sup>. La SOFC est utilisée principalement comme générateur électrique stationnaire.

La pile à combustible à membrane échangeuse de protons (PEMFC) fonctionne au dihydrogène et au dioxygène avec échange de protons à travers une membrane. La température de fonctionnement est comprise entre 60 °C et 200 °C avec une puissance pouvant atteindre 500 kW<sup>9</sup>. Son succès est lié à la mise au point par l'entreprise DuPont, au début des années 1970, d'une membrane polymère conductrice des protons, le Nafion®. Cette membrane est utilisée dans la plupart des PEMFC et a permis le développement de cette technologie. Le rôle de l'électrolyte/membrane est triple. Il permet l'échange des protons, il est imperméable aux électrons et empêche les gaz de diffuser au sein de la PAC. Les PEMFC équipent actuellement la majorité des véhicules électriques fonctionnant avec une PAC. La faible température de fonctionnement autorise aussi une utilisation dans le domaine des appareils électroniques portables.

### 1.3 Les principales caractéristiques des piles PEMFC

### 1.3.1 Principe d'une PEMCF

Le principe général d'une PAC repose sur la transformation d'une énergie chimique en une énergie électrique. Le fonctionnement d'une PEMFC utilisant du dihydrogène et du dioxygène peut être décrit par les réactions suivantes :

 $2 H_2 \rightarrow 4 H^+ + 4 e^- \text{ (à l'anode)}$   $O_2 + 4 e^- \rightarrow 2 O^{2-} \text{ (à la cathode)}$   $2 H_2 + O_2 \rightarrow 2 H_2O \text{ (réaction globale)}$ 

Plus précisément, l'hydrogène est décomposé à l'anode en électrons et en protons. Les protons diffusent à travers la membrane en polymère jusqu'à la cathode. Le flux d'électrons circule à travers le circuit jusqu'à la cathode où le dioxygène provenant de l'air est réduit en ions oxydes qui réagissent avec les protons pour former des molécules H<sub>2</sub>O (Figure 1.3-1).



Figure 1.3-1 : schéma et réactions d'une PEMFC<sup>9</sup>

La cinétique de réaction est améliorée grâce à l'utilisation de catalyseurs. Les catalyseurs permettent d'accélérer les réactions au sein de la PAC sans pour autant être consommés. Ils

sont utilisés en très faible quantité et sont principalement à base de métaux du groupe platine (PGM, platinum group metals).

### 1.3.2 Les catalyseurs de PEMCF

#### 1.3.2.1 Les catalyseurs à base de platine

Le platine est le matériau le plus répandu en catalyse mais il reste un matériau très onéreux. Il est utilisé dans de nombreuses réactions. Dès le début du 19<sup>ème</sup> siècle, il est utilisé comme électrode pour l'électrolyse de l'eau. De nos jours, il est principalement utilisé en tant que convertisseur catalytique dans les échappements en catalysant les réactions redox qui permettent de diminuer les rejets de monoxyde de carbone et d'hydrocarbures en les oxydants en dioxyde de carbone et en eau alors que les rejets d'oxydes d'azote sont réduits en diazote. Dans l'industrie pétrolière, il est utilisé pour le reformage catalytique afin d'augmenter l'indice octane des carburants.

Dans les PAC, il est utilisé en tant que catalyseur à l'anode pour décomposer le dihydrogène en espèces atomiques et à la cathode pour aider à réduire le dioxygène. Une utilisation des PEMFC à grande échelle impliquerait donc une forte consommation d'un matériau dont les ressources s'épuisent et qui a un coût élevé. Une des solutions à ce problème est de réduire la charge en platine au sein des matériaux catalytiques. Pour cela il est important de contrôler parfaitement la dispersion du platine dans sa matrice et qu'il soit le plus accessible possible afin d'améliorer son efficacité. C'est pour cela que plusieurs méthodes ont été développées afin d'améliorer la dispersion mais aussi les propriétés catalytiques du platine. Dans la majorité des cas, le platine métallique se trouve sous forme de particules dispersées sur une membrane de carbone. Ces particules peuvent être obtenues par différentes techniques telles que : l'électrodéposition, l'imprégnation, le procédé sol-gel ou les techniques de dépôts sous vide.

### 1.3.2.2 Les catalyseurs avec une charge en platine réduite

Une solution apparemment simple pour diminuer la charge en platine consiste à substituer une partie de ce métal par un autre matériau en cherchant à ne pas diminuer l'efficacité du catalyseur. Des chercheurs ont montré que le platine pouvait être remplacé partiellement par un autre métal tel que le cobalt ou le ruthénium afin d'obtenir un alliage métallique qui exalte l'activité du catalyseur. <sup>11,12,13</sup>

Cependant, le prix des métaux utilisés ne permettant pas une utilisation à grande échelle de part un coût trop onéreux, une alternative consiste à diminuer la charge de platine en le remplaçant par un oxyde. Plusieurs études ainsi ont montré que l'activité catalytique des catalyseurs au platine pouvait être améliorée en utilisant par exemple  $TiO_2^{14,15}$ ,  $WO_3^{16,17}$ ,  $ZrO_2^{18,19}$ ,  $SnO_2^{20,21}$  ou  $CeO_2^{22,23}$ .

L'oxyde de cérium est largement utilisé comme catalyseur depuis quelques années<sup>24</sup>. L'avantage de ce matériau est sa grande capacité à stocker l'oxygène du fait de la coexistence possible de deux états d'oxydation ( $Ce^{3+}$  et  $Ce^{4+}$ ) qui permet un échange rapide de l'oxygène<sup>25</sup>. De plus, il a été montré que l'utilisation combinée de l'oxyde de cérium et d'un métal noble tel que le platine augmente l'activité catalytique en améliorant la réductibilité de la surface<sup>22,23,26</sup>. Des études expérimentales et théoriques ont ainsi démontré que les ions Pt<sup>2+</sup> incorporés dans une matrice CeO<sub>2</sub> accélèrent la réaction de dissociation du dihydrogène en protons et augmente la capacité de stockage de l'hydrogène actif pour la réaction au sein du

<sup>24</sup> A. Trovalleri, Catalysis Reviews. 38 (1996) 439–520.

<sup>&</sup>lt;sup>11</sup> E. Lust, E. Härk, J. Nerut, K. Vaarmets, Electrochimica Acta 101 (2013) 130-141.

<sup>&</sup>lt;sup>12</sup> H., A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, Applied Catalysis B: Environmental 56 (2005) 9-35.

<sup>&</sup>lt;sup>13</sup> A. Chen, P. Holt-Hindle, Chemical Reviews. 110 (2010) 3767-3804.

<sup>&</sup>lt;sup>14</sup> S. Sun, G. Zhang, X. Sun, M. Cai, M. Ruthkosky, Journal of Nanotechnology 2012 (2012).

<sup>&</sup>lt;sup>15</sup> J. Parrondoa , T. Hanb , E. Niangarb, C. Wangb , N. Daleb , K. Adjemianb , V. Ramania, PNAS 111 (1) (2014), 45-50.

<sup>&</sup>lt;sup>16</sup> J. Shim, C-R. Lee, H-K Lee, J-S Lee, E. J. Cairns, Journal of Power Sources 102 (2001) 172-177.

<sup>&</sup>lt;sup>17</sup> E. Antolini, E. R. Gonzalez, Applied Catalysis B : Environmental 96 (2010) 245-266.

<sup>&</sup>lt;sup>18</sup> Y. Bai, J. Wu, J. Xi, J. Wang, W. Zhu, L. Chen, Xi. Qiu, Electrochemistry Communications. 7 (2005) 1087-1090.

<sup>&</sup>lt;sup>19</sup> P. O. Graf, D. J. M. de Vlieger, B. L. Mojet, L. Lefferts, Journal of Catalysis 262 (2009) 181-187.

<sup>&</sup>lt;sup>20</sup> E. Higuchi, K. Miyata, T. Takase, H. Inoue, Journal of Power Sources (2011) 1730-1737.

<sup>&</sup>lt;sup>21</sup> Y. Chen, J. Wang, X. Meng, Y. Zhong, R. Li, X. Sun, S. Ye, S. Knights, International Journal of Hydrogen Energy 36 (2011) 11085-11092.

<sup>&</sup>lt;sup>22</sup> H. C. Yao, Y. F. Yu Yao, Journal of Catalysis 86 (1984) 254-265.

<sup>&</sup>lt;sup>23</sup> D. Pierre, W. Deng, M. Flytzani-Stephanopoulos, Topics in Catalysis. 46 (2007) 363–373.

<sup>25</sup> N. V. Skorodumova, S. I. Simak, B. I. Lundqvist, I. A. Abrikosov, B. Johansson, Physical Review Letters 89, 166601 (2002).

<sup>&</sup>lt;sup>26</sup> O. Pozdnyakova, D. Teschner, A. Wootsch, J. Kröhnert, B. Steinhauer, H. Sauer, L.Toth, F.C. Jentoft, A. Knop-Gericke, Z. Paál, R. Schlögl, Journal of Catalysis 237 (2006) 1–16.

catalyseur<sup>27</sup>. Ces propriétés font de l'oxyde de cérium dopé au platine un matériau pouvant être utilisé à l'anode ou à la cathode d'une PEMFC.

Une seconde alternative consiste à diminuer la charge du platine en le substituant partiellement par un carbure. En effet, il a été montré dès 1973, que les carbures de métaux de transitions et plus particulièrement les carbures de tungstène<sup>28</sup> possèdent des propriétés catalytiques équivalentes à celle du platine de par la proximité de leur niveau de Fermi<sup>29</sup>. Pt-WC possède ainsi un effet synergique et augmente donc l'activité catalytique des catalyseurs<sup>30,31</sup>.

Cependant, les principaux inconvénients des catalyseurs composés en partie seulement de platine sont une durée de vie trop courte du fait notamment de l'empoisonnement au monoxyde de carbone<sup>32,33</sup> ceci en dépit d'un coût malgré tout élevé.

### 1.3.2.3 Les catalyseurs ne contenant pas de métaux nobles

Une alternative au platine et, d'une manière plus générale, aux métaux nobles, consiste à utiliser des métaux de transitions liés à des atomes d'azote dans des macrocycles supportés sur carbone (M-N<sub>x</sub>/C) et plus particulièrement des macrocycles de métaux de transition - N<sub>4</sub>. Les premières études datant des années 1960 ont montré l'intérêt du phtalocyanine de cobalt dans la réaction de réduction de l'oxygène<sup>34</sup>. Par ailleurs, il a été mis en évidence que l'activité catalytique de ces matériaux ainsi que leur stabilité sont améliorés lorsqu'ils sont recuits à des températures entre 400 °C et 1000 °C<sup>35</sup>. Plusieurs métaux de transition présentent de bons résultats mais le fer et le cobalt permettent d'obtenir les meilleures activités catalytiques<sup>36</sup>.

<sup>&</sup>lt;sup>27</sup> G. Dutta, U.V. Waghmare, T. Baidya, M.S. Hegde, Chemistry of Materials 19 (2007) 6430-6436.

<sup>&</sup>lt;sup>28</sup> R. B. Levy, M. Boudart, Science 181 (1973) 547-549.

<sup>&</sup>lt;sup>29</sup> R. J. Colton, J. W. Rabalais, Inorganic Chemistry. 15 (1) (1976) 236-238.

<sup>&</sup>lt;sup>30</sup> D. V. Esposito, J. G. Chen, Energy & Environmental Science 4 (2011) 3900-3912.

<sup>&</sup>lt;sup>31</sup> M. B. Zellner, J. G. Chen, Journal of the Electrochemistry Society 152 (8) (2005) A1483-A1494.

<sup>&</sup>lt;sup>32</sup> Q. Li, R. He, J-A. Gao, J. O. Jensen N. J. Bjerrum, Journal of the Electrochemistry Society 150 (12) (2003) A1599-A1605.

<sup>&</sup>lt;sup>33</sup> S. K. Das, A. Reis, K. J. Berry, Journal of Power Sources 193 (2) (2009) 691-698.

<sup>&</sup>lt;sup>34</sup> R. Jasinski, Nature 201 (1964) 1212.

<sup>&</sup>lt;sup>35</sup> R. Franke, D. Ohms and K. Wiesener, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry 260 (1989) 63–73.

<sup>&</sup>lt;sup>36</sup> V. Nallathambi, J. W. Lee, S. P. Kumaraguru, G. Wu, B. N. Popov, ournal of Power Sources 183 (2008) 34–42.

L'oxyde de manganèse  $MnO_2$  est utilisé dans certaines PAC<sup>37</sup>. Lorsqu'il est modifié par du fer, du nickel ou du ruthénium cela a pour effet d'améliorer les propriétés catalytiques<sup>38,39</sup>.

Le carbure de tungstène possède les propriétés idéales pour être utilisé dans les piles à combustibles<sup>17</sup>. Dès le début des années 1960 le carbure de tungstène a été utilisé comme matériaux pour anode dans les PAC<sup>40</sup>. Plus récemment, des études ont montré le fort potentiel de ce matériau lorsqu'il est nanostructuré. Le broyage planétaire d'un mélange stœchiométrique de poudres d'oxyde de tungstène WO<sub>3</sub> et de carbone a permis l'obtention d'un mélange de différentes phases de carbures de tungstène. Ce mélange présente les caractéristiques catalytiques proches d'un catalyseur au platine permettant le remplacement des catalyseurs actuels<sup>41</sup>. Les propriétés catalytiques du carbure de tungstène sont liées aux lacunes de carbone dans le réseau de WC. Les sites vacants sont alors occupés par des atomes d'oxygène<sup>42</sup> modifiant les interactions de surface entre le catalyseur et l'électrolyte ce qui a pour effet de créer des liaisons W-O. Aussi, les oxycarbures sont-ils une alternative intéressante au regard des différents travaux récents réalisés soulignant les propriétés catalytiques d'oxycarbures de titane<sup>43,44</sup>, de molybdène<sup>45,46</sup> ou de tungstène<sup>47,48</sup>.

# 1.4 Les principales voies d'élaboration des matériaux catalytiques des PAC

Il existe de nombreuses techniques pour synthétiser les catalyseurs de PAC. Dans cette partie, seules les principales techniques d'élaboration seront décrites succinctement.

<sup>&</sup>lt;sup>37</sup> D. Zhang, D. Chi, T. Okajima, T. Ohsaka, Electrochimica Acta 52 (2007) 5400–5406.

<sup>&</sup>lt;sup>38</sup> J. S. rebello, P. V. Samant, J. L. Figuierdo, J. B. Fernandes, Journal of Power Sources 153 (1) (2006) 36-40

<sup>&</sup>lt;sup>39</sup> P. V. Samant, J. B. Fernandes, Journal of Power Sources 79 (1) (1999) 114-118.

<sup>&</sup>lt;sup>40</sup> H. Binder, A. Kohling, W. Kuhn, W. Lindner, G. Sandstede, Nature 224 (1969) 1299–1300.

<sup>&</sup>lt;sup>41</sup> X.G. Yang, C.Y. Wang, Applied Physics Letters 86 (2005) 224104–224112.

<sup>&</sup>lt;sup>42</sup> P.N. Ross, P. Stonehart, Journal of Catalysis 48 (1977) 42–59.

<sup>&</sup>lt;sup>43</sup> A. Sinha, D. N. Miller, J. T. S. Irvine, Journal of Materials Chemistry A 4 (2016) 11117

<sup>&</sup>lt;sup>44</sup> K. Huang, YF. Li, YC. Xing, Journal of Mater. Research. 28 (3) (2013) 454-460

<sup>&</sup>lt;sup>45</sup> P. Delporte, F. Meunier, C. Pham-Huu, P. Vennegues, M. J. Ledoux, J. Guille, Catalysis Today 23 (1995) 251-267

<sup>&</sup>lt;sup>46</sup> P. Lui, J. A. Rodriguez, The Journal of Physical Chemistry B 110 (39) (2006) 19418-19425

<sup>&</sup>lt;sup>47</sup> N. Liu, S. A. Rykov, J. G. Chen, Surface Science 487 (2001) 107-117

<sup>&</sup>lt;sup>48</sup> J. A. J. Rodrigues, G. M. Cruz, G. Bugli, M. Boudart ; G. D. Djéga-Maiadassou, Catalysis Letters 45 (1997) 1-3

### 1.4.1 L' « electroless metal deposition »

Une des premières techniques majeures fût développée par Brenner et Riddell, au milieu des années 1940, qu'ils nommèrent « electroless metal deposition »<sup>49,50</sup>. Il s'agit d'un procédé de dépôt autocatalytique de métal en l'absence d'une source externe d'électricité par l'intermédiaire d'un agent réducteur tel que l'hydrazine ou le diméthylamine borane. Cette technique fût d'une grande importance dans les avancées technologiques modernes principalement en électronique, en traitement de surface et dans les batteries.

### 1.4.2 L'électrodéposition :

L'électrodéposition repose sur le principe inverse de la pile voltaïque. C'est un procédé utilisant un courant électrique pour réduire ou oxyder les cations de sels métalliques dissouts dans une solution. Le matériau catalytique est déposé sur un substrat jouant le rôle de cathode. Cette technique est très répandue dans le domaine de la synthèse de catalyseur car elle est peu onéreuse. De plus, le contrôle de l'épaisseur et de la composition du matériau déposé est simple. Cependant, cette technique n'est pas spécifiquement adaptée pour obtenir des couches ou des particules nanométriques.

### 1.4.3 L'imprégnation

L'imprégnation est une technique de dépôt qui est divisée en trois étapes. Dans un premier temps, le support est immergé dans une solution contenant le précurseur métallique. Seul un volume de solution de précurseur égal au volume des pores est utilisé afin de ne pas avoir une perte de précurseur. Il s'en suit une étape de séchage puis une dernière étape de calcinationactivation. Afin d'augmenter la charge en catalyseur, l'opération d'imprégnation peut être répétée.

<sup>&</sup>lt;sup>49</sup> A. Brenner, G.E. Riddell, Journal of Research of the National Bureau of Standards 37 (1946) 31.

<sup>&</sup>lt;sup>50</sup> A. Brenner, G.E. Riddell, Journal of Research of the National Bureau of Standards 39 (1947) 385.

L'imprégnation est utilisée pour sa facilité de mise en œuvre et pour des concentrations faibles en catalyseurs mais il est difficile de contrôler la dispersion des phases catalytiques sur le matériau support.

### 1.4.4 Les procédés sol-gel

Les dépôts sol-gels sont réalisés à partir d'une solution colloïdale au sein de laquelle un gel est obtenu par polymérisation ou polycondensation. Deux cas sont alors à distinguer : soit une réticulation des micelles formant un hydrogel ; soit une agrégation résultant de la neutralisation des charges formant des floculats. Il s'en suit une étape de séparation par décantation, filtration, centrifugation ou lavage. Le gel ou les floculats sont alors séchés pour éliminer le solvant puis sont calcinés.

Cette technique est utilisée en catalyse car elle permet d'obtenir des matériaux très purs parfaitement dispersés avec une granularité contrôlée et homogène. Cependant il n'est pas possible de limiter la surface de dépôt sur le support et parfois le solvant peut ne pas être éliminé en totalité.

### 1.4.5 Les techniques de dépôts sous vide par voie physique

Les dépôts physiques en phase vapeur (PVD) regroupent deux principales méthodes de dépôt. La première, nommée pulvérisation cathodique utilise un gaz plasmagène ainsi qu'une différence de potentiel appliquée entre une cathode (la cible) et une anode (le substrat) permettant d'obtenir un dépôt nanostructuré. La composition de ce dépôt dépendra de la cible et de l'utilisation ou non d'un gaz réactif dans l'enceinte de dépôt. A partir d'un plasma uniquement constitué d'argon, des couches minces métalliques sont obtenues. Il est possible de déposer des films d'oxyde, de nitrure ou de carbure en ajoutant un gaz réactif. Dans ce cas, le gaz est constitué d'un mélange d'argon et d'un gaz réactif qui peut être du dioxygène, du diazote ou du méthane selon que l'on souhaite synthétiser respectivement un oxyde, un nitrure ou un carbure. L'avantage de cette technique est la possibilité de contrôler parfaitement la composition du matériau tout en maîtrisant son épaisseur. De plus, un grand éventail de matériaux en fonction des applications visées peut être obtenu par cette technique. En effet, l'utilisation conjointe de plusieurs cathodes et donc de différentes cibles permet d'obtenir des mélanges binaires, ternaires, voire quaternaires.

La seconde méthode PVD est l'évaporation sous vide qui consiste à chauffer un matériau afin de le sublimer pour qu'il se dépose sur un substrat. Pour cela, il existe plusieurs méthodes. Il est notamment possible de chauffer par effet Joules ou par induction, de bombarder la cible avec un faisceau d'électrons, d'utiliser un faisceau laser ou bien encore un arc électrique. Cette technique est principalement utilisée pour la synthèse de métaux ou alliages. L'utilisation de plusieurs cibles permet d'obtenir des matériaux plus ou moins complexes. Cette technique possède les mêmes avantages et inconvénients que la pulvérisation, bien que l'éventail de matériaux déposables soit réduit en particulier du fait de la difficulté d'obtenir ainsi des oxydes, des nitrures ou des carbures.

### 1.4.6 Les dépôts chimiques en phase vapeur

Les techniques de dépôts sous vide par voie chimique regroupent un grand nombre de méthodes parfois extrêmement diverses qui chacune met en jeu une ou plusieurs réactions chimiques à partir d'un ou plusieurs précurseurs.

Parmi les différentes techniques de dépôts chimiques, la pyrolyse consiste à nébuliser un complexe organométallique qui sera décomposé par la chaleur. Cette technique est utilisée pour sa facilité de mise en œuvre car le matériau ne nécessite pas d'étapes complémentaires pour être utilisé. De plus, une grande gamme de précurseur peut être employée. Cependant, une utilisation à grande échelle est compliquée du fait des faibles rendements obtenus et le risque élevé de problème sanitaire lié à la taille nanométrique des grains.

Plus généralement, le terme « dépôt chimique en phase vapeur (CVD) » regroupe différentes techniques reposant sur un principe équivalent : un précurseur est évaporé ou sublimé par l'intermédiaire d'une source d'énergie thermique, photonique ou via l'utilisation d'un plasma. Deux types de réactions peuvent alors avoir lieu : une réaction homogène en phase gazeuse pour l'obtention d'une poudre ou une réaction dite hétérogène sur une surface chauffée (un substrat) pour l'obtention d'un film. Selon le type de vide, le type de précurseur utilisé et/ou le type d'activation choisi, différents types de CVD peuvent être distingués.

La CVD à pression atmosphérique (APCVD) permet par exemple d'obtenir des dépôts à pression atmosphérique. Un chauffage par induction ou par infra-rouge chauffe le substrat sur lequel vient réagir le précurseur transporté à l'aide d'un gaz vecteur.

La CVD « basse pression » (LPCVD) est une technique similaire en son principe à l'APCVD. Elle se différencie par l'usage d'un système de pompage permettant un meilleur contrôle de la pureté des matériaux et une meilleure homogénéité.

La CVD à ultra-haut-vide (UHVCVD) est une technique qui permet d'obtenir des matériaux très purs à partir du contrôle parfait de l'atmosphère au sein de la chambre de réaction. Le système de pompage doit permettre de dépasser 10<sup>-5</sup> Pa dans la chambre de réaction c'est-àdire d'obtenir des pressions partielles de dioxygène et d'eau très faible.

La CVD à précurseur organométallique (OMCVD pour organo-metallic CVD s'il y a une liaison carbone-métal ou MOCVD pour metalorganic si le métal n'est pas lié à la molécule via des atomes de carbone) se distingue par l'utilisation de précurseurs organométalliques. Ces précurseurs ont une température de décomposition beaucoup plus basse que les précurseurs utilisés pour une CVD conventionnelle.

La CVD assisté par plasma (PECVD) consiste à activer les précurseurs à l'aide d'un plasma. Ceci permet de diminuer les températures de dépôts et ainsi d'utiliser des polymères comme substrat. Cela permet aussi d'obtenir un meilleur taux de conversions des précurseurs. L'Atomic layer deposition (ALD) est une technique de dépôts séquentiels, couche par couche. Ce type de CVD utilise deux espèces chimiques. Un premier réactif est adsorbé sur la surface du substrat sous la forme d'une monocouche, l'excès est alors purgé. Un second réactif est ensuite injecté et réagit avec le premier ce qui produit une monocouche du matériau définitif sur laquelle le premier réactive pourra être à nouveau adsorbé La répétition de ce cycle permet la croissance de couches nanométriques avec un contrôle parfait de l'épaisseur. De plus, les réactions étant exothermiques, la température de dépôt peut être abaissée ce qui permet d'utiliser des polymères comme substrat.

La CVD à injection directe de liquide (DLI-CVD pour direct liquid injection CVD) est une technique innovante qui permet de ne pas être limité par les pressions de vapeur saturante des précurseurs. En effet, le précurseur est dissout ou dilué dans un solvant qui est directement injecté sous forme liquide dans une chambre de vaporisation. L'aérosol formé est alors chauffé et le solvant évaporé. Par l'intermédiaire d'un gaz vecteur, le précurseur est transporté jusqu'à la chambre de réaction. Les avantages de cette technique sont multiples : un grand éventail de précurseurs utilisables, une vitesse de croissance élevée, un contrôle de la porosité, l'obtention de films conformes et un parfait contrôle de l'épaisseur des dépôts.

L'avantage des techniques CVD est la possibilité de pouvoir obtenir des dépôts assez conformes malgré l'utilisation de supports ayant une géométrie complexe. C'est notamment la caractéristique première de l'ALD. En outre, les différents types de CVD sont combinables. Ainsi il est tout à fait possible de travailler avec une MOCVD à pression atmosphérique ou une DLI-CVD assistée par plasma.

### 2 Techniques expérimentales

Dans ce chapitre sont présentées la technique d'élaboration des films minces (DLI-CVD) ainsi que les techniques de caractérisations mises en œuvre (XPS, MEB, MET, DRX).

# 2.1 Dépôt chimique en phase vapeur à injection directe de liquide (DLI-CVD)

L'appareil de dépôt décrit ci-après a permis de réaliser la totalité des films minces étudiés lors de ce travail. Il s'agit du modèle MC050 commercialisé par AnnealSys, entreprise localisée en France, à Montpellier. Ce modèle offre la possibilité de travailler en mode ALD ou en mode CVD selon les caractéristiques du dépôt souhaitées. Par ailleurs, le procédé de chauffage infra-rouge RTP (rapid thermal processing) intégré, permet de chauffer et de refroidir l'échantillon de manière relativement rapide (plusieurs degrés par seconde) comparé à un système de chauffage par induction. En outre, la reproductibilité des dépôts est assurée par un système automatisé permettant d'avoir un débit de solution de précurseur, une température de dépôt et une pression de travail constants tout au long de la phase de dépôt. Enfin, le système d'injection de liquide autorise l'utilisation d'un grand éventail de précurseurs solide ou liquide. Le choix de ces derniers sera détaillé dans les chapitres consacrés aux résultats.

### 2.1.1 Aspects techniques

Le modèle que nous utilisons est équipé de deux sources distinctes pour les solutions de précurseurs reliées chacune à un injecteur permettant la formation d'aérosols dans la chambre de vaporisation. Un troisième injecteur permet d'introduire le réactif oxydant lors de dépôts en mode ALD mais aussi d'injecter des nanoparticules<sup>51</sup>.

<sup>&</sup>lt;sup>51</sup> L. Avril, S. Bourgeois, M.C. Marco de Lucas, B. Domenichini, P. Simon, F. Addou, J. Boudon, V. Potin, L. Imhoff, Vacuum 122 (2015) 314-320

Le substrat et le suscepteur sont chauffés par l'intermédiaire de lampes infrarouge placées autour de la chambre de réaction cylindrique à parois froides. Cette chambre de réaction est constituée d'un tube et d'un contre-tube en quartz transparent à l'infrarouge. Le suscepteur est en graphite recouvert de carbure de silicium. Ce matériau est connu pour ses propriétés réfractaires et sa stabilité chimique : il ne pollue donc pas les films déposés. Un thermocouple permet le contrôle de la température du substrat qui peut être chauffé jusqu'à 1200 °C à la vitesse de 50 °C.s<sup>-1</sup> si le suscepteur est utilisé et jusqu'à 200 °C.s<sup>-1</sup> si un wafer de silicium 2 pouces est utilisé sans le suscepteur.

Le vide est obtenu à l'aide d'une pompe primaire à palettes et peut atteindre 4 Pa. Un capteur de pression et une électrovanne permettent de réguler la pression de travail au sein de la chambre de réaction.



2.1.2 Schéma du procédé en configuration « codéposition »

Figure 2.1-1 : schéma du procédé DLI-CVD

La Figure 2.1-1 présente le schéma de fonctionnement du procédé DLI-CVD.

### 2.1.3 Principe de fonctionnement des injecteurs

L'injection directe de liquide est rendue possible par l'utilisation d'injecteurs spéciaux et d'une chambre de vaporisation (vapbox 1500) (Figure 2.1-2) développés par Kemstream<sup>52</sup>, entreprise localisée à Montpellier.



Figure 2.1-2 : schéma de la Vapbox 1500 et de l'injecteur développés par Kemstream

Le liquide est préalablement mélangé à un gaz vecteur puis le mélange passe dans les injecteurs qui permettent d'obtenir un aérosol composé de microgouttelettes rendant possible le dépôt. Une électrovanne permet de contrôler le débit de solution injectée et il est possible de modifier la fréquence et le temps d'ouverture de la vanne pour contrôler et optimiser la morphologie et la structure du dépôt. Le débit de gaz injecté est compris entre 150 SCCM (Standard Cubic Centimeter per Minute) et 2000 SCCM. Le débit massique de liquide est quant à lui compris entre 0.1 g.min<sup>-1</sup> et 2 g.min<sup>-1</sup>.

<sup>&</sup>lt;sup>52</sup> M. Vervaele, B. De Roo, O. Deschaume, Ma. Rajala, H. Guillon, M. Sousa, C. Bartic, C. Van Haesendonck, J. W. Seo, J-P. Locquet, Review Of Scientific Instruments 87 (2016), 025101

### 2.2 Spectroscopie de photoélectrons X (XPS)

### 2.2.1 Principe de l'XPS

La spectroscopie de photoélectrons initiés par une source de rayon X est une technique basée sur l'effet photoélectrique. L'interaction entre un rayonnement et un matériau provoque l'ionisation des atomes. Une partie de l'énergie transférée permet de rompre la liaison entre un électron et son atome, le reste lui étant cédé sous forme d'énergie cinétique.

Le rayonnement étant monochromatique, l'effet photoélectrique s'exprime selon la formule suivante :

$$h\nu = E_c + E_l + \Phi$$

où hv est l'énergie des photons,  $E_c$  est l'énergie cinétique de l'électron,  $E_l$  est l'énergie de liaison initiale de l'électron sur une orbitale donnée et  $\Phi$  est le travail de sortie du spectromètre avec une valeur de 4,7 eV pour l'appareillage utilisé. En mesurant l'énergie cinétique des électrons émis, il est donc possible de calculer l'énergie de liaison de l'électron et ainsi de faire une analyse qualitative élémentaire mais aussi chimique du matériau caractérisé. Il est notamment possible, sous certaines conditions, de connaître le degré d'oxydation ou l'environnement chimique de l'élément étudié.

### 2.2.2 Aspects techniques

L'XPS utilisé possède une double source de rayon X qui utilise la raie K $\alpha$  de l'aluminium à 1486,6 eV et la raie K $\alpha$  du magnésium à 1254,6 eV. La majorité des analyses ont été effectuées avec la source en aluminium. La détection des électrons est faite par un analyseur hémisphérique CLAM 4 MCD de chez Thermo VG Scientific de 150 mm de diamètre. Quatre fentes d'entrée de diamètre allant de 0,5 mm à 5 mm permettent d'augmenter ou de diminuer le nombre d'électrons transmis ce qui permet de trouver le meilleur compris entre intensité du signal et résolution. En utilisation normale, la fente sélectionnée a un diamètre de 2 mm.

L'intensité du flux d'électrons à détecter en sortie d'analyseur est amplifiée par neuf channeltrons.

Au sein de l'analyseur hémisphérique, des champs électrostatiques sont modulés dans le but de filtrer les électrons ayant une énergie donnée, appelé énergie de passage (Pass Energy), ils peuvent être choisies entre 2 eV et 200 eV. Les spectres globaux ont été enregistrés avec une énergie de passage de 100 eV et les acquisitions plus précises des niveaux de cœur ont été réalisées avec une énergie de passage de 20 eV.

En outre, un manipulateur rotatif permet de caractériser les échantillons à plusieurs angles d'émission des électrons. Ceci permet de révéler de potentielles différences de compositions entre les couches extrêmes de surface et la partie sub-surfacique du matériau (cf. Figure 2.2-1).



<u>Figure 2.2-1</u>: schéma de principe de la caractérisation XPS d'un échantillon à différents angles d'émission des électrons

Ce mode d'analyse particulier est autorisé par la profondeur d'extraction limitée des électrons qui dépend de leur libre parcours moyen. Ce paramètre correspond à la distance que parcourt un électron entre deux chocs inélastiques et donc sans perte d'énergie. En augmentant l'angle par rapport à la normale, la profondeur analysée diminue ce qui a pour effet d'exalter l'intensité des pics des éléments se trouvant à la surface.

### 2.2.3 Analyse des spectres XPS

Le traitement des spectres a été effectué à l'aide du logiciel CasaXPS<sup>53</sup>. L'analyse d'une couche métallique de platine a permis de mettre en évidence un décalage non-linéaire du spectromètre. En effet, le décalage des pics n'est pas constant en fonction de l'énergie cinétique à laquelle doit se situer le pic. La formule appliquée pour recaler en énergie les spectres est la suivante :

$$E_l = E_{l \text{ mesurée}} + 0.0018 \times E_{l \text{ mesurée}} - 1,3838$$

Cette formule a été appliquée sur le pic principal de chaque spectre enregistré afin de déterminer son énergie de liaison exacte.

Par ailleurs, des phénomènes de charges à la surface des échantillons peuvent, dans certains cas, décaler les spectres. Les spectres ont donc en totalité été recalés mais de manières différentes en fonction de la nature du dépôt. Les dépôts à base d'oxyde de cérium ont été recalés à l'aide de la composante 4f<sup>0</sup> du massif correspondant à Ce3d et située à 916,9 eV<sup>54</sup>. Cette composante est caractéristique de la présence de Ce<sup>4+</sup> et sa position est fixe. Dans les autres cas, les pics étaient recalés à l'aide de la position du carbone C1s ou de l'oxygène O1s pour les phases oxydes, voire à partir du signal Si2p du silicium si l'épaisseur du dépôt le permettait. Il est à noter que la calibration à partir du carbone C1s n'est pas la manière la plus optimale du fait de la nature organométallique des précurseurs qui peut laisser en surface des atomes de carbone de diverses natures.

<sup>53</sup> http://www.casaxps.com

<sup>&</sup>lt;sup>54</sup> E. Bêche, P. Charvin, D. Perarnau, S. Abanades, G. Flamant, Surface and Interface Analysis 40 (2008) 264–267.

### 2.3 Microscopie électronique à balayage (MEB)

Le principe du MEB repose sur l'interaction d'un faisceau d'électrons balayant l'échantillon étudié. Lorsque que les électrons pénètrent dans le matériau il peut se produire deux types d'interactions différentes, élastiques ou inélastiques, ce qui entraîne respectivement l'émission d'électrons rétrodiffusés et secondaires. Les électrons rétrodiffusés permettent d'obtenir une information élémentaire quant aux électrons secondaires, ils permettent d'obtenir une information sur la morphologie de l'échantillon.

Le MEB utilisé lors de ce travail est un JEOL 7600F équipé d'un canon à électron de type Schottky à émission de champ travaillant généralement à une tension d'accélération de 15 kV. Ce microscope a permis d'estimer l'épaisseur des films ainsi que leur porosité à partir des clichés obtenus sur des coupes transverses des dépôts. L'étude de la surface des matériaux a permis d'apprécier la taille des grains et particules.

### 2.4 Microscopie électronique en transmission (MET)

### 2.4.1 Principe du MET

Le principe du MET repose sur l'interaction d'un faisceau d'électrons à très haute énergie (quelques centaines de kV) avec le matériau analysé.

Contrairement au MEB, les électrons doivent traverser l'échantillon ce qui implique de longues étapes de préparation des échantillons, l'épaisseur de l'échantillon devant être d'une dizaine de nanomètres. Pour cela, le wafer de silicium de 500 µm est d'abord poli mécaniquement puis subit un bombardement ionique afin d'obtenir la transparence aux électrons. Ces différentes étapes peuvent polluer l'échantillon, voire modifier sa morphologie. Les électrons qui traversent l'échantillon peuvent servir à former une image en champ clair (électrons transmis) ou une image en champ sombre (électrons diffractés). Les contrastes
observés sur les images dépendent de l'épaisseur de l'échantillon, de son numéro atomique et de son orientation par rapport au faisceau incident (contraste de diffraction). Les interférences entre le faisceau transmis et les faisceaux diffractés permet d'obtenir des images MET en haute résolution (HRTEM) et donc d'avoir une image du réseau cristallin de l'échantillon. Le travail en mode diffraction permet aussi de vérifier la nature cristallographique de certains dépôts.

Au cours de cette étude, deux dispositifs ont été utilisé, un JEOL JEM-2100 LaB<sub>6</sub> et un JEOL JEM-2100 FEG tous deux travaillant à une tension d'accélération de 200 kV.

# 2.4.2 Technique sans préparation d'analyse chimique et microstructurale des matériaux

Une technique de dépôt sur grille (EMS CF300-Cu) initialement prévue pour l'analyse de poudre a permis de connaître rapidement la composition ainsi que la morphologie des couches minces en s'affranchissant de toute étape de préparation.



Figure 2.4-1 : morphologie des grilles MET

La morphologie initiale de la grille est présentée sur la Figure 2.4-1. Elle est composée d'une grille en cuivre avec un diamètre adéquat pour le dispositif de microscopie. La grille est recouverte d'un film de carbone dit « holey ». Ce film présente une morphologie idéale pour la caractérisation des dépôts, il s'agit d'un film mince transparent aux électrons avec la résistance mécanique nécessaire pour résister aux flux de gaz et aux températures de dépôts.

Cette technique permet de s'affranchir des modifications de morphologie que peuvent entraîner les différentes étapes de préparation habituellement utilisées pour l'observation de couches minces déposées sur des substrats de silicium.

La Figure 2.4-2 présente deux exemples de dépôts élaborés sur grille. La Figure 2.4-2 (a) montre un dépôt d'oxyde de cérium et la Figure 2.4-2 (b) montre un dépôt d'oxyde de tungstène.



Figure 2.4-2 : dépôts élaborés sur grille (a) oxyde de cérium et (b) oxyde de tungstène

## 2.5 Diffraction des rayons X

Le principe de la DRX repose sur l'interaction entre un faisceau de rayon X et la matière cristallisée. Un phénomène de diffraction est observé en fonction de la direction des familles de plans réticulaires (h, k, l).

Les pics de diffraction respectent la condition de Bragg selon l'équation suivante :

$$n \cdot \lambda = 2d_{hkl} \sin \theta$$

où n est l'ordre de diffraction,  $\lambda$  est la longueur d'onde des rayons X, d est la distance interréticulaire d'une famille de plan et  $\theta$  est le demi-angle de déviation. Cette technique permet donc l'identification des phases cristallines.

Compte tenu de la faible épaisseur des échantillons, les analyses DRX ont été réalisées en incidence rasante avec un angle de l'ordre du degré. En effet, la profondeur de pénétration des rayons X étant de l'ordre du micromètre, le pic du substrat (silicium) aurait masqué certains pics en configuration thêta-deux thêta.

La DRX utilisée lors de ce travail est composée d'un diffractomètre Inel CPS 120T équipé d'un monochromateur Ge (111) et d'une source à rayon X au cuivre travaillant à 40 kV et 40 mA.

## 3 Films minces d'oxyde de cérium

Depuis quelques années, les films d'oxyde à base de cérium sont étudiés pour leur capacité à stocker l'oxygène, ce qui les rend très efficaces pour les réactions de réduction de l'oxygène. C'est pour cette raison que l'oxyde de cérium a été retenu pour la conception de nouveaux matériaux pour PEMFC. Il a par ailleurs été montré que le dopage des films d'oxyde de CeO<sub>2</sub> par le platine améliore considérablement les propriétés catalytiques de ce dernier. Afin de répondre au cahier des charges, il était nécessaire d'obtenir un film poreux, conforme et avec une charge en platine et une épaisseur parfaitement contrôlées. Cela a été rendu possible par l'utilisation de la DLI-CVD.

Les différentes études menées sur les dépôts d'oxyde de cérium non dopé dans le but de comprendre les mécanismes de croissance de ces films et ainsi permettre de trouver les paramètres optimaux pour la conception de couches minces dopées sont présentées dans ce chapitre.

Dans une première partie, les précurseurs retenus pour l'élaboration des couches sont présentés. Une seconde partie se focalise sur l'étude de la croissance d'oxyde de cérium permettant de trouver les paramètres optimaux et nécessaires à l'obtention de films poreux.

## 3.1 Choix du précurseur

Un des intérêts de la DLI-CVD repose sur un grand choix de précurseurs solides ou liquides. De plus, l'efficacité de la majorité des procédés CVD est fonction de la pression de vapeur saturante du précurseur, contrairement à la DLI-CVD qui permet d'injecter directement une solution de précurseur dilué dans un solvant. Le volume de précurseur pur injecté pour une même épaisseur de dépôt est donc beaucoup plus faible ce qui permet de diminuer les coûts. Il existe de nombreuses études présentant différents précurseurs utilisés pour la croissance de couches d'oxyde de cérium (Tableau 3.1-1). Le Ce(mmp)<sub>4</sub>, tetrakis(1-methoxy-2-methyl-2propanolate) de cérium (IV)<sup>55,56</sup> (Figure 3.1-1) a été retenu comme précurseur pour cette étude. Il présente l'avantage de pouvoir être utilisé en ALD ou en CVD contrairement au Ce(iPrCp)<sub>3</sub> qui n'est utilisé qu'en ALD. Un des critères de sélection a été aussi sa disponibilité auprès des fournisseurs contrairement au Ce(Mp)<sub>4</sub> et au Ce(fod)<sub>4</sub> qui sont des précurseurs synthétisés en laboratoire et non commercialisés. En outre, lors de cette étude, le Ce(thd)<sub>4</sub> a également été retenu mais les premières expérimentations ont montré que son affinité chimique avec le solvant utilisé n'était pas assez grande. Cela a entraîné une évaporation prématurée du solvant provoquant la formation de particules qui ont obturées l'injecteur liquide de la DLI-CVD. Enfin, le Ce(mmp)<sub>4</sub> a été choisi car c'est un des précurseurs les moins onéreux.

Précurseur	Procédé	gaz réactif	température de dépôt	prix
Ce(mmp) <sub>4</sub>	ALD	$H_2O$	150 - 350°C	210/-
	CVD	O <sub>2</sub>	350-600°C	31€/g
Ce(thd) <sub>4</sub> <sup>57</sup>	ALD	O <sub>3</sub>	200 - 275 °C	520/-
	CVD	Ar-O <sub>2</sub>	400 - 900 °C	53€/g
Ce(iPrCp) <sub>3</sub> <sup>58</sup>	ALD	H <sub>2</sub> O	175 - 250°C	118€/g
Ce(Mp) <sub>4</sub> <sup>59</sup>	CVD	O <sub>2</sub>	300 - 350°C	non commercialisé
$Ce(fod)_4^{60}$	CVD	O <sub>2</sub>	225 - 400 °C	non commercialisé

Tableau 3.1-1 : précurseurs à base de cérium pour la synthèse par voie chimique

<sup>55</sup> P.J. King, M. Werner, P.R. Chalker, A.C. Jones, H.C. Aspinall, J. Basca, J.S. Wrench, K. Black, H.O. Davies, P.N. Heys, Thin Solid Films 519 (2011) 4192 – 4195. <sup>56</sup> J. S. Wrench, K. Black, H. C. Aspinall, A. C. Jones, J. Bacsa, P. R. Chalker, P. J. King, M. Werner, H. O. Davies, and P. N. Heys,

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<sup>58</sup> W. H. Kim, M. K. Kim, W. J. Maeng, J. Gatineau, V. pallem, C. Dussarrat, A. Noori, D. Thompson, S. Chu, H. Kim, Journal of Electrochemical Society 158 (2011) G169 - G172.

<sup>59</sup> H. Ohno, K. Sakurai, K. Tagui, T. Morita, S. Suzuki, K. Ishibashi, and Y. Yamamoto, Electrochemical and Solid-State Letters 9 (2006) G87 - G89

<sup>&</sup>lt;sup>60</sup> J. McAleese, J. C. Plakatouras, B. C. H. Steele, Thin Solid Films 280 (1996) 152 - 159.



Figure 3.1-1 : molécule de Ce(mmp)<sub>4</sub>

## 3.2 Croissance de films poreux sur substrat de silicium

Cette étude porte sur la croissance de films minces poreux d'oxyde de cérium obtenus par DLI-CVD sur des substrats de silicium. Les résultats ont été publiés dans Surface & Coatings Technology en 2015.

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## MOCVD growth of porous cerium oxide thin films on silicon substrate



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## ABSTRACT

Porous cerium oxide thin films were grown by pulsed direct liquid injection metal organic chemical vapor deposition (DLI-MOCVD) on silicon substrate, using cerium tetrakis (1-methoxy-2-methyl-2-propanolate) dissolved in cyclohexane as precursor as well as oxygen as oxidant agent. The chemical and morphological characteristics of the films were investigated by XPS, SEM and TEM. The influence of the growth conditions on the morphological features of the thin films and the cerium chemical states are reported and discussed. The decrease of the oxygen and/or alkoxide flow rate induces the decrease of both the film thickness and the porosity of the layer. Moreover, the growth of silicate at the interface between the silicon substrate and the grown film is evidenced.

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## 1. Introduction

Chemical vapor deposition (CVD) method has been used since many years in the synthesis of dense and continuous thin films with applications in several fields. This technique allows the production of deposits with a good conformal coverage, good thickness uniformity and on a large scale. In addition it has been developed to produce catalytically active materials in the form of nanoparticles [1], nanotubes [2] or porous films [3]. As this method prevents most of the problems linked to solvents which are always present in classical liquid-phase impregnation processes and produces deposits in a well-controlled way [4,5], there is an increasing interest for its use in the preparation of supported catalysts.

It is known that cerium dioxide (CeO<sub>2</sub>) is an interesting material in many catalytic reactions, like NO reduction under oxidizing conditions or CO oxidation under reducing conditions in automotive exhaust catalysts [6–8]. In all the applications involving cerium oxide, the ability of cerium to cycle between Ce<sup>+3</sup> and Ce<sup>+4</sup> is crucial. Controlling the properties of ceria is thus important. These properties are strongly affected by the preparation method and it is thus fundamental to prepare cerium oxide films in a well controlled way. In addition, for many applications involving supported catalysts, it is necessary to obtain materials with a high specific surface area. There is thus a high interest in preparing porous thin films [9–11].

In this work, direct liquid injection (DLI) metal organic CVD (MOCVD) was used for  $CeO_2$  thin film deposition. Although the most used precursors for this kind of deposition are beta-diketonate ones [12,13], cerium tetrakis (1-methoxy-2-methyl-2-propanolate),

 $[Ce(mmp)_4]$  was used here. Indeed, Ce(IV) alkoxides are less used than beta-diketonate precursors [14] because, due to their lower stability, they are difficult to implement without the use of DLI MOCVD. However this low stability allows lower deposition temperature and can induce a different, potentially interesting, reactivity. Indeed it was shown that using Ce(IV) alkoxides volatile precursors lead to high purity  $CeO_2$  thin films with low carbon contamination using either MOCVD or atomic layer deposition (ALD) techniques [15,16].

Cerium oxide layers were grown on silicon substrates, especially because silicon was widely used to grow  $CeO_2$  epitaxial thin films using different deposition techniques [17]. Some experiments were also performed using a carbon foil instead of silicon substrates in order to get some insight on the influence of the nature of the substrate. The influence of main deposition parameters on the morphology and the chemical properties of the deposited cerium oxide films were here studied.

## 2. Experimental procedure

DLI-MOCVD experiments were carried out on an Annealsys MC-050 system equipped with a cold wall reactor, a direct liquid injection system and infrared lamps for rapid thermal heating [18]. Thin cerium oxide films were elaborated at a substrate temperature of 400 °C under a reactor pressure of 10 mbar using a 0.01 M solution of  $[Ce(mmp)_4]$  (Sigma-Aldrich, SAFC Hitech) diluted in anhydrous cyclohexane (C<sub>6</sub>H<sub>12</sub>, Sigma Aldrich, 99.99%).

CeO<sub>2</sub> layers were elaborated either on silicon Si(100) substrates (Si-Mat Silicon Materials, 99.99%) or on carbon foils (Alfa Aesar, 99.8%), oxygen being used as the oxidant with flow rates in 100–500 sccm. The precursor flow rate was either 0.5 or 1 g  $\cdot$  min<sup>-1</sup> and the N<sub>2</sub> carrier gas flow was chosen equal to 1000 sccm.

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The thickness of the films was measured by a Veeco Dektak surface profilometer. Scanning electron microscopy (SEM) experiments were performed to study the surface morphology of the layers. A JEOL 7600F microscope was used for this purpose, working at an accelerating voltage of 15 kV. Transmission Electron Microscopy (TEM) experiments were performed on a JEOL 2100 LaB<sub>6</sub> while High Angle Annular Dark Field (HAADF)-Scanning Transmission Electron Microscopy experiments were carried out on a JEOL 2100 FEG microscope with a 1 nm probe size. Both microscopes were operated at 200 kV. The samples were prepared for TEM cross-section observation by mechanical thinning with a final argon ion polishing.

Characterizations of the composition and the stoichiometry of cerium oxide films were performed by X-ray Photoelectron Spectroscopy (XPS), using an Al K $\alpha$  X-ray source (h $\nu$  = 1486.6 eV). Electron detection was provided by a hemispheric analyzer CLAM 4 MCD (Thermo VG Scientific). Photoelectrons were collected with an analyzer slit of 1 mm and a pass energy of 100 eV for survey spectra and 20 eV for more precise acquisition of core level spectra, i.e. windows around C1s and Ce4s at ca. 285 eV; O1s at ca. 530 eV; Ce3d at ca. 920 eV and Si2p at ca. 100 eV. Moreover, thanks to a high precision manipulator, it is possible to modify the photoelectron detection angle from 0 to 85° with respect to the normal to the surface. In this way, this device is well adapted not only for regular XPS analyses but also for Angle Dependent XPS (AD-XPS) which can give in-depth information, and, after data treatment, thickness and surface coverage of deposited film [19].

In order to have Ce3d XPS reference spectra corresponding to cerium in Ce<sup>4+</sup> and Ce<sup>3+</sup> oxidation states, Ce3d spectra were acquired respectively on CeO<sub>2</sub> (Alfa Aesar, 99.5%) and Ce<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> (Alfa Aesar, 99.9%) powders.

#### 3. Results and discussion

#### 3.1. Thin film morphology

The different experimental conditions as well as the thicknesses of the corresponding layers determined by surface profiles are summarized in Table 1.

The surface morphology of the as-deposited films was studied by SEM and the results are presented in Fig. 1. First, the effect of deposition times on the layer morphology can be evidenced. For the 5 nm thick film (S2), SEM observations show a homogeneous surface with small particles fully covering the substrate (Fig. 1a). When the film thickness increases to 15 nm (Fig. 1b, S3), the particles seem to agglomerate in grains leaving room for pores which are homogeneously spread on the whole surface. This is even more obvious for the thickest deposit (85 nm) which exhibits higher pore volumes (Fig. 1c, S4).

Then the influence of other parameters such as oxygen and precursor flow rates was studied. Results are presented in Fig. 2. Decreasing the oxidant amount, i.e. using 100 sccm instead of 500 sccm induces a decrease of the thickness of the film (50 nm compared to 85 nm) as well as of the porosity (Fig. 2a). In the same way, decreasing the precursor flow rate from 1 to  $0.5 \text{ g} \cdot \text{min}^{-1}$  results in a huge decrease of the thickness (10 nm instead of 50 nm) and in a much more compact layer (Fig. 2b).

#### Table 1

Conditions of elaboration and thicknesses of the different CeO<sub>2</sub> thin films labeled S1 to S6 deposited at 400 °C on a Si(100) wafer at a working pressure of 10 mbar with a N<sub>2</sub> carrier gas flow equal to 1000 sccm.

	S1	S2	S3	S4	S5	S6
$Ce(mmp)_4$ flow rate $(g \cdot min^{-1})$	1	1	1	1	1	0.5
Time deposition (min)	5	10	15	30	30	30
O <sub>2</sub> gas flow (sccm)	500	500	500	500	100	100
Film thickness (nm)	x(*)	5	15	85	50	10

(\*) No possible measurement because of a too small thickness.



**Fig. 1.** SEM images of CeO<sub>2</sub> thin films deposited on silicon substrate at 400 °C with a precursor flow rate of 1 g  $\cdot$  min<sup>-1</sup>, an oxygen flow rate of 500 sccm and after deposition times of (a) 10 min (sample S2), (b) 15 min (sample S3), and (c) 30 min (sample S4).

In order to go further in the study of the morphology of the layers, TEM studies have been performed in addition to SEM ones. Results of both TEM and Dark Field STEM experiments are presented in Fig. 3a and b for the S4 layer. It appears in TEM images (Fig. 3a) that the layer is homogenous and presents a columnar grain growth. This is in agreement with results obtained using other kinds of precursor [12]. In addition in the HAADF images (Fig. 3b), a bright contrast is visible in the lower part of the films, indicating a higher density of the layer at the beginning of the deposition which is typical for CVD elaboration. The S4 layer thickness has been measured after a careful alignment of the specimens in the TEM using silicon substrate. It is about 90 nm,



**Fig. 2.** SEM images of CeO<sub>2</sub> thin films deposited during 30 min on silicon substrate at 400 °C with an oxygen flow rate of 100 sccm and a precursor flow rate of (a) 1 g.min<sup>-1</sup> (sample S5), (b) 0.5 g.min<sup>-1</sup> (sample S6).

in good agreement with the value obtained with the profilometer. In addition the ceria thin films also present intergrain porosities as can be seen in Fig. 3a. The porosity of the layer is confirmed by HAADF image (Fig. 3b) where the chemical contrast in the sample is enhanced and where black contrasts are visible between the grain columns.

In the following, deposition conditions leading to as porous as possible layers were chosen. The processing conditions were thus precursor flow rate of 1 g  $\cdot$  min<sup>-1</sup> and oxygen flow rate of 500 sccm except otherwise specified. It is interesting to notice that the porosity exhibited by these cerium oxide films deposited by CVD directly on silicon substrates is much higher than the one obtained for films of the same thicknesses processed by physical vapor deposition [20].

#### 3.2. Chemical characterization

As already underlined, the chemical state of cerium in cerium oxide thin layers ( $Ce^{3+}$  and  $Ce^{4+}$ ) is of high importance for the subsequent properties of the films. An XPS study of the films prepared in different conditions has thus been performed in order to get information on the variations of surface cerium chemical state related to deposition parameters. For seek of comparison, spectra of reference compounds, a micrometric  $CeO_2$  powder for  $Ce^{4+}$  reference (Spectrum (d) in Fig. 4) and cerium tungstate  $Ce_2(WO_4)_3$  for  $Ce^{3+}$  reference (Spectrum (e) in Fig. 4) are also presented. Indeed it has been shown that whereas  $CeO_2$  is a correct reference for  $Ce^{4+}$ , eventual use of  $Ce_2O_3$  powder as a  $Ce^{3+}$  reference would not be possible because the surface of  $Ce_2O_3$ might be oxidized to mixture of  $Ce^{3+}$  and  $Ce^{4+}$ .  $Ce_2(WO_4)_3$  powder



Fig. 3. TEM (a) and HAADF-STEM (b) images of CeO<sub>2</sub> thin films deposited during 30 min on silicon substrate at 400 °C with a precursor flow rate of 1 g  $\cdot$  min<sup>-1</sup> and an oxygen flow rate of 500 sccm (sample S4).

was revealed as totally inactive towards air or carboneous species, it was used as XPS Ce<sup>3+</sup> reference.

From Fig. 4 it appears that the Ce3d spectrum centered on 900 eV is quite complex. It has been the topic of a lot of researches and a long debate [21,22]. Indeed, six peaks corresponding to three pairs of spin-orbit doublets can be identified in the Ce3d spectrum from oxidized CeO<sub>2</sub> (spectrum (d) in Fig. 4) while the Ce3d spectrum from the Ce<sup>3+</sup> compound shows different doublets (spectrum (e) in Fig. 4). These multiple states arise from different Ce4f level occupancies in the final state and have been widely discussed [23]. A decomposition of the Ce3d peak can be used to get a quantification of the relative amount of Ce<sup>3+</sup> and Ce<sup>4+</sup> [24] although it is quite difficult to obtain this value precisely. Anyway, it is clear that the presence of Ce<sup>3+</sup> in addition to Ce<sup>4+</sup> at the surface of the film can be evidenced by the observation of a shoulder or even a peak around 885 eV corresponding to the Ce<sup>3+</sup> ad<sub>5/2</sub> 4f<sup>1</sup> 3d<sup>9</sup> state in between the major Ce<sup>4+</sup> gat<sub>3</sub> at 883 eV and 889 eV corresponding to a mixture of final states Ce<sup>4+</sup> 3d<sub>5/2</sub> 4f<sup>2</sup> 3d<sup>9</sup>



**Fig. 4.** Normalized Ce3d XPS spectra of CeO<sub>2</sub> thin films deposited on silicon substrates at 400 °C, with a precursor flow rate of 1 g  $\cdot$  min<sup>-1</sup>, an oxygen flow rate of 500 cm<sup>3</sup>  $\cdot$  min<sup>-1</sup> and different deposition times. (a) 30 min (Sample S4), (b) 10 min (Sample S2), (c) 5 min (Sample S1). (d) Ce<sup>4+</sup> reference and (e) Ce<sup>3+</sup> reference. The dotted line corresponds to the Ce<sup>3+</sup> 3d<sub>5/2</sub> 4f<sup>1</sup> state used to evidence the presence of Ce<sup>3+</sup> in addition to Ce<sup>4+</sup> in the thin films.

and  $Ce^{4+} 3d_{5/2} 4f^1 3d^9$  [25]. The localization of this  $Ce^{3+}$  state is shown by a dotted line in Figs. 4 to 6. Moreover the only feature of the spectrum which can unequivocally be assigned to cerium in the 4 + oxidation state is the one at 916.7 eV which is attributed to  $Ce^{4+} 3d_{3/2}$  $4f^0 3d^9$  final state. This peak, which is absent in  $Ce^{3+}$  compounds, has been used as a quantitative measure of the amount of  $Ce^{4+}$  in the sample [26].

The influence of the chemical state of cerium upon the layer thickness is shown in Fig. 4. In this figure are presented, in addition to the Ce3d spectra of reference Ce<sup>4+</sup> (spectrum (d) in Fig. 4) and Ce<sup>3+</sup> (spectrum (e) in Fig. 4), three experimental spectra obtained for decreasing deposition time of the films. Clear changes can be seen, evidencing that cerium chemical state determined by XPS is function of the thickness of the layer. Indeed, a progressive decrease of the Ce<sup>3+</sup> amount to the benefit of Ce<sup>4+</sup> when the thickness of the layer increases is evidenced on the Ce3d XPS spectra through the relative



**Fig. 5.** Normalized Ce3d XPS spectra of CeO<sub>2</sub> thin film deposited on silicon substrates during 5 min (sample S1) with a detection angle normal to the surface (a) and at grazing angle (75° from the normal to the surface) (b). The dotted line corresponds to the Ce<sup>3+</sup>  $3d_{5/2}4f^1$  state used to evidence the presence of Ce<sup>3+</sup>.



**Fig. 6.** O1s spectra of  $CeO_2$  deposited on silicon during 5 min (Sample S1) recorded with a detection angle normal to the surface (full black line) and at grazing angle (75° from the normal to the surface, dotted red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

intensity of the peak located at 916.7 eV which is attributed to cerium in the 4 + oxidation state. Especially, for the thickest deposit (85 nm, spectrum (a) in Fig. 4), cerium ions appear mostly in the  $Ce^{4+}$  form in the part of the film analyzed by XPS technique, i.e. in the superficial part of the film. In contrary, for the thinnest film (thickness lower than 5 nm, spectrum (c) in Fig. 4), mostly  $Ce^{3+}$  is revealed. For an intermediate thickness (5 nm, spectrum (b) in Fig. 4), the presence of  $Ce^{3+}$  is evidenced in addition to  $Ce^{4+}$  thanks to the presence of a shoulder at a binding energy corresponding to the  $Ce^{3+} 3d_{5/2} 4f^1$  state (dotted line on the figure).

The presence of mostly Ce<sup>3+</sup> for the thinnest oxide layers deposited on silicon may be related to a specific localization of Ce<sup>3+</sup> ions at the interface between the silicon substrate and the cerium oxide layer. In order to prove (or not) this hypothesis, the depth distribution of the chemical state of cerium, was probed by means of comparison of XPS data recorded using a detection angle normal to the surface and a grazing one (75° from the normal to the surface) in the case of the thinnest film (sample S1) (Fig. 5 spectra (a) and (b) respectively). From comparison with  $Ce^{4+}$  and  $Ce^{3+}$  reference spectra (Fig. 4 spectra (d) and (e) respectively), it is clear that most of the cerium is in  $Ce^{3+}$ state. However, a small contribution of Ce<sup>4+</sup> is evidenced through a feature at 916.7 eV on the XPS spectrum which is higher for grazing detection (spectrum (b)), i.e. for the top most layers of material. The fact that cerium is mainly in  $Ce^{3+}$  state may be here the consequence of a reaction between cerium species and native silicon oxide which is always present on silicon wafer. In order to go further, O1s (Fig. 6) and Si2p (Fig. 7) XPS spectra were studied in the case of this thinnest layer with photoelectrons detected either normally to the surface or at grazing angle. In the thinnest CeO<sub>2</sub> film (sample S1), the O1s spectrum (Fig. 6) exhibits both a peak at 532.8 eV which corresponds to the oxygen of SiO<sub>2</sub> and a shoulder which appears at a binding energy of 531.0 eV. This component, which is more intense for photoelectrons detected at grazing angle (Fig. 6 dotted line), i.e. emitted from atoms closer to the surface, corresponds to a less covalent oxide such as a silicate phase (Si-O-Ce) rather than pure cerium oxides which exhibit an O1s line at 529.6 eV [27].

Concerning the Si2p line (Fig. 7), a reference of the Si substrate is also presented for comparison (Fig. 8 spectrum (c)). In the reference spectrum two peaks are present and correspond to non-oxidized silicon (Si°) at 99.6 eV and silicon oxide SiO<sub>2</sub> at 103.5 eV. For the Si2p line obtained after 5 min of cerium oxide deposition (Sample 1) (Fig. 7 spectra (a) and (b)), the spectrum obtained at grazing angle (Fig. 7 spectrum



Fig. 7. Si2p XPS spectra of CeO<sub>2</sub> deposited on silicon during 5 min (Sample S1) recorded with a grazing detection angle (75° from the normal to the surface) (a) and with a detection angle normal to the surface (b). Reference Si2p spectrum obtained on silicon substrate (c).

(a)) is different from the one obtained at normal angle (Fig. 7 spectrum (b)). The relative higher contribution of the component at 103.5 eV compared to the one at 99.6 eV is due to the smaller information depth for grazing detection angle. This induces a higher contribution of the surface silicon oxide with respect to the "bulk" silicon component. Moreover additional features exist with binding energies from 102 to 103 eV which are clearer for the spectrum recorded at grazing incidence. They can be assigned to silicon in lower oxidation states such as in a mixed Ce-Si oxide.

Besides, the presence of  $Ce^{4+}$  ions in the top most film layers simply evidences an increase of  $Ce^{4+}$  site concentration on this part of the material, i. e. far from the interface between silicon oxide and the film where cerium is as a majority as  $Ce^{3+}$  state.

In order to confirm the reaction between the cerium precursor and the silicon substrate, similar depositions were performed on a siliconfree substrate, i.e. a carbon foil. The corresponding XPS Ce3d lines are presented in Fig. 8 for the three deposition times, 30 min (spectrum (a)), 10 min (spectrum (b)) and 5 min (spectrum (c)). It should be



Fig. 8. Normalized Ce3d XPS spectra of CeO2 thin films deposited on graphite with different deposition times. (a) 30 min, (b) 10 min, (c) 5 min. The dotted line corresponds to the  $Ce^{3+} 3d_{5/2} 4f^1$  state used to evidence the presence of  $Ce^{3+}$  in addition to  $Ce^{4+}$  in the thin films.

noticed that these depositions do not give the same results as the ones performed on silicon. Indeed, when depositions are carried out on a carbon foil cerium is only in the Ce<sup>4+</sup> state whatever the deposited amount is, even for the thinnest one. In other words, Ce<sup>3+</sup> occurs at interface in the presence of silicon only.

All these results can be interpreted by the formation of cerium silicates at the interface between the silicon substrate and the growing layer. Such a kind of interfacial interaction between a growing oxide overlayer and silicon surfaces leading to the formation of a silicate phase of subnanometric thickness was also observed by various techniques among different thin films deposited on silicon substrates [28-30]. In particular high resolution photoemission electron spectroscopy has been used for cerium oxide evaporated on silicon substrate: several oxygen and silicon components whose intensities are varying with the overlayer thickness were also evidenced indicating the presence of different oxide phases at the interface [31].

Hence, Ce<sup>3+</sup> occurring during the first steps of the growth can be explained by the presence of a reactive Si-Ce-O interface leading, at the beginning of the growth only, to the formation of subnanometric cerium silicate layer. This one is further followed by the growth of a cerium oxide layer. In the case of a silicon-free support, no reaction can occur and cerium oxide, containing mainly Ce4+ ions, grows from the first steps.

#### 4. Conclusion

Cerium oxide films have been obtained on silicon or carbon foil substrates using DLI-MOCVD with Ce(mmp)<sub>4</sub> as a precursor. The influence of deposition parameters on the thin film morphology has been studied using SEM and TEM and the possibility of obtaining high porous films, especially using higher oxygen flow, has been demonstrated. In addition, thanks to XPS results, it was shown that in the obtained films, cerium is mainly in the Ce4+ state corresponding to the growth of CeO<sub>2</sub>. Moreover, an additional compound where cerium is a  $Ce^{3+}$ state is present at the interface when depositions are performed on a silicon substrate and absent in the case of a silicon-free substrate such as a carbon foil. This is attributed to the formation of a silicate phase at the interface between the silicon based substrate and the growing layer.

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## 3.3 Croissance de films sur substrats de carbone

Des dépôts d'oxyde de cérium ont été obtenus sur des substrats de carbone et les résultats ont été publiés dans Materials Today : Proceedings.



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# Observation of surface reduction in porous ceria thin film grown on graphite foil substrate

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## Abstract

In this study, we report transmission electron microscopy and electron energy loss spectroscopy study of cerium oxide thin layer grown on graphite foil substrate by direct liquid injection chemical vapour deposition. Transmission electron microscopy experiments have revealed the porous morphology of the deposited layer. Energy electron loss spectroscopy measurements were also performed in scanning mode to study the evolution of the cerium valence. In addition to  $Ce^{4+}$  inside the layer, the presence of reduced cerium oxide with  $Ce^{3+}$  valence is pointed out at the layer surface and at the surface of the porosity developed by the layer. Besides, studies of high resolution images coupled to electron energy loss spectroscopy have indicated the presence of crystallized ceria nanoparticles, and the absence of cerium carbide.

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Keywords: Transmission electron microscopy; electron energy loss spectroscopy; cerium oxide; fuel cells

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## 1. Introduction

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In the last decades, cerium oxide materials have gained great interest due to their wide range of applications in different areas such as catalysis, electrochemistry, photochemistry and materials science[1–4]. Moreover, this material is considered as one of the most promising oxide for anode materials used for fuel cells applications.

Platinum is well known as an efficient catalyst and it is usually used in the proton exchange membrane fuel cell electrochemical reactions. As it is expensive, low Pt content Pt-CeO<sub>2</sub> anode samples have been investigated[5]. When combined with platinum, the system exhibits excellent catalytic properties for a variety of reactions: CO oxidation[6], hydrogen production[3], and decomposition of methanol[7]. Previously, it has also been shown that when used as an anode material for proton exchange membrane fuel cells, Pt-doped cerium oxide thin films deposited on carbon nanotubes exhibit very high specific power (up to 30 W/mg Pt)[8]. This is due to the existence of two stable oxidation states (Ce<sup>3+</sup> and Ce<sup>4+</sup>), which allows cerium oxides to undergo oxidation and reduction relatively easily[9,10], coupled with its ability to absorb and release oxygen[11].

Investigations by high resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS) have already been performed on ceria systems[12–14] but mainly for ceria nanopowders[10,15–18] and not for thin films. The combination of the two techniques allows the correlation of spectroscopic information with detailed structural knowledge of a material. The Ce<sup>4+</sup> M<sub>4,5</sub> edge shape, intensity, and energy differ from those of Ce<sup>3+</sup>. Therefore, changes in edge shape, peaks position and peaks area give information about the valence of Ce atoms.

Previous studies of  $CeO_2$  thin films deposited on silicon substrate using radio frequency magnetron sputtering have shown that the surface layer is relatively flat in contrast with porous structure obtained with an intermediate carbon layer[19–21]. In contrary, studies of  $CeO_2$  thin films deposited on silicon substrate using Chemical Vapour Deposition (CVD) have shown that the layers are grown with a porous structure, without addition of an intermediate layer[22]. However, studies of  $CeO_2$  thin films morphology on carbonaceous substrates by CVD have not been performed yet[23].

Before the study of Pt-doped ceria thin films for fuel cells applications[24], this study aims at characterization of undoped ceria nanoporous and nanostructured  $CeO_2$  thin films directly deposited on a graphite foil substrate by Direct Liquid Injection Chemical Vapour Deposition (DLI-CVD). This study will be used to obtain references before studying the effect of Pt co-deposition. Coating morphology observations, crystallographic structures determination, elemental chemical analyses and cerium oxidation states determination by HRTEM and EELS measurements have been performed.

## 2. Experimental details

CeO<sub>2</sub> thin films were deposited on graphite foil substrates, purchased from Alfa Aesar (graphite foils 99.8%). DLI-MOCVD experiments were carried out on an Annealsys MC-050 system equipped with a direct liquid injection system and infrared lamps for rapid thermal heating[25]. Thin cerium oxide films were deposited under a reactor pressure of 10 mbar using 0.01M solution of  $[Ce(mmp)_4]$  in anhydrous cyclohexane (C<sub>6</sub>H<sub>12</sub>, Sigma Aldrich, 99.99%). CeO<sub>2</sub> layer was elaborated at deposition temperature of 400°C, oxygen being used as the oxidant with flow rates of 100 sccm. The precursor flow rate was 0.5 g.min<sup>-1</sup>.

For TEM characterization, samples were prepared with Focus Ion Beam (FIB) (Tescan LYRA FIB-SEM) technique in form of thin lamellas cut from the catalyst films. A protective  $SiO_2$  layer was systematically deposited on the area of interest prior to milling.

High Resolution (HRTEM) and High Angle Annular Dark Field (HAADF)-Scanning Transmission Electron Microscopy (STEM) experiments were performed on a JEOL JEM 2100F microscope operated at 200 kV. Experimental crystallographic structures were compared with simulated ones obtained using Java Electron Microscopy Software[26]. STEM-EELS experiments were carried out on a Gatan GIF-TRIDIEM spectrometer with a 1 eV energy resolution and a STEM probe size of 1 nm. Short acquisition times (less than 1 second) were used in all STEM-EELS experiments, in order to limit electron-beam damage of the deposits[16].

Oxidation state of Ce in the layer was determined using cerium  $M_{4,5}$  edges and by measuring the  $M_4/M_5$  area ratio. The  $M_{4,5}$  cerium spectra are characterized by sharp white lines corresponding to transitions from  $3d_{3/2}$  to  $4f_{5/2}$  ( $M_4$ ) and  $3d_{5/2}$  to  $4f_{7/2}$  ( $M_5$ )[27]. The position and the relative intensity of the  $M_{4,5}$  edges can give an insight into the valence state of cerium. Indeed, the intensity of the  $M_4$  edge is higher than  $M_5$  one in Ce<sup>4+</sup>, and reversed in Ce<sup>3+</sup>[17]. Numerous methods have been developed to measure the ratio[16,28]. In this work we choose the second derivative method since it is insensitive to thickness variation[17]. After background removal by fitting an inverse power-law of the form AR<sup>-r</sup> for a range of 40 eV before CeM<sub>4,5</sub> edge, the second derivative was calculated numerically using Digital Micrograph (DM) software. The ratio between  $M_5$  and  $M_4$  peaks areas was then calculated using only the positive area of the  $M_5$  and  $M_4$  second derivative peaks, for each EELS spectrum. The  $M_5/M_4$  area ratios were firstly determined for Ce<sup>3+</sup> (Ce<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub>) and Ce<sup>4+</sup> (CeO<sub>2</sub>) commercial reference powders. The  $M_5/M_4$  area ratios were 0.90 for Ce<sup>4+</sup> and 1.29 for Ce<sup>3+</sup> from these standards, in good agreement with literature results [17,18]. For our samples, after spectrum-imaging (SI) experiments, the  $M_4/M_5$  area ratio were then plotted following a color code (blue for Ce<sup>4+</sup> and red for Ce<sup>3+</sup>) to generate Ce<sup>4+</sup> and Ce<sup>3+</sup> maps of our layer.

## 3. Results and discussion

## 3.1. Thin film morphology

The morphology of the layer was studied by TEM for cross-section samples (Fig. 1). The TEM image evidences the presence of nanostructured thin films on top of the amorphous graphite foil substrate. The layer/substrate interface appears to be very sharp. The thickness of the deposited layer is estimated to be around 100 nm. At the layer/substrate interface, a darker contrast is visible (Fig. 1). This contrast is due to the first step of elaboration, in which the layer is grown with a dense structure. By collecting scattered electrons over a wide angular range, STEM-HAADF technique is highly sensitive to mass-thickness contrast[29]. Thus, the presence of a dense part in the layer is confirmed by the HAADF image on Fig. 2(a), where a brighter contrast is visible in the lower part of the layer. This type of dense growth is typical for CVD elaboration[30]. However, the dense part of the layer is only around 12 nm thick. From there, the layer presents well defined leaf-like structures which denote a columnar grain growth. It also seems to present important intercolumns porosity. This is emphasized in the HAADF image, where the mass-contrast in the samples is enhanced and where darker contrasts between the grain columns can be seen (Fig. 2a). This observation is in agreement with thin films elaborated in same conditions on silicon substrates[22] and confirms that the processes involved during cerium oxide deposition by DLI-CVD naturally lead to porous layers with a potential high specific area.



Fig. 1. Cross section TEM image of CeO<sub>2</sub> layer deposited on graphite foil substrate.

## 3.2. Electron Energy Loss Spectroscopy measurements

The cerium chemical state along the layer was determined by EELS measurements in STEM acquisition mode. EELS measurements allow to obtain information about the chemistry of materials and this technique has been successfully applied to study the oxidation states of cerium via the cerium  $M_{4,5}$  edge. Cerium oxidation state mapping was carried out after acquisition of spectrum-image by scanning the focused electron beam while, at each pixel in a two dimensional pattern (SI indicated by the white rectangle), an EEL spectrum was collected (Fig. 2a). This SI allows precise correlation between spatial and spectral features. Color-coded maps of the cerium valence (blue for Ce<sup>4+</sup> and red for Ce<sup>3+</sup>) are superimposed on the dark field STEM images. Moreover, Fig. 2(b) presents two spectra extracted from SI in area 2. They are displayed for energy loss corresponding to Ce $M_{4,5}$  edges close to 900 eV.

The relative quantity of  $Ce^{3+}$  and  $Ce^{4+}$  was calculated by extrapolation from the ratio values supposing a linear relationship. Pure  $Ce^{4+}$  and  $Ce^{3+}$  states are characterized by second derivative  $M_5/M_4$  peaks areas ratio close to 0.9 (100%  $Ce^{4+}$ ) and 1.3 (0%  $Ce^{4+}$ ) respectively[15,17,18], whereas results within these limits correspond to sample areas with multiple cerium valence states. Since cerium does not adopt any other valence than +3 and +4, an intermediate value corresponds to a mixed composition of both oxidation levels superimposed in projection and simultaneously crossed by the electron beam.

From Fig. 2(b), we calculated that the second derivative  $M_5/M_4$  area ratio at the interface of CeO<sub>2</sub> layer with the substrate is  $0.90 \pm 0.05$ , in good agreement with values reported in the literature for Ce<sup>4+</sup>. By comparing the different spectra, an inversion of the  $M_{4,5}$  peaks maximum intensity is qualitatively observed when going from the interface with the substrate (Fig. 2(b), bottom spectrum) to the surface of the layer (Fig. 2(c), upper spectrum). Close to the interface, the  $M_5$  edge is less intense than the  $M_4$  one inside the deposit. At the surface,  $M_5$  peak intensity is more intense than  $M_4$  one. These results are confirmed by the color-coded maps shown in Fig. 2(a) where the cerium is oxidized at the interface (blue color) and reduced at the surface (red color). In between, the cerium presents a mixed valence (purple color). We can thus conclude that a change of valence state of Ce is taking place at the surface.

Whilst the cerium valence at the graphite foil interface corresponds to  $Ce^{4+}$ , the cerium localized at the surface is almost completely reduced to  $Ce^{3+}$ . Between the upper layers and the lowers ones, the cerium presents a mixed valence. Moreover, we can note that the reduction of cerium valence does not only take place at the very surface of the layer. Cerium is also reduced at the surface of the leaf-like structures. It means that cerium is not only reduced at the very surface of the layer, but is also reduced in the porosity developed by the layer. This observation is true for every area that was analyzed. The presence of  $Ce^{3+}$  at the surface has already been pointed out for  $CeO_2$ nanopowders[17]. It was shown for pure  $CeO_2$  particles that the top atomic layer is almost fully reduced. Whilst the underlying atomic layers were intermixed, the number of layers with  $Ce^{3+}$  depends on the surface type[10]. The presence of  $Ce^{3+}$  at the particle surface can be linked to oxygen vacancies which were predicted to be unstable inside the particles and to tend to migrate to the surface[12]. So the ceria reduction at the surface of the layer and of the leaf-like structures would be linked in our layer to oxygen vacancies diffusion toward the surface of cerium oxide nanostructures in all directions. This observation is another proof of the presence of inter-columns porosity of the layer.



Fig. 2. (a) EELS color-coded maps superposed on dark-field STEM images. The color-coded maps display the ratio values obtained from second derivative  $M_5/M_4$  peak areas (Ce<sup>4+</sup> in blue and Ce<sup>3+</sup> in red); (b,c) EELS spectra extracted from area 2 in Figure 2(a) covering the region of Ce- $M_{4,5}$  edge around 900 eV. Spectrum (b) is extracted at the layer/substrate interface and spectrum (c) is extracted at the surface of the layer.  $M_5:M_4$  indicated values correspond to the second derivative  $M_5/M_4$  area ratio.

Spatially resolved EELS analysis, based on the core loss edges, has been used for the quantification of cerium, oxygen and carbon composition. EELS spectrum images were acquired for C-K, O-K and Ce- $M_{4,5}$  edges. Moreover, spectrum images were acquired in the zero-loss area of the spectra to determine the relative thickness of the sample. The relative concentrations of carbon and cerium, as well as the relative thickness extracted from spectrum image of area 2 in Fig. 2(a) were calculated using DM and are displayed as temperature color coded maps in Fig. 3 where black color corresponds to low values and white color to high values. Oxygen relative concentration map is not presented here. Indeed, SiO<sub>2</sub> protective layer used for FIB preparation induces an oxygen contamination on the entire sample. The measured relative oxygen concentration is then unusable for this study. For comparison, the dark field image extracted from area 2 in Fig. 2(a) is also presented (Fig. 3(a)).

Observation of the relative thickness map (Fig. 3(b)) shows that it is correlated with the cerium concentration map (Fig. 3(c)). The cerium concentration increases in the leaf-like structure and decreases in between. In the same way, the thickness decrease between the cerium oxide leaf-like structures. This observation confirms well that the layer presents inter-column porosity.

The study of carbon maps (Fig. 3(d)) indicates that the relative carbon concentration decreases in the cerium oxide structures. Moreover, when compared to the film thickness, the relative carbon amount increases in the porosity and at the surface of the cerium oxide structures. This observation shows that it is very unlikely that the formation of cerium carbides occurs at the interface with graphite foil substrate. Indeed, it would have resulted in an increase of carbon relative content in the nanostructure instead of its decrease.

Despite known interaction with substrate when cerium oxide is deposited on silicon substrate, and subsequent formation of cerium silicates[23,31], no presence of cerium carbide can thus be evidenced in deposition on graphite foil substrates at the layer/substrate interface by EELS measurements. The carbon content is thus only attributed to the contamination from cerium precursor which contains carbon and from redeposition in the layer during FIB preparation.



Fig. 3. Dark Field image and temperature color coded maps extracted from SI in area 2 of Fig. 2(a). (a) Dark field image; (b) relative thickness of the layer; (c) relative quantification for cerium; (d) relative quantification for carbon. For temperature color coded maps, high values are in white/clear and low values in black/dark).

## 3.3. High Resolution Transmission Electron Microscopy measurements

HRTEM experiments have been performed to study the crystallography of the layer. The cerium oxide film is very well crystallized, in both dense and porous parts of the deposit. Fig. 4 presents two examples of HR pictures, one in the upper part of the layer in squared area 1 (Fig. 4(b)) and the other one in the lower and dense part of the layer in squared area 2 (Fig. 4(c)). For all HR measurements, the only type of crystallites evidenced was cerium dioxide CeO<sub>2</sub>. On Fig. 4(b), measurements of interplanar distances and angles between crystallographic planes indicate that the visible CeO<sub>2</sub> crystallite is oriented along [101] zone axis. It is characterized by distances d<sub>(11-1)</sub> = 0.315 nm, d<sub>(0-20)</sub> = 0.272 nm and angles d<sub>(11-1)</sub>d<sub>(1-1-1)</sub> = 70° and d<sub>(1-1-1)</sub>d<sub>(0-20)</sub> = 55°. On Fig. 4(c), the visible CeO<sub>2</sub> crystallite is oriented along [114] zone axis. It is characterized by distances d<sub>(-220)</sub> = 0.193 nm, d<sub>(-3-11)</sub> = d<sub>(-1-31)</sub> = 0.164 nm, and angles d<sub>(-220)</sub>d<sub>(-3-11)</sub> = 65° and d<sub>(-3-11)</sub>d<sub>(-1-31)</sub> = 50°.

Unlike deposition on silicon substrate where cerium silicates were evidenced by EELS measurements[31], deposition of cerium oxide on graphite foil substrate doesn't induce the formation of cerium carbides. However, despite the absence of this kind of interaction between the precursor and the substrate even at 400°C, the

layer/substrate interface is still very sharp without voids or cracks. This observation can be linked to EELS measurements, where no evidence of cerium carbide presence was found.



Fig. 4. (a) Cross section TEM image of the layer; (b) Experimental HR image from squared area 1 in Fig. 4(a) with a CeO<sub>2</sub> crystallite oriented along [101] zone axis (distances  $d_1 = d_{(11-1)} = 0.315$  nm,  $d_2 = d_{(1-1)} = 0.315$  nm and  $d_3 = d_{(0-20)} = 0.274$  nm); (c) Experimental HR image from squared area 2 in Fig. 4(a) with a CeO<sub>2</sub> crystallite oriented along [114] zone axis (distances  $d_1 = d_{(-3-11)} = 0.166$  nm,  $d_2 = d_{(-220)} = 0.198$  nm and  $d_3 = d_{(-3-11)} = 0.166$  nm,  $d_2 = d_{(-220)} = 0.198$  nm and  $d_3 = d_{(-3-11)} = 0.166$  nm).

## 4. Conclusion

TEM experiments have revealed the porous morphology of the deposited layer with formation of leaf-like structures (Fig. 1). We can also note sharp interface between the deposit and the carbon substrate. In addition, studies of high resolution images have indicated that the layer is well crystallized with  $CeO_2$  structure. No evidence of cerium carbide crystallites was found. EELS measurements were also performed in scanning mode to study the evolution of the cerium valence. In addition to  $Ce^{4+}$  inside the layer and at the interface with the substrate, the presence of reduced cerium with valence +3 is pointed out at the surface of the layer as well as in the porosity. This is consistent with surface reduction of ceria observed in nanostructured systems.

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## 3.4 Conclusion

Des films d'oxyde de cérium ont été obtenus par DLI-CVD sur des substrats en silicium et en carbone. L'optimisation des paramètres a notamment permis d'obtenir dans les deux cas des couches poreuses. Les caractérisations par XPS ont montrées que l'état d'oxydation du cérium est +IV, ce qui correspond à du CeO<sub>2</sub>. Une forme réduite de type Ce<sup>3+</sup> a aussi été mise en évidence à l'interface entre le silicium et le cérium et correspond très probablement à la formation de silicates. En outre, une étude des clichés MET en haute résolution a montré une réduction partielle du cérium à la surface des dépôts obtenus sur des substrats en carbone. Cette réductibilité de la surface est cohérente par rapport à ce qui a déjà été observé sur les couches de cérium nanostructurés<sup>61</sup>.

<sup>&</sup>lt;sup>61</sup> V. Potin, J. Lavkova, S. Bourgeois, M. Dubau, I. Matolinova and V. Matolin; Materials Today Proceedings 2 (2015) 101 - 107.

## 4 Films d'oxyde de cérium dopé au platine

Le chapitre précédent a montré la possibilité d'obtenir des couches d'oxyde de cérium poreuses, dont la microstructure semble idéale pour une utilisation en tant que catalyseurs. Ce chapitre traite de l'étude de couches d'oxyde de cérium dopé au platine, cet élément pourrait améliorer les propriétés catalytiques de l'oxyde de cérium.

## 4.1 Choix du précurseur

Tout comme pour le cérium, le choix des précurseurs de platine est large (Tableau 4.1-1). Le précurseur retenu est le MeCpPtMe<sub>3</sub>, triméthyl(méthylcyclopentadiényl) de platine  $(IV)^{62,63}$  (Figure 4.1-1). Il a été choisi car il peut être utilisé tant en mode ALD qu'en mode CVD à la différence du Pt(hfa)<sub>2</sub> et du Pt(cod) qui n'ont été utilisé qu'en CVD. De plus, il peut être facilement mis en œuvre car il ne nécessite pas l'utilisation de dihydrogène comme gaz réactif contrairement au Pt(acac)<sub>2</sub>.

Précurseur	Procédé	gaz réactif	température de dépôt	prix	
<b>D</b> t(acco) 64	CVD	$O_2/H_2$	280 - 600°C	89€/g	
$Pt(acac)_2^{\circ 1}$	ALD	$\mathrm{H}_{2}$	250°C		
Pt(hfa) <sub>2</sub> <sup>65</sup>	CVD	$\mathrm{H}_{2}$	350°C	330€/g	
Pt(cod) <sup>66</sup>	CVD	O <sub>2</sub>	320°C	256€/g	
MeCpPtMe <sub>3</sub>	CVD	$O_2/H_2$	350 - 400°C	2550/	
	ALD	O <sub>2</sub>	250 - 350°C-	255€/g	

<u>Tableau 4.1-1 : précurseurs à base de platine pour la synthèse par voie chimique</u>

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Figure 4.1-1 : molécule de MeCpPtMe<sub>3</sub>

## 4.2 Dépôt de films minces d'oxyde de cérium dopé au platine

Dans cette étude l'oxyde de cérium dopé au platine a été obtenu sur des substrats de silicium. Les résultats ont été publiés dans Thin Solid Films en 2015. Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

## Direct liquid injection chemical vapor deposition of platinum doped cerium oxide thin films



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## 1. Introduction

In recent years, ceria based oxides have been widely used as catalysts [1] or as electrolyte material for fuel cells. This is due to the fact that cerium ions can be present in the oxide skeleton in two stable oxidation states (Ce<sup>3+</sup> and Ce<sup>4+</sup>). Cerium oxide is thus used for catalytic applications in which alternating oxidation and reduction in the material is needed [1]. Some of the applications of ceria based materials are water-gas shift reaction [2], CO oxidation [3], NO reduction [4], automotive exhaust catalyst [5], and fuel cell catalysts [6]. Moreover, it has been observed that interaction between noble metal such as Pt with ceria enhances its catalytic activity by improving the reducibility of the surface [2,7–9]. The promoting action of ceria has been underlined in several reactions and different ways of preparing Pt/CeO<sub>2</sub> catalysts have been studied. For example a 1% Pt/CeO<sub>2</sub> catalyst prepared by the solution combustion method shows a higher catalytic activity for CO oxidation by O<sub>2</sub> compared to Pt metal particles [10]. In addition, it has been shown that such an enhanced catalytic activity phenomenon increases with the presence of non-metallic platinum,  $Pt^{2+,4+}$  [10–13]. For instance, it was demonstrated from both experiments and density functional theory calculations that Pt ions incorporated in a CeO2 matrix mostly in + II oxidation state enhance hydrogen molecule dissociation to protonic hydrogen and increase hydrogen storage capacity of the catalyst [14].

Besides, for economical reason, the amount of platinum has to be as low as possible and a perfect control of the doping content is necessary.

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### ABSTRACT

Thin films of Pt-doped CeO<sub>2</sub> were grown by direct liquid injection chemical vapor deposition on silicon wafer covered by native oxide at 400 °C using Ce(IV) alkoxide and organoplatinum(IV) as precursors. X-ray photoelectron spectra evidenced that the platinum oxidation state is linked to the deposition way. For platinum deposited on top of cerium oxide thin films previously grown, metallic platinum particles were obtained. Cerium and platinum codeposition allowed obtaining a Pt<sup>0</sup> and Pt<sup>2+</sup> mixture with the Pt<sup>2+</sup> to Pt ratio strongly dependent on the platinum flow rate during the deposition. Indeed, the lower the platinum precursor flow rate is, the higher the Pt<sup>2+</sup> to Pt ratio is. Moreover, surface and cross-sectional morphologies obtained by scanning electron microscopy evidenced porous layers in any case.

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In addition a strong relationship between the morphology and the catalytic performance of  $Pt/CeO_2$  catalysts has been shown for example in the case of impregnation of different kinds of  $CeO_2$  supports with platinum precursor [15]. It is thus very important to prepare in a controlled way nanostructured  $Pt/CeO_2$  catalysts. Different ways have been proposed such as hydrothermal treatment processing [16] or the use of mesoporous silica template [17]. Among the methods developed in order to obtain porous thin film catalysts, electrochemical routes [18,19] or magnetron sputtering [20,21] allow a good control of the physical and chemical properties of catalysts.

However, there was no previous study of chemical vapor deposition (CVD) growth of platinum doped cerium oxide thin films, this paper deals with a method for depositing those thin films by direct liquid injection chemical vapor deposition (DLI-CVD). This technique has been chosen for its capacity to produce conformal coverage on a large area. It also allows depositing layers with good doping and thickness controls [22,23].

Cerium chosen precursor was cerium tetrakis (1-methoxy-2-methyl-2-propanolate),  $[Ce(mmp)_4]$ , i.e. a cerium alkoxide. This metal alkoxide precursor is widely used in metalorganic chemical vapor deposition (MOCVD) because it allows depositing pure oxide films i.e. free of carbon at rather low temperature [24,25]. Platinum precursor was trimethyl (methylcyclopentadienyl) platinum(IV), [MeCpPtMe<sub>3</sub>], i.e. an organometallic compound. Moreover, both compounds present a low decomposition temperature with a high chemical stability while the use of oxygen allows decomposing the precursor with a low carbon contamination [26–29].

Hence, this study is about different routes for elaborating porous Ptdoped ceria thin films by means of DLI-CVD. Three different protocols



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were studied, the aim being obtaining the most porous film containing the higher amount of platinum in ionic state localized in the top most of the layers. The morphology and the chemical properties of the films deposited using the different routes were studied by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS).

### 2. Experimental

#### 2.1. DLI-CVD process

DLI-CVD experiments were carried out with an Annealsys MC-050 system equipped with a cold wall reactor, a direct liquid injection system Kemstream and infrared lamps for rapid thermal heating of substrates. Platinum and cerium oxides were deposited using a reactor pressure of 10 hPa with 0.01 mol·dm<sup>-3</sup> solution of [Ce(mmp)<sub>4</sub>] (Sigma-Aldrich, SAFC Hitech) and 0.001 mol·dm<sup>-3</sup> solution of [MeCpPtMe<sub>3</sub>] (Sigma-Aldrich, SAFC Hitech) both diluted in anhydrous cyclohexane (C<sub>6</sub>H<sub>12</sub>, Sigma Aldrich, 99.99%).

Pt–CeO<sub>2</sub> layers were elaborated on silicon Si(100) substrates (Si-Mat Silicon Materials, 99.99%) covered by native oxide. The deposition temperature was 400 °C while oxygen was used as oxidant with flow rate of 500 sccm. The cerium precursor flow rate was 1 g·min<sup>-1</sup> and platinum flow rates can be tuned between 0.25 and 1.0 g·min<sup>-1</sup>. Thin film thicknesses were estimated between 40 and 80 nm depending upon the chosen protocol for deposition.

The three deposition protocols were:

- (i). deposition of platinum on a previously elaborated cerium oxide film,
- (ii). elaboration of a film through platinum and cerium oxide co-deposition,
- (iii). co-deposition of platinum and cerium oxide film on a previously grown cerium oxide film.

#### Experimental parameters are summarized in Table 1.

#### 2.2. Thin film characterization

SEM was used to both estimate the film thickness and porosity through cross section images and observe the surface morphology of the material. A JEOL 7600F microscope was used for this purpose, working at an accelerating voltage of 15 kV.

Characterizations of the composition and stoichiometry of platinum doped cerium oxide films were performed by XPS, using an Al K $\alpha$  X-ray source (h $\nu$  = 1486.6 eV). Electron detection was provided by a hemispheric analyzer CLAM 4 MCD (Thermo VG Scientific). The spectra were referenced to the C1s line of the residual carbon. Photoelectrons were collected with pass energy of 100 eV for survey spectra, 20 eV for more precise acquisition of Ce3d and 50 eV for Pt4f and Ce4d in order to increase the signal of doping platinum. Photoemission peak areas were determined after smoothing and background subtraction using a Shirley routine. Pt/Ce atomic ratio of the Pt–CeO<sub>2</sub> catalysts was calculated from Ce4d and Pt4f XPS peaks area instead of Ce3d. Indeed, although Ce4d has a lower intensity, the kinetic energies of Ce4d and

#### Table 1

Experimental conditions used	for DLI-MOCVD	elaboration of C	2eO <sub>2</sub> and platinum	thin film
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Working pressure (hPa)	10
Substrate temperature (°C)	400
Deposition time (min)	15
Ce(mmp) <sub>4</sub> concentration in cyclohexane (mol·dm <sup>-3</sup> )	0.01
$Ce(mmp)_4$ solution flow rate $(g \cdot min^{-1})$	1
MeCpPtMe <sub>3</sub> concentration in cyclohexane (mol·dm <sup>-3</sup> )	0.001
MeCpPtMe <sub>3</sub> solution flow rates $(g \cdot min^{-1})$	0.25, 0.50, 1.0

Pt4f are very close (both in 1400–1350 eV range) leading to equivalent analysis depth for cerium and platinum species. Pt/Ce atomic ratio was thus calculated by correcting peak areas by the photoionization cross sections [30]. Desummations of platinum spectra were done by fitting the peaks with asymmetrical Lorentzian shapes for metallic platinum peaks and Gaussian (70%)–Lorentzian (30%) shapes for nonmetallic platinum.

The crystalline structure was investigated through X-ray diffraction (XRD) with small incidence angle  $(2^{\circ})$  using a diffractometer (Inel-CPS 120T) equipped with a Ge(111) monochromator and a Cu X-ray tube working at 40 kV and 40 mA.

## 3. Results and discussion

#### 3.1. Deposition of platinum on CeO<sub>2</sub> film

Platinum was deposited with a platinum solution flow rate of  $1 \text{ g} \cdot \text{min}^{-1}$  on 50 nm thick porous CeO<sub>2</sub> films grown according to conditions given in Table 1. Fig. 1a presents a cross section image related to such a deposit, showing the expected high porous character of the deposit. The SEM observations of the film surface carried out with secondary electrons show grains with a size in the order of 30 nm with particles smaller than 10 nm on top (Fig. 1b). SEM image obtained with backscattered electrons reveals that these dispersed nanoparticles are made of a material heavier than cerium, probably metallic platinum, which could have grown on the surface of cerium oxide layer (Fig. 1c).

XPS analysis was performed on such a sample in order to go further about the chemistry of material (Fig. 2). Concerning the platinum



Fig. 1. SEM images of Pt particles deposited on  $CeO_2$  films at 400 °C with precursor flow rates of 1 g·min<sup>-1</sup>; (a) side view obtained with secondary electrons, (b) surface image obtained with secondary electrons, and (c) surface image obtained with backscattered electrons.



Fig. 2. Pt4f X-ray photoelectron spectrum for Pt thin film deposited on CeO<sub>2</sub> substrate.

chemistry, Pt4f core level spectrum exhibits a main doublet composed of Pt4f<sub>7/2</sub> and Pt4f<sub>5/2</sub> lines at binding energies 71.0 eV and 74.3 eV, respectively. These components are related to metallic platinum [31–33]. Furthermore, an additional doublet is also present, where Pt4f<sub>7/2</sub> binding energy is at approximately 72.5 eV. This binding energy value corresponds to Pt<sup>2+</sup> state [34]. Hence, the platinum deposit is mainly composed of metallic platinum particles but a low amount (ca. 10%) of Pt<sup>2+</sup> is also revealed.

## 3.2. Pt CeO<sub>2</sub> co-deposition on silicon substrate

In order to dope ceria, cerium and platinum were deposited at the same time in an oxygen atmosphere. Such co-depositions were performed in conditions reported in Table 1 using different platinum precursor flow rates from  $1.0 \text{ g} \cdot \text{min}^{-1}$  to  $0.25 \text{ g} \cdot \text{min}^{-1}$  of precursor solution. The thicknesses of the samples for  $1.0 \text{ g} \cdot \text{min}^{-1}$ ,  $0.50 \text{ g} \cdot \text{min}^{-1}$  and  $0.25 \text{ g} \cdot \text{min}^{-1}$  were respectively 40 nm, 60 nm and 80 nm. Fig. 3 presents XPS analysis showing a Pt4f core level exhibiting two doublets at ca. 71 eV and 72.5 eV for the Pt4f<sub>7/2</sub> peak corresponding to Pt<sup>0</sup> and Pt<sup>2+</sup>, respectively. It is clear in Fig. 3 that the relative amount of Pt<sup>2+</sup> compared to Pt<sup>0</sup> varies as a function of platinum flow rate: for the higher concentration of platinum precursor, Pt<sup>0</sup> is mostly observed while the



**Fig. 3.** Pt4f X-ray photoelectron spectra for thin films obtained by co-deposition of Pt and CeO<sub>2</sub> on Si substrates with three different platinum flow rates: 1 g·min<sup>-1</sup> (top), 0.5 g·min<sup>-1</sup> (middle), and 0.25 g·min<sup>-1</sup> (bottom).

opposite occurs when decreasing the platinum flow rate. Platinum state was followed through the relative intensities of these two doublets, more precisely through the ratio between  $Pt^{2+}$  peak area and the total  $Pt4f_{7/2}$  area. Results are presented in Fig. 4. Indeed, decomposition of the Pt4f spectra reveals that the  $Pt^{2+}/Pt$  ratio decreases from 0.8 to 0.4 when the flow rate increases from 0.25 to 1 g·min<sup>-1</sup>.

The cerium to platinum atomic ratio was determined using Ce4d and Pt4f core levels and results are presented also in Fig. 4. It is shown that the Pt loading in the cerium oxide film is proportional to platinum flow rate. Indeed, the higher the flow rate, the higher the Pt/Ce ratio is with a variation from 1% to 5% for precursor flow rates varying from 0.25 to 1 g $\cdot$ min<sup>-1</sup>. In Fig. 5 are presented the backscattered electron SEM surface and cross sectional images for three different platinum precursor flow rates. First of all, surface images (Fig. 5(a),(b),(c)) reveal the presence of nanoparticles made of a material heavier than cerium, i.e. probably metallic platinum. However, it appears that surface density of clusters depends on the platinum precursor flow rates: it increases with increasing flow rate. Moreover, cross section SEM images of the same layers (Fig. 5(d),(e),(f)), also studied with backscattered electrons, show the presence of platinum clusters at the interface between Si wafer and the deposited film. Hence, whether co-deposition of Pt and Ce on Si wafer allows obtaining Pt<sup>2+</sup> ions in ceria films, platinum particles are anyway present at the substrate surface. This point can be explained by the fact that, on silica, the platinum precursor decomposition, i.e. the platinum growth, may be faster than the cerium oxide one, leading to an agglomeration of platinum at the interface. When ceria growth finally occurs, deposit conditions change for platinum leading to the formation of  $Pt^{2+}$ . This behavior could explain the presence of Pt<sup>2+</sup> when platinum is deposited on top of cerium oxide. Pt<sup>2+</sup> should be mainly located at the interface between metallic platinum particles and cerium oxide layer. During the germination of platinum clusters, platinum might react with cerium oxide causing the oxidation of platinum: co-deposition allows increasing the interaction between growing platinum and cerium oxide thereby increasing nonmetallic to metallic platinum ratio. Besides, the platinum precursor flow rate controls the loading of platinum but also influence the platinum chemical state. As the higher Pt<sup>2+</sup>/Pt ratio is observed for the lower platinum precursor flow rate (Fig. 4), it seems that the possible embedding of platinum in ceria has a major role in Pt<sup>2+</sup> formation.

Cerium 3d core level spectra for the three samples elaborated with different platinum precursor flow rates are presented on Fig. 6. Ce3d core level spectrum is centered at around 900 eV and presents a complex shape. Six peaks corresponding to three pairs of spin–orbit doublets can be identified in the Ce3d spectrum of CeO<sub>2</sub> reference (Fig. 6(d)) characteristic of Ce<sup>4+</sup> states [35] and two pairs of 3d<sub>5/2</sub>– 3d<sub>3/2</sub> spin–orbit doublets characteristic of Ce3 + states appear in the Ce3d spectrum of Ce<sub>2</sub>(WO4)<sub>3</sub> reference (Fig. 6(e)). These states arise



Fig. 4. Relative amounts of platinum and cerium (in black) and of Pt<sup>2+</sup> and Pt species (in gray) in co-deposited thin films on Si substrates as function of the platinum precursor flow rate.



Fig. 5. Backscattered electrons SEM images of Pt and CeO<sub>2</sub> co-deposited thin films on Si substrates with different platinum flow rates. (a) and (d) 1.0 g·min<sup>-1</sup>, (b) and (e) 0.50 g·min<sup>-1</sup>, and (c) and (f) 0.25 g·min<sup>-1</sup>.

from different Ce4f level occupancies in the final state and have been widely discussed [36,37]. It is quite difficult to obtain a quantification of the relative amount of  $Ce^{3+}$  and  $Ce^{4+}$  through a fitting of the Ce3d peak but it is clear that the presence of  $Ce^{3+}$  in addition to  $Ce^{4+}$  at the surface of the film can be evidenced by the observation of a shoulder or even a peak at around 885 eV corresponding to the  $Ce^{3+}$   $3d_{5/2}$   $4f^1$   $3d^9$  state in between the  $Ce^{4+}$  peaks at 883 eV and 889 eV corresponding to a mixture of final states  $Ce^{4+}$   $3d_{5/2}$   $4f^2$   $3d^9$  and  $Ce^{4+}$   $3d_{5/2}$   $4f^1$   $3d^9$  [38]. The localization of this  $Ce^{3+}$  state is shown by a dotted line in Fig. 6.

For all three samples, the major contribution corresponds to  $Ce^{4+}$  with a very low contribution of  $Ce^{3+}$ . A small increase of the component corresponding to  $Ce^{3+}$  can be observed on Fig. 6c, that is when the platinum flow rate is the lowest, 0.25 g·min<sup>-1</sup>. This can be linked to the results obtained for Pt4f: in Fig. 4 it was shown that the relative amount of  $Pt^{2+}$  is the highest for the lowest platinum flow rate. Although doping with platinum does not seem to change the chemistry of the cerium oxide which remains mainly  $CeO_2$ , a small reduction occurs in link with the formation of  $Pt^{2+}$  states.

In addition XRD experiments have been performed on thin films elaborated on silicon with and without platinum. For platinum-doped sample a platinum precursor flow rate equal to  $0.25 \text{ g}\cdot\text{min}^{-1}$  was chosen and the cerium precursor flow rate was  $1 \text{ g}\cdot\text{min}^{-1}$  for both



**Fig. 6.** Ce3d X-ray photoelectron spectra for co-deposited thin films on Si substrates prepared with platinum flow rates of  $1 \text{ g-min}^{-1}(a)$ , 0.5  $\text{ g-min}^{-1}(b)$ , and 0.25  $\text{ g-min}^{-1}(c)$ . Reference Ce3d spectra are presented at the bottom: Ce<sup>4+</sup> from a CeO<sub>2</sub> pellet (d) and Ce<sup>3+</sup> from a cerium tungstate Ce<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> (e).

doped and undoped films. Some representative X-ray diffractograms are displayed in Fig. 7. The two diffractograms exhibit, in addition to the peak corresponding to silicon at 55.6°, the ones of  $CeO_2$  fluorite structure [39]. It can thus be inferred, that the two diffractograms of Fig. 7 are characteristic of crystallized  $CeO_2$  films exhibiting no preferential orientation. Moreover the very similar diffractograms observed for undoped and Pt-doped thin films attest that introduction of platinum during the growth does not change significantly the crystalline structure of ceria thin films.

## 3.3. Pt CeO<sub>2</sub> co-deposition on CeO<sub>2</sub> buffer layer

To reduce the platinum loading, a third deposition route was chosen with platinum and cerium oxide deposited during 5 min on a ceria buffer layer. This layer was obtained with a deposition time of 10 min and the total thickness of the sample was 70 nm. The cerium precursor flow rate was  $1 \text{ g} \cdot \text{min}^{-1}$  while the platinum precursor flow rate was  $0.25 \text{ g} \cdot \text{min}^{-1}$  in order to be in conditions allowing higher Pt<sup>2+</sup>/Pt ratio as demonstrated (see Section 3.2). The platinum versus cerium atomic ratio is here equal to about 0.01, comparable to the value obtained for platinum and cerium co-deposited directly on silicon in the same conditions. After such a growth, XPS analysis shows a Pt4f core level exhibiting two doublets with Pt4f<sub>7/2</sub> line at 71.7 eV and 73.2 eV, respectively (Fig. 8). The component at 71.7 eV is related to metallic platinum whereas the second one corresponds to Pt<sup>2+</sup> [31,32]. If compared to the



Fig. 7. X-ray diffraction patterns of CeO\_2 (bottom) and Pt–CeO\_2 thin films co–deposited on Si: x: Si, \*: CeO\_2, and °: Pt.



Fig. 8. Pt 4f X-ray photoelectron spectrum of Pt and CeO<sub>2</sub> thin films co-deposited on CeO<sub>2</sub> buffer layer.

previous depositions, the doublets are shifted [13,27]. This shift should be explained by a very small size of the particles. Indeed it is known that, for metallic nanoparticles in interaction with an oxide, a decrease in the size induces a core level shift towards higher binding energy [40]. This has been explained by both initial and final state effects such as strain in the nanoparticle for the first one and different screening of the core hole for the second [41].

The decomposition of the Pt4f spectrum shows that the Pt<sup>2+</sup>/Pt ratio is 0.85, i.e. a value close to the one obtained for platinum and cerium codeposited in the same conditions directly on silicon (previous section). Fig. 9 shows surface and cross-section backscattered electrons SEM images of the deposit. It is clear that the porosity of the layer is not changed but no particle is now observed at the interface. Although XPS experiments clearly evidence the presence of platinum at the surface of the deposit. Indeed, when co-deposition is performed on silicon, platinum agglomerates at the interface between silica and cerium oxide. It is no more the case when co-deposition is performed on a CeO<sub>2</sub> buffer layer: the faster growth of platinum on silicon if compared to the one on cerium oxide is no more present and no platinum clusters can be observed at the substrate interface. Platinum might still react with cerium



Fig. 9. Backscattered electrons SEM images of Pt and  $CeO_2$  thin films co-deposited on  $CeO_2$  buffer layer: (a) surface morphology, and (b) side view.

oxide allowing obtaining nonmetallic platinum as evidenced by the high  $Pt^{2+}/Pt$  ratio given by decomposition of Pt4f line. No loss of platinum in the form of particles localized at the interface occurs in this case and that, for the same amount of platinum. Actually metallic platinum is now present in very low amount in the sample in the form of very small clusters as attested by SEM results as well as XPS ones.

## 4. Conclusion

Pt-doped cerium oxide films were obtained using chemical vapor deposition methods with [Ce(mmp)<sub>4</sub>] and [MeCpPtMe<sub>3</sub>] as precursors. Indeed the use of liquid injection (DLI-CVD) allows this deposition. XPS and SEM have been performed on the obtained samples and reveal the presence of platinum having two oxidation states: metallic platinum forming clusters and Pt<sup>2+</sup> probably dispersed into or on ceria grains. The ratio between these two platinum states is a function of deposition conditions. If platinum is deposited on top of cerium oxide, the state is mainly metallic even though a low amount of platinum (ca. 10%) is oxidized. If platinum and cerium oxide are co-deposited, the  $Pt^{2+}$  state proportion increases. Besides, the Pt<sup>2+</sup> to Pt ratio is linked to the platinum precursor flow rate in that the lower the flow rate, the higher the ratio is. Moreover, by performing the co-deposition on cerium oxide buffer layer, the global loading of platinum was decreased but without changing the morphology of deposit as well as the amount of platinum detected by XPS, i.e. present in the top most layers of the material. This way seems thus to be effective in order to perform porous films having a high amount of surface Pt<sup>2+</sup> species, especially for low platinum loading.

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## 4.3 Localisation du platine dans les couches minces d'oxyde de cérium dopé

Ce travail avait pour but de tenter de localiser le platine dans les films minces afin de comprendre les mécanismes de croissance. Les résultats ont donné lieu à un article soumis pour publication en août 2016 dans Advanced Materials Interfaces et qui est actuellement en cours de revue.

## Nanoporous Platinum doped Cerium Oxides Thin Films Grown on Silicon Substrates: Ionic Platinum Localization and Stability

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## Abstract

In this study, we report the characterization of nanostructured Pt-doped CeO<sub>2</sub> films with low platinum content and porous structure, deposited on silicon substrate by direct liquid injection chemical vapour deposition. The platinum localization and concentration in the nanocomposite were determined by scanning transmission electron microscopy (STEM) associated with energy dispersive X-ray spectroscopy (EDS). Films are made of ca. 3 nm diameter particles and platinum is homogeneously dispersed through the layers. X-ray photoelectron spectroscopy (XPS) also showed that platinum is mainly in an ionic Pt<sup>2+</sup> state. After diffusion through the preformed ceria films porosity, the platinum precursor decomposes at the surface of each ceria particle forming the films, producing a homogeneous

platinum-doped CeO<sub>2</sub> nanocomposite. This result was supported by synchrotron radiation XPS experiment where the measured relative Pt concentration demonstrated that platinum is decomposed only at the surface of ceria particles. Finally, when the saturation of  $Pt^{2+}$  sites at the surface of ceria particles is reached, metallic nanoclusters are formed from platinum excess.

## 1. Introduction

In recent years, ceria based materials have been widely studied as catalysts for CO oxidation<sup>[1–3]</sup> or as electrolyte materials for fuel cells<sup>[4]</sup> and as supports for heterogeneous catalytic reactions<sup>[5,6]</sup>. As cerium can be present in two stable oxidation states (Ce<sup>3+</sup> and Ce<sup>4+</sup>) which allow it to undergo oxidation and reduction relatively easily<sup>[5,7]</sup>, cerium oxide act as an efficient oxygen storage component<sup>[8,9]</sup>. When combined with platinum, the system exhibits excellent catalytic properties for a variety of reactions: CO oxidation<sup>[10]</sup>, hydrogen production<sup>[11]</sup>, and decomposition of methanol<sup>[12]</sup>. Previously, it has also been shown that when used as an anode material for proton exchange membrane fuel cells, Pt-doped cerium oxide thin films deposited on carbon nanotubes exhibit very high specific power (up to 30 W/mg Pt)<sup>[13]</sup>.

An important issue concerning the development of platinum based catalysts is to reduce the Pt loading in the catalyst layers. In order to maximize the catalyst efficiency, Pt should be dispersed and located at the very surface of the layer only. Recently, density functional theory calculations have predicted that atomically dispersed platinum is stabilized in specific oxidation state Pt<sup>2+</sup> at the surface of CeO<sub>2</sub> {100} type nanofacets<sup>[14]</sup>. Moreover when Pt is only present in the 2+ state, Pt-CeO<sub>2</sub> nanofilms reveal very high performances as anode catalyst for fuel cells and allow enhanced hydrogen molecule dissociation as compared to metallic platinum<sup>[15]</sup>.

This study was made in the context of a recent approach which consists in the development of fuel cells on silicon substrates to be used as on-chip miniaturized fuel cells<sup>[16]</sup>. To achieve a high catalytic yield and improve the use of the catalyst, it is necessary to control the geometry (thickness and porosity) of the catalyst layer. Thereby, working on flat silicon substrates may induce difficulties in controlling the morphology and porosity of the catalytic layer. One possibility to obtain porous structures is to work with porous silicon which is generally formed by electrochemical etching (anodic dissolution) of crystalline silicon wafers in hydrofluoric acid-based electrolytes<sup>[17]</sup>. Another possibility is to add an intermediate carbonaceous layer on silicon substrate prior to the deposition of catalyst layer<sup>[18]</sup>. An alternative to these methods which both involve several preparation steps is the direct deposition of porous catalyst thin films on flat silicon substrates.

In a previous study, we demonstrated the possibility of elaborating porous Pt-CeO<sub>2</sub> catalyst layers on silicon substrates, with platinum in the favorable  $Pt^{2+}$  ionic state<sup>[19]</sup> using chemical vapour deposition (CVD) direct deposition. In this paper, using spatially resolved energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) with conventional Al K $\alpha$  X-ray source and synchrotron radiation (SR) source, we propose a growth model of the porous catalyst layers based on the influence of process parameters on the morphology and composition of the films.

## 2. Experimental

The Pt-CeO<sub>2</sub> films were grown on silicon (100) substrates (Si-Mat Silicon Materials, 99.99 %), using a direct liquid injection (DLI) CVD process (Annealsys MC-050) with rapid thermal heating. The films were synthesized using Ce(mmp)<sub>4</sub> (Sigma-Aldrich, SAFC Hitech)
and MeCpPtMe<sub>3</sub> (Sigma-Aldrich, SAFC Hitech) as liquid precursors for cerium oxide and platinum. The detailed experimental setup has been presented in a previous paper<sup>[19]</sup>.

The deposition protocol of the two films presented in this article is a sequential deposition and consists in a deposition of pure cerium oxide by injecting only the cerium precursor, followed by a co-deposition of platinum and cerium oxide. Both samples were elaborated with a total injection time of cerium precursor of 15 minutes. Sample A was elaborated with a Pt precursor injection time of 5 minutes and sample B with a Pt precursor injection time of 2 minutes. Details of the deposition parameters are presented in Table 4.3-1. In addition, sample A was further annealed 10 h under air at 700 °C to study the stability of platinum states in the layer. The annealed sample will be subsequently named sample A-annealed.

TEM experiments were performed on a JEOL JEM 2100F microscope operating at 200 kV. Cross-section samples were mechanically thinned using a Gatan dimple grinder and electron transparency was achieved by argon-ion beam sputtering with a Gatan Precision Ion Polishing System. Crystallographic structures were obtained by means of high resolution (HRTEM) measurements. The platinum concentration in the layers was determined by EDS in scanning mode (STEM) with a 1 nm probe size using a Bruker Quantax X-flash® 5030T SDD spectrometer.

Characterizations of the chemical composition of nanocomposite films were performed by XPS, using Al K $\alpha$  as X-ray source (hv = 1486.6 eV). Electron detection was provided by a hemispheric analyzer CLAM 4 MCD (Thermo VG Scientific). Photoelectrons were collected with an analyzer slit of 2 mm and a pass energy of 20 eV for Ce3d core level spectra and 50 eV for Pt4f and Ce4d core level spectra. The binding energies (BE) were referenced to the Ce4f<sup>0</sup> peak, the binding energy of which was set at 917.0 eV, corresponding to stoechiometric CeO<sub>2</sub>. Photoemission peak areas were determined after a Shirley background substraction<sup>[20]</sup> and Pt4f and Ce4d peak areas were used to calculate the Pt/Ce atomic ratio using the Scofield

photoionization cross-sections<sup>[21]</sup>. Decomposition of platinum spectra were done by fitting the peaks with asymmetrical Lorentzian shapes for metallic platinum peaks and Gaussian–Lorentzian curves with a 30% Lorentzian contribution for non metallic platinum.

In addition, other photoemission experiments were carried out on Matline, a beamline dedicated to photoemission and located at the ASTRID2 synchrotron source present at ISA, the Centre for Storage Ring Facilities (Åarhus). Thanks to the use of a multipole wiggler and of a Zeiss SX700 plane grating monochromator, the usable photon energy range was from 20 to 700 eV. The setup was equipped with a hemispherical Scienta SES-200 electron energy analyser and a micro channelplate as detector. All data were obtained with a pass energy of 75 eV and an exit slit width of 56 µm. Overall resolution was around 0.3 eV at working photon energy i.e. 300 eV. The pressure in the ultra high vacuum chamber was around 5.10<sup>-10</sup> mbar. The use of a synchrotron radiation (SR) source instead of a conventional photon source allows changing the photon energies and thus varying the escape depth of out coming photoelectrons. Experiments on Ce4d and Pt4f core level spectra were performed by adjusting the incident energy to get a comparable photoelectron kinetic energy at these core levels. The incident energy was thus set to 320 eV and 270 eV for Ce4d and Pt4f core level spectra respectively. When compared to conventional experiments using Al K $\alpha$  as X-ray source, the inelastic mean free path (IMFP) of Pt4f photoelectrons in ceria is thus divided by a factor close to 3.7<sup>[22]</sup> i.e. 2.2 nm with K $\alpha$  source and 0.6 nm with SR source.

Parameters	Sample A	Sample B	Sample A annealed
Pure Ce precursor injection time / min	10	13	10
Pt + Ce precursors injection time / min	5	2	5
Mean grain size / nm	3.3	3.1	11.2
Pt/Ce / at.% (EDS)	$1.1 \pm 0.1$	$1.0\pm0.1$	/
Pt/Ce / at.% (XPS, Al K $\alpha$ X-ray source)	1.0	0.6	0.7
Pt/Ce / at.% (XPS, SR source)	5.8	/	/
$Pt^{2+}$ (XPS) / at.%	86	100	68

<u>Table 4.3-1</u>: Summary of the deposition parameters and associated mean grain size and Pt and Pt<sup>2+</sup> relative atomic concentrations obtained by EDS and XPS measurements.

## 3. Results and discussion

The TEM cross section images of the two Pt-CeO<sub>2</sub> thin films deposited on silicon substrates with two different platinum precursor injection times are shown in Figure 4.3-1(a) and (b). The morphologies of both Pt-CeO<sub>2</sub> films are very similar. On the cross-section views, the layers exhibit a rather homogenous structure with a sharp interface towards the Si substrate. The layer thicknesses have been measured and are around 65 nm for sample A and 50 nm for sample B.

At the layer/substrate interface, for both samples a darker contrast is visible (Figure 4.3-1(a) and (b)). This contrast is due to the first step of elaboration, in which the layer is grown with a dense structure. This type of dense growth is typical for CVD elaboration<sup>[23]</sup>. The dense part of the layer is only around 2-3 nm thick. From there, the layers seem very porous and present a columnar grain growth, with intergrain porosity. This observation is in agreement with the results obtained in a previous study<sup>[19]</sup> and shows that the process involved during cerium

oxide deposition by DLI-CVD naturally leads to porous layers with a potential high specific area.



<u>Fig. 4.3-1</u>: TEM cross-section images of Pt-CeO<sub>2</sub> thin films. (a) Sample A (injection of platinum precursor for 5 minutes); (b) sample B (injection of platinum precursor for 2 minutes); (c) Size distribution of cerium oxide grains for samples A and B.

Concerning the platinum insertion in the layers, TEM cross-section views show no evidence of platinum grains for both films whatever the platinum injection time is. Moreover, when compared to pure ceria layers obtained in previous work<sup>[19]</sup>, no modification of the layer morphology is found.

The cerium oxide grain size has been measured on TEM images and is in the range 1.8-5.9 nm for both samples (Figure 4.3-1(c)). The distribution size is centered on 3.3 nm for sample A and 3.1 nm for sample B. The measured mean grain sizes are summarized in Table 4.3-1. High resolution TEM was used to characterize the crystallographic structure of the layers. HRTEM observations show that both films are well crystallized. Figure 2 shows the shape of one particle at the upper part of sample A. Measurements of interplanar distances and angles between crystallographic planes indicate that the crystallites are cerium dioxide CeO<sub>2</sub> ones. This is consistent with XRD analysis shown in a previous study<sup>[19]</sup>. Moreover, the CeO<sub>2</sub> particles, which are present at the surface of the film, expose {111} planes (with an interplanar distance equal to 0.317 nm). As shown in Figure 2, this peculiar orientation allows the presence of {100} nanofacets at the surface of the films. It is important to underline that theses CeO<sub>2</sub> nanofacets were predicted by DFT calculation to be able to stabilize platinum atoms in specific oxidation state Pt<sup>2+[14]</sup>.



<u>Fig. 4.3-2</u> : HRTEM image at the upper part of sample A. The crystallized grain is identified to CeO<sub>2</sub> aligned along [101] zone axis. The distances and angles are  $d_1 = d_2 = 0.317$  nm;  $d_3 = 0.274$  nm;  $d_1d_2 = 70^\circ$ ,  $d_2d_3 = 54^\circ$ . The grain exhibits several {100} type nanofacets.

To determine the platinum loading and localization, EDS measurements in STEM mode have been performed on both samples. Several points and linescan acquisitions show that the platinum concentration is homogeneous for both layers. Figure 4.3-3 shows an example of an EDS-STEM linescan image associated with Pt and Ce relative atomic concentration profiles. The Pt and Ce profiles exhibit a constant concentration along the layer's depth. When comparing the Pt concentrations for the two sequential depositions, we found out that the same amount of platinum was incorporated, even with different injection times of platinum precursor. The measured relative platinum concentration is around 1 % throughout the volume of both layers. Thus the incorporation of platinum in both layers is very low and corresponds to a total Pt loading calculated from the film thicknesses of 0.53 µg.cm-2 for sample A and 0.41 µg.cm-2 for sample B. Moreover, EDS results show that even when reducing the total platinum precursor injection time during the sample elaboration, it is possible to induce a constant incorporation of platinum in the ceria layer. These results are summarized in Table 4.3-1.



<u>Fig. 4.3-3</u>: (a) STEM-linescan image from sample B and (b) Pt and Ce relative atomic concentration profiling (right part). The white arrow on STEM image indicates the beam path on the sample.

As STEM-EDS experiments provide information on the elemental composition inside the layers, XPS measurements have been performed to characterize the platinum and cerium oxidation states in the upper part of the films. Figure 4 presents the XPS Ce3d, Pt4f and Ce4d core level spectra for the two samples.

In Figure 4.3-4(a) are presented Ce3d core level spectra for the two samples A (bottom-curve) and B (upper-curve) obtained with conventional XPS. Both spectra look very similar consisting mainly of three pairs of spin–orbit doublets arising from different Ce4f level occupancies in the final state<sup>[24,25]</sup>. They can be identified as characteristic of Ce<sup>4+</sup> states<sup>[13,24,26]</sup>. The presence of Ce<sup>3+</sup> in addition to Ce<sup>4+</sup> at the surface of the film, if any, can be evidenced by the observation of a shoulder around 885 eV corresponding to the Ce<sup>3+</sup>  $3d_{5/2}$  4f<sup>1</sup>  $3d^9$  state in between the major Ce<sup>4+</sup> peaks at 883 eV and 889 eV corresponding to a mixture

of final states  $Ce^{4+} 3d_{5/2} 4f^2 3d^9$  and  $Ce^{4+} 3d_{5/2} 4f^1 3d^9$  [27]. It is clear in Figure 4(a) that a small contribution of sub-stoichiometric cerium oxide (Ce<sup>3+</sup>) is present in both samples. However, the presence of an intense peak located at 917 eV, which is the only feature of the spectrum which can unequivocally be assigned to cerium in the 4+ oxidation state, attests that CeO<sub>2</sub> is formed in both layers<sup>[28]</sup>. As no significant differences in the spectra of samples A and B are evidenced, the modification of precursor injection times does not seem to modify the chemistry of the cerium oxide. Moreover, similar results, that is the predominant formation of stoichiometric cerium oxide, have been found when no platinum is incorporated in the cerium oxide layer as shown in previous work<sup>[19]</sup>. Figure 4(b) shows the XPS spectra of Pt4f core level for samples A and B. For both samples, the Pt4f spectrum exhibits a main doublet corresponding to  $Pt4f_{7/2}$  and  $Pt4f_{5/2}$  lines with binding energies respectively of 73.6 eV and 77.0 eV. These binding energies are characteristic of Pt<sup>2+</sup> state<sup>[29]</sup>. However, for sample A with the highest platinum precursor injection time, Pt4f spectrum presents another small spinorbit doublet. It corresponds to Pt4f<sub>7/2</sub> and Pt4f<sub>5/2</sub> lines with binding energies of 71.7 eV and 75.0 eV which both exhibit an asymmetry at high binding energy. This contribution is characteristic of the presence of metallic platinum<sup>[30]</sup>. The concentration of metallic and oxidized platinum at the surface for sample A has been determined from areas of Pt<sup>0</sup> and Pt<sup>2+</sup> decomposition on Pt4f spectrum. The Pt<sup>2+</sup> concentration is 86 % at the surface of sample A. Despite the presence of metallic platinum, Pt4f spectra reveal that, for both samples, the platinum present at the surface of the layers is mostly in Pt<sup>2+</sup> specific oxidation state.

Figure 4(c) shows the XPS spectra of Ce4d core level for the two samples. They look very similar, and several distinct features can be identified. The two highest binding energy peaks localized at 122.6 and 125.9 eV can be assigned to Ce4d<sub>5/2</sub> and Ce4d<sub>3/2</sub> respectively, in fully oxidized CeO<sub>2</sub><sup>[31,32]</sup>. The spin-orbit splitting is 3.3 eV.

The relative platinum concentration ratio has been calculated from XPS measurements to compare concentrations in the upper part of the film with volume concentrations obtained by EDS (Table 4.3-1). It was determined from global areas of XPS Pt4f (Figure 4.3-4(b)) and Ce4d (Figure 4.3-4(c)) spectra. The relative Pt concentration was found equal to 1.0 % for sample A and 0.6 % for sample B when using an Al K  $\Box$  photon source.



<u>Fig. 4.3-4</u>: (a) XPS Ce3d core level spectra of sample A (bottom part, sequential deposition  $10^{7}$ ) and sample B (upper part, sequential deposition  $12^{7}$ ). (b) XPS Pt4f core level spectra of samples A and B. The decomposition of Pt4f spectra are represented as dotes lines and the associated envelopes are sureimposed to the spectyra. (c) XPS Ce4d core level spectre of samples A and B.

In addition, SR XPS measurements have been performed on sample A. The results are summarized in Table 4.3-1. Figure 4.3-5 shows Ce4d and Pt4f core level spectra that have been recorded at 320 eV and 270 eV respectively. The escape depth for photoelectron is thus reduced by a factor around 3.7 as compared to Al K $\alpha$  X-ray source, and the spectra are representative of the very top of the film. The kinetic energy scales in the figure are not corrected for charging effects or for the work function of the sample. Ce4d spectrum is similar

to the one obtain by conventional XPS, and presents the two peaks corresponding to Ce4d5/2 and Ce4d3/2 in stoichiometric CeO2 respectively localized at 195.0 eV and 191.7 eV in kinetic energy; this corresponds to a spin-orbit splitting of 3.3 eV, which is consistent with experiments obtained by conventional XPS. As previously, Pt4f spectrum also presents two pairs of spin-orbit doublet which have both a splitting of 3.3 eV. They correspond to Pt2+ and Pt<sup>0</sup> contributions. Once again, the concentration of metallic and oxidized platinum has been determined from Pt4f spectrum decomposition. The measured Pt2+ concentration is now 82 % at the extreme surface of sample A. This result is consistent with measurement made by conventional XPS. The relative Pt concentration has also been determined from global Pt4f and Ce4d spectra areas and is now equal to 5.8 % whereas it was found equal to 1% with conventional XPS experiments.



Fig. 4.3-5 : (a) Ce4d spectra on sample A, primary photon energy: 320 eV. (b) Pt4f spectra on sample A, primary photon energy: 270 eV.

The preparation of platinum-doped cerium oxide thin films by DLI-CVD using different protocols leads to very similar layers, in both morphology and chemical composition, as it can be seen in Table 4.3-1. Indeed, regardless of the platinum precursor injection time, both grain size and platinum content in the volume are alike. Moreover, even though the platinum precursor was injected after a prior deposition of cerium oxide, platinum is found throughout the whole layer. EDS measurements of Pt content in the layer volume and XPS measurements of Pt content at the layer surface are in a rather good agreement and show that Pt incorporation is nearly the same for both injection times. However, some differences should be underlined: The Pt relative concentration is slightly lower at the surface when platinum injection time decreases (sample B) and sample B presents only ionic Pt<sup>2+</sup>, sample A having, in addition, a small metallic platinum contribution at the surface. Moreover, when decreasing the incident photon energy for XPS experiments, and thus probing only a very small depth on the film, we observed that the relative Pt concentration increases by a factor 5 for sample A. EDS measurements allow to probe the elementary composition of the films, according to linescans spectrum acquisitions through the deposit depth. As the transmitted electron beam goes through the whole cross section, i.e. more than one hundred of nm, it passes through several particles and particle boundaries and thus an average value of the platinum content inside the whole depth of the layer is obtained. With this measurement way, platinum relative concentration is found homogeneous and equal to 1 % throughout the whole layer depth, from the surface to the interface with the substrate. This observation is true for each film whatever the platinum precursor injection time. The presence of platinum in the whole layer depth, even in the part of the ceria film grown before injection of platinum precursor, comes thus likely from the diffusion of platinum precursor through the preformed ceria grains. We can thus assume that the cerium oxide films initially develop a high porosity.

Conventional XPS measurements (i.e. with Al K $\alpha$  X-ray source) show a similar Pt relative concentration at the surface of the films. However, when considering the incident photon energy and the material, the Pt4f photoelectron escape depth, guessed equal to 3 IMFP, is around 6.7 nm<sup>[22]</sup>. Considering now the cerium oxide particles mean size, which is around 3.2 nm for both samples, we can assume that conventional XPS signal with Al K $\alpha$  X-ray source is representative of more than the first particle layer in the film. The measured Pt relative concentrations are therefore not representative of the concentration in the top most atomic layers but correspond to an analysis on at least an entire particle. It is thus consistent to find with Al K $\alpha$  X-ray source, a relative Pt concentration similar to the one determined by EDS in the entire film.

However, SR XPS measurements with lower incident photon energy have shown that the relative Pt concentration is increased up to 5.8 % as compared to conventional XPS for sample A. One should point that with SR photon beam, the analysis thickness is here decreased far below the size of a single particle. Indeed, in this case, one can estimate that the IMFP of Pt4f photoelectrons is around 0.6 nm<sup>[22]</sup>. This value is very close to the actual lattice constant of nanocrystalline ceria with particle size around 3 nm which is around 0.56 nm<sup>[33]</sup>. That means that with this photon incident energy the measurement is extremely sensitive to the top most atomic layers of the material. As the Pt relative content strongly increases when the probing depth decreases from the entire particle to its top most atomic layers only, we can conclude that the spatial distribution of Pt through the particle is not homogeneous and, more precisely, we can assume that Pt is rather localized at the surface of the ceria particles instead of in their volume.

Besides, we have determined that the platinum is mostly in  $Pt^{2+}$  ionic state, which is consistent with the presence of {100} type nanofacets at the surface of the ceria grains<sup>[14]</sup>. However, one can notice that while sample A presents a small metallic Pt contribution, platinum in sample B consists only of ionic platinum. For sample A, as only 84 % of total platinum is in  $Pt^{2+}$  state, 0.84 %  $Pt^{2+}/Ce$  relative concentration is reached (sample A). For sample B, 100 % of the platinum is in  $Pt^{2+}$  state, which corresponds to a  $Pt^{2+}/Ce$  relative concentration of 0.6 %. As a consequence, when the platinum precursor injection time is increased by a factor 2.5 (from 2 to 5 minutes), the  $Pt^{2+}/Ce$  relative concentration is only increased by a factor 1.4 (from 0.6 to 0.84 %). These observations may be consistent with the fact that the saturation of  $Pt^{2+}$  available sites at ceria particles surface is reached for sample A. When the saturation is obtained, the decomposition of platinum precursor excess leads then to the formation of metallic platinum. However, as no evidence of metallic platinum particles was revealed in the layers by HRTEM, we can assume that in such case, nucleation of Pt metallic nanoclusters leads to very small size of particles, unrevealed by HRTEM.

To support this hypothesis, we performed an annealing under air, at 700 °C and under ambient pressure on sample A. In these conditions, metallic platinum is the thermodynamically stable species, according to Ellingham diagram, as compared to pure platinum oxide<sup>[34]</sup>. Figure 4.3-6 shows the evolution of XPS Pt4f core level spectra of sample A after annealing. The spectrum still presents two spin orbit doublets corresponding to Pt<sup>2+</sup> and Pt<sup>0</sup> species. We can also observe that the metallic contribution has increased from 14 % to 32 % after annealing. However, as the ionic platinum was not totally reduced to metallic platinum, it means that ionic platinum is still the most stable species in this system. The origin of the ionic platinum amount decrease is thus not the temperature.



Fig. 4.3-6: XPS Pt4f core level spectra of samples A and sample A-annealed. The decomposition of Pt4f spectra are represented as dotted lines and the associated envelopes are superimposed to the spectra.

To go further, the morphology of sample A after annealing was characterized by TEM crosssection measurement leading to the image presented on Figure 4.3-7 where the grain size distribution is also showed. We can observe that after annealing there is a significant increase in the average grain size, from 3.3 nm to 11.2 nm. This corresponds to a significant decrease of the surface area. The decrease of the Pt<sup>2+</sup> proportion at the surface of the film can thus be correlated to this decrease of the surface area. As the surface/volume ratio decreases when the particle diameter increases, the number of specific sites able to stabilize Pt<sup>2+</sup>, at the surface of ceria particles decreases according to Bruix et al.<sup>[14]</sup>. This observation is thus an indirect evidence of the stabilization of ionic platinum at the surface of ceria particles.



<u>Fig. 4.3-7</u>: (a) TEM cross-section images of sample A after annealing. (b) Size distribution of cerium oxide grains.

From all these observations, a growth model for the Pt-CeO<sub>2</sub> layers grown by DLI-CVD with a sequential deposition can be proposed, as summarized on Figure 8. After injection of CeO<sub>2</sub> precursor (Figure 4.3-8(a)), a porous cerium oxide thin film is formed. During platinum precursor injection mixed with CeO<sub>2</sub> precursor (Figure 4.3-8(b)), it is very likely that both CeO<sub>2</sub> and platinum precursors diffuses throughout ceria grain porosities. Every ceria particles go onto grow, but as the platinum precursor also reacts at the whole surface developed by ceria grains, cationic Pt<sup>2+</sup> species occur on their surface (Figure 4.3-8(c)). The preferential formation of ionic Pt<sup>2+</sup> species rather than metallic platinum can directly be linked to the presence of CeO<sub>2</sub> surface {100} nanofacets (Figure 4.3-2) which are known to be the anchor of Pt<sup>2+</sup> species. Then, when the saturation of Pt<sup>2+</sup> available sites on the surface is reached, either by an excess introduction of precursor or by the removal of these surface sites, platinum excess precipitates as metallic nanoclusters.



<u>Fig. 4.3-8</u>: Growth model for the formation of porous Pt-doped CeO<sub>2</sub> thin films by DLI-CVD with a sequential deposition. (a) Injection of pure CeO<sub>2</sub> precursor and formation of porous ceria layer. (b) Injection of mixed CeO<sub>2</sub> and Pt precursors and their diffusion through the preformed ceria layer. (c) Formation of  $Pt^{2+}$  species due to the decomposition of Pt precursor at the surface of CeO<sub>2</sub> particles.

## 4.Conclusions

Pt-doped cerium oxide catalyst films were prepared by DLI-CVD sequential deposition. TEM analyses reveal that the processes involved during deposition on silicon substrate lead naturally to porous layers with columnar structure. The columns are composed of well crystallized particles in 2-4 nm size range and present intergrain porosity. The obtained layers are homogeneous and present well defined interface with the Si substrate without addition of intermediate layer prior to deposition. The injection of platinum leads to mostly cationic platinum in Pt<sup>2+</sup> oxidation states. This may be explained by the presence of nanofacets with adequate orientation at the surface of ceria grain, which can be the anchor of Pt<sup>2+</sup> platinum can be obtained. Moreover, the platinum incorporated during elaboration is found homogeneously dispersed in the whole layer even in the preformed CeO<sub>2</sub> part of the layer and no rupture in the structure is observed. This can be explained by the diffusion of platinum precursor

throughout the ceria film porosity during platinum precursor injection and the incorporation of ionic platinum only at the surface of  $CeO_2$  particles.

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## 4.4 Conclusion

Des films minces d'oxyde de cérium dopé au platine ont été obtenus par DLI-CVD par dépôts séquentiels. Les différents dépôts réalisés ont permis d'obtenir des films poreux, le dopage en platine ne modifiant pas la morphologie par rapport aux films non dopés. Par ailleurs, les caractérisations chimiques ont permis de montrer que l'injection simultanée de cérium et de platine permet d'obtenir du Pt<sup>2+</sup> à la surface des particules composant le film. Cet état d'oxydation peut être expliqué par la présence, en surface des particules d'oxyde de cérium, de nanofacettes ayant une orientation adéquate à la stabilisation du platine cationique<sup>67</sup>.

<sup>&</sup>lt;sup>67</sup> A. Bruix, Y. Lykhach, I. Matolínová, A. Neitzel, T. Skála, N. Tsud, M. Vorokhta, V. Stetsovych, K. Ševčíková, J. Mysliveček, R. Fiala, M. Václavů, K. C. Prince, S. Bruyère, V. Potin, F. Illas, V. Matolín, J. Libuda, K. M. Neyman, Angewandte Chemie International Edition. 53 (2014) 10525 – 10530.

# 5 Cas particulier de l'oxyde de titane dopé au platine

Le chapitre précédent a montré que l'état d'oxydation du platine peut être modifié en fonction du type de dépôt choisi, « séquentiel » ou non, et que le platine injecté au cours des dépôts réagit préférentiellement avec les clusters de platine métallique déjà formés. Cela entraîne une diminution du rapport Pt<sup>2+</sup> / Pt lorsque le flux de la solution de précurseur de platine augmente.

Dans ce chapitre, l'oxyde de cérium est remplacé par de l'oxyde de titane afin d'étudier le comportement du platine vis-à-vis d'un autre oxyde.

## 5.1 Choix du précurseur de titane

L'oxyde de titane est un matériau utilisé en catalyse et en photocatalyse pour son coût peu onéreux et sa non-toxicité. De plus, lorsqu'il est dopé par un métal noble ses propriétés catalytiques sont accrues. C'est pour ces raisons qu'il a été choisi pour remplacer l'oxyde de cérium.

Le précurseur retenu pour cette étude est l'isopropoxyde de titane (TTIP) (Figure 5.1-1) car il s'agit d'un précurseur peu onéreux, largement utilisé, permettant d'obtenir des couches poreuses et déjà étudié au sein de l'équipe lors de travaux antérieurs<sup>68,69,70</sup>.

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Figure 5.1-1 : molecule de TTIP

# 5.2 Croissance du dioxyde de titane dopé au platine

Cette étude porte sur la croissance de dioxyde de titane dopé au platine. Les résultats ont été publiés dans Thin Solid Films en 2015.



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# Nanostructured Pt–TiO<sub>2</sub> composite thin films obtained by direct liquid injection metal organic chemical vapor deposition: Control of chemical state by X-ray photoelectron spectroscopy



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#### ABSTRACT

Nanostructured Pt–TiO<sub>2</sub> composite thin films were synthesized by direct liquid injection metal organic chemical vapor deposition process, using trimethyl(methylcyclopentadienyl)platinum and titanium isopropoxide as precursors. Surface and cross-sectional morphologies obtained by scanning electron microscopy and transmission electron microscopy evidenced the uniform distribution of platinum nanoparticles in the TiO<sub>2</sub> matrix. At higher Pt content, the X-ray diffraction analysis showed that the face-centered cubic phase of platinum appeared together with an anatase TiO<sub>2</sub> structure. In addition, as far as the platinum chemical state is concerned, the co-deposition of TiO<sub>2</sub> and Pt allowed obtaining Pt<sup>2+</sup> or Pt<sup>o</sup>, in a ratio strongly dependent on the Pt content. Indeed, X-ray photoelectron spectroscopy characterization evidenced the presence of only Pt<sup>2+</sup> for lower Pt content and only Pt<sup>o</sup> for higher one. The variation of platinum content in the TiO<sub>2</sub> films resulted in a change of the chemical state of platinum.

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#### 1. Introduction

Semiconductor photocatalysis has received much attention during the last decades as a promising solution for energy generation such as hydrogen production. When a metal is in contact with the semiconductor, the photocatalytic efficiency is greatly enhanced [1–3].

Although a large number of materials for hydrogen production has been recently reported on semiconductor oxides [4,5], sulfides [6,7], and nitrides [8,9], titanium dioxide (TiO<sub>2</sub>) is proven to be an attractive catalyst due to its large availability, cheapness, stability and nontoxicity [10–12]. Nevertheless, its wide band gap allows appreciable photocatalytic activity only under UV light irradiation and the fast electron-hole recombination decreases the photocatalytic efficiency [13,14].

The availability and separation of photogenerated charges in photocatalytic materials are key issues which can be improved by loading noble metal. Indeed,  $TiO_2$  modified by noble metal nanoparticles still remains the model system for  $H_2$  production. Several noble metals have been used as titania co-catalyst, looking for the best photocatalytic performance [15,16]. The main reason of this behavior relies on the separation of photogenerated charge carriers generally attributed to the

formation of a Schottky barrier at the metal/TiO2 interface. This barrier facilitates electron capture and therefore hinders the recombination between electrons and holes [17,18]. Among noble metals, platinum (Pt) is one of the most active for photocatalytic enhancement TiO2 activity. In early work, Bamwenda et al. [19] reported on the photocatalytic effects of Au and Pt nanoparticles on TiO<sub>2</sub>. The hydrogen production from water/ethanol solution was more improved by platinum deposition on TiO2 than by gold deposition. Vorontsov and Dubovitskaya [20] investigated photocatalytic oxidation of ethanol at different Pt concentrations on TiO2 surface: the presence of Pt-TiO2 nanoparticles increased the ethanol photo-oxidation rate by twice compared to pure TiO2. A very small amount of platinum is sufficient for photocatalytic activity. Indeed, Li and Li [21] reported that 0.75 wt.% of platinum in TiO<sub>2</sub> film allowed photocatalytic activity in the degradation of methyl blue and methyl orange. However Pt-TiO2 photocatalyst performance is strongly dependent on the quantity, structure and electronic state of Pt in TiO<sub>2</sub> film.

Not many works on Pt–TiO<sub>2</sub> films by chemical vapor co-deposition have been reported [22]. Trimethyl(methylcyclopentadienyl)platinum which is used in atomic layer deposition [23–26] and CVD [27–29] processes for deposition of Pt nanoparticles supported on different materials and of Pt thin films was chosen in this work. In the present paper, we report on the synthesis of nanostructured Pt–TiO<sub>2</sub> composite thin films on silicon substrates using direct liquid injection metal organic chemical vapor deposition process (DLI-MOCVD). Titanium tetraisopropoxide

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#### Table 1

Experimental conditions used for DLI-MOCVD elaboration of nanostructured  $\rm Pt-TiO_2$  composite thin films.

Working pressure (mbar)	10
Substrate temperature (°C)	400
MeCpPtMe <sub>3</sub> solution concentration in anhydrous cyclohexane (mol $\cdot l^{-1}$ )	$10^{-3}$
MeCpPtMe₃ flow rate (g·min <sup>-1</sup> )	0.5 - 2
TTIP solution concentration in anhydrous cyclohexane (mol·l <sup>-1</sup> )	0.2
TTIP flow rate (g·min <sup>−1</sup> )	0.2
Deposition time (min)	6
$O_2$ gas flow (sccm)	600
N2 carrier gas flow (sccm)	1000

and trimethyl(methylcyclopentadienyl)platinum were used as metallic precursors. The effect of Pt content in the nanocomposite films on morphology, crystallinity and chemical state of platinum was investigated.

#### 2. Experimental procedure

Nanocomposite Pt-TiO<sub>2</sub> thin films were grown by direct liquid injection metal organic chemical vapor deposition. The experimental set-up was composed of a cold wall reactor, direct liquid injection system and infrared lamps for rapid thermal heating [30]. Oxygen  $(O_2)$ and nitrogen (N<sub>2</sub>) were used as reactive and carrier gasses, respectively. The precursors were titanium tetraisopropoxide (TTIP, Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>, Strem, 99.99%) and trimethyl(methylcyclopentadienyl)platinum (MeCpPtMe3, (CH3)3(CH3C5H4)Pt, Strem, 99%) which were dissolved in anhydrous cyclohexane (C<sub>6</sub>H<sub>12</sub>, Sigma Aldrich, 99.99%) in order to obtain 0.2 M and  $10^{-3}$  M concentrations, respectively. The titanium and platinum precursor solutions were kept in vessels at room temperature and pressurized under 3.5 bar in N<sub>2</sub> atmosphere. The MOCVD chamber was pumped down to  $6.10^{-2}$  mbar and the working pressure was 10 mbar, using a dry pump and a regulated valve. The deposition was performed by injecting simultaneously the two precursors at the temperature of 400 °C under an O2 flow rate of 600 sccm with different flow rates of platinum precursor. The different parameters used for elaboration are summarized in Table 1.

X-ray diffraction (XRD) was used to investigate the crystallographic structure of the films. XRD patterns were obtained by an INEL CPS-120 curved detector, at an incidence of 2° using Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm). The crystallite size determination was performed



Fig. 1. XPS depth profiles of 150 nm Pt-TiO<sub>2</sub> film elaborated at 400 °C with  $F_{Pt} = 1 \text{ g} \cdot \text{min}^{-1}$ .



**Fig. 2.** X-ray diffraction patterns of nanostructured Pt–TiO<sub>2</sub> composite films elaborated at 400 °C with a platinum precursor flow rate of (a) 0.5, (b) 1 and (c)  $2 \text{ g} \cdot \text{min}^{-1}$ . Insert shows the XRD patterns in the (111)Pt plane.

with a commercial software TOPAS, using a modified Thompson–Cox–Hastings pseudo-Voigt function [31].

The morphology of the films was characterized by field-emission scanning electron microscope (FE-SEM, JEOL 7600F) working at 15 kV. Nanostructured Pt–TiO<sub>2</sub> films were also investigated by transmission electron microscopy (TEM) using a JEOL 2100 FEG operating at 200 kV. Cross-section samples were mechanically thinned using a Gatan dimple grinder and electron transparency was achieved by argon-ion beam sputtering with a Gatan Precision Ion Polishing System. The crystallographic structure was studied by High Resolution TEM (HRTEM). Images were acquired with a GATAN Ultrascan camera.

X-ray photoelectron spectroscopy (XPS) depth profiles and characterizations of the chemical states of Pt–TiO<sub>2</sub> films were performed using a Thermo VG Scientific. Photoelectrons were excited by an Al K $\alpha$  radiation (1486.6 eV) and electron detection was provided by a hemispheric analyzer CLAM 4 MCD. Photoelectrons were collected with an analyzer slit of 2 mm and a pass energy of 100 eV for survey spectra and 20 eV



**Fig. 3.** X-ray diffraction patterns of nanostructured  $Pt-TiO_2$  composite film elaborated at 400 °C with a platinum precursor flow rate of 1 g·min<sup>-1</sup> after annealing at (a) 600 °C. (b) As-deposited film.

for more precise acquisition. Argon ion sputtering of 2 kV accelerating voltage was applied to obtain the relative element concentration depth. The sputtering rate was determined to be about 4 nm  $\cdot$  min<sup>-1</sup>. The binding energies were referenced to the Ti2p peak fixed at 459.0  $\pm$  0.1 eV. Photoemission peak areas were determined after smoothing and background subtraction using a Shirley routine. Quantifications were performed by correcting peak areas with relative sensitivity factors: 15.5 for Pt4f and 7.81 for Ti2p.

#### 3. Results and discussion

#### 3.1. Film composition

XPS composition profiles were performed on a 150 nm Pt–TiO<sub>2</sub> film elaborated with  $F_{\rm Pt} = 1 \ g \cdot min^{-1}$  (Fig. 1). Prior to analysis of the depth chemical composition, the surface contamination was removed by ion etching. The depth profiling of the film shows the weak Pt content which was about 1.2 at.%. Titanium and oxygen contents are constant

through the whole film thickness whereas the carbon impurity content was small, below 1 at.%. The ratio between O and Ti atomic contents is about 2, which shows the growth of stoichiometric  $TiO_2$ . At the interface, the small increase of the carbon content can be due to the contamination of the substrate surface. The Pt loading did not change the stoichiometric  $TiO_2$  formation.

#### 3.2. Crystallographic characterizations

XRD was used to characterize the crystalline structure of nanocomposite Pt–TiO<sub>2</sub> films versus platinum precursor (MeCpPtMe<sub>3</sub>) flow rate ( $F_{Pt}$ ). Results are presented in Fig. 2. No peak characteristic of platinum is observed for Pt–TiO<sub>2</sub> film with  $F_{Pt} = 0.5 \text{ g} \cdot \text{min}^{-1}$  (pattern (a) of Fig. 2). This may be due to very weak Pt content. When increasing the MeCpPtMe<sub>3</sub> flow rate ( $F_{Pt} = 1 \text{ and } 2 \text{ g} \cdot \text{min}^{-1}$ ), the XRD patterns show that a weak broad peak appears at 39.8° (patterns (b) and (c) of Fig. 2). This reflection is identified as the (111) plane of the face-centered cubic structure of platinum (file 00-004-0802 in ICCD). The presence of this



Fig. 4. FE-SEM images of nanostructured Pt-TiO<sub>2</sub> composite films elaborated at 400 °C with a platinum precursor flow rate of (a,b) 0.5, (c,d) 1 and (e,f) 2 g·min<sup>-1</sup>. FE-SEM images were taken in (a,c,e) secondary electron mode and (b,d,f) backscattered electron mode.



Fig. 5. FE-SEM cross-section images of nanostructured Pt-TiO<sub>2</sub> composite films elaborated at 400 °C with a platinum precursor flow rate of (a,b) 0.5, (c,d) 1 and (e,f) 2 g·min<sup>-1</sup>. FE-SEM images were taken in (a,ce) secondary electron mode and (b,d,f) backscattered electron.

broad peak in the XRD pattern could indicate that platinum is in the form of nanoparticles dispersed in the film. The TiO<sub>2</sub> matrix is composed only by anatase phase which is revealed by the peaks at  $2\theta$  values of  $25.4^{\circ}$ , 38.7° and 48.2° (file 03-065-5714 in ICDD). All films are textured with an orientation in the (101) direction and the crystallite size is about 50-100 nm, using software TOPAS. In addition, no evident differences are noticed in the texture of the films grown as a function platinum precursor flow rate, as observed by Battiston et al. on the Pt-TiO2 mixed films with different atomic Pt/Ti ratios [22]. For the Pt-TiO<sub>2</sub> film elaborated with  $F_{Pt} = 0.5 \text{ g} \cdot \text{min}^{-1}$ , the XRD peak intensities in the (101) and (200) planes are 3 times larger than the ones for the Pt-TiO2 film elaborated with  $F_{Pt} = 2 \text{ g} \cdot \text{min}^{-1}$ . It seems that the Pt introduction in the TiO<sub>2</sub> films leads to less crystallized TiO<sub>2</sub> anatase phase evidenced by the small intensities of the diffraction peaks. However, the absence of a broad band background in the XRD patterns allows to discard the growth of amorphous TiO<sub>2</sub>. In order to verify this assumption, a Pt-TiO<sub>2</sub> film elaborated with  $F_{Pt} = 1 \text{ g} \cdot \text{min}^{-1}$  was annealed at 600 °C for 30 min in N<sub>2</sub> atmosphere. No changes are observed in the XRD patterns of the annealed film (Fig. 3) indicating the absence of an amorphous phase in the as-deposited films.

#### 3.3. Morphological characterizations

SEM is used to study the surface film morphologies as well as the film cross sections. The presence of platinum nanoparticles (Pt NPs) is evidenced on the film surfaces, when considering images obtained using backscattered electrons thanks to the chemical contrast provided by this technique (Fig. 4(b,d,f)). Cross section SEM images (Fig. 5) demonstrate that Pt–TiO<sub>2</sub> films exhibit a columnar growth with a porous structure and the presence of platinum nanoparticles all along the TiO<sub>2</sub> films. Thus SEM observations show the nanostructuration of the films, which are in good agreement with the XRD and XPS profile results. The nanocomposite film deposited at 400 °C with  $F_{Pt} = 1 \text{ g} \cdot \text{min}^{-1}$  was annealed at 600°C during 30 min in N<sub>2</sub> atmosphere. No change of the film and Pt NP morphology is observed (Fig. 6) after annealing, proving the good stability of the nanocomposite film.



Fig. 6. FE-SEM surface (a,b) and cross-section (c,d) images of nanostructured Pt-TiO<sub>2</sub> composite film after annealing at 600 °C. The nanocomposite was elaborated at 400 °C with a platinum precursor flow rate of 1 g·min<sup>-1</sup>. FE-SEM images were taken in (a,c) secondary electron mode and (b,d) backscattered electron mode.

The TEM cross-section view of the nanocomposite film deposited at 400 °C with  $F_{Pt} = 1 \text{ g} \cdot \text{min}^{-1}$  is shown on Fig. 7. The morphology of the layer is shown in Fig. 7(a). The nanocomposite is grown with a columnar and porous structure. The layer thickness measured is around 145 nm. Fig. 7(a) also exhibits the presence of a lot of small round shaped nanoparticles inside and between the columns, in a good agreement with SEM observations. The diameter size of the particles is in the 1.5–5.5 nm range with a size distribution centered at 2.5  $\pm$  0.8 nm (Fig. 7(b)). Fig. 7(c) shows a HRTEM image of the layer. The film is composed of a well crystallized TiO<sub>2</sub> matrix. Moreover, a crystallized nanoparticle is isible on Fig. 7(c). The measurement of interplanar distances allows one to determine that the crystallite is a platinum particle oriented along a {111} plane. Finally the platinum nanoparticles are well inserted in the TiO<sub>2</sub> films with no void around them.

#### 3.4. Film chemical state characterizations

The chemical state of the nanocomposite Pt–TiO<sub>2</sub> films versus Pt precursor flow rate was investigated by XPS. In particular, a detailed analysis was performed of the Ti2p, O1s and Pt4f binding energy regions (Table 2). Measured binding energies are reported in Table 2 referenced to the Ti2p<sub>3/2</sub> line set at  $459.0 \pm 0.1$  eV. Actually this value is characteristic of Ti element in the chemical state Ti<sup>4+</sup>, which is characteristic of TiO<sub>2</sub> [32–34]. The stoichiometry of TiO<sub>2</sub> is confirmed thanks to the XPS spectra of titanium and oxygen presented in Fig. 8: the Ti2p<sub>3/2</sub> and Ti2p<sub>1/2</sub> peaks are perfectly symmetrical and present a spin–orbit splitting equal to 5.7 eV (Fig. 8(a)) This indicates that the Ti element mainly existed in the chemical state of Ti<sup>4+</sup> in TiO<sub>2</sub>. The O1s XPS spectra are asymmetric (Fig. 8(b)), the left side is wider than the right, indicating that at least two kinds of oxygen species are present. The dominant peak at about 530.2  $\pm$  0.1 eV is assigned to O<sub>2</sub> constituent of TiO<sub>2</sub> [35,

36]. The minor one at 531.2  $\pm$  0.1 eV is related to the presence of Ti–OH species and/or to some surface hydroxyl [37,38].

The XPS spectra of platinum show variations of the Pt4f peak positions versus Pt precursor flow rate (Fig. 9 and Table 2). Indeed, for the nanocomposite film elaborated with  $F_{Pt} = 0.5 \text{ g} \cdot \text{min}^{-1}$ , the Pt4f<sub>7/2</sub> and Pt4f\_{5/2} binding energies are located at 72.7  $\pm$  0.1 eV and 76.1  $\pm$  0.1 eV (spectrum (a) of Fig. 9), respectively. This corresponds to the presence of pure  $Pt^{2+}$  [39,40] with a Pt/Ti ratio of 0.02. As Pt precursor flow rate increases, a binding energy of the Pt4f<sub>7/2</sub> line at 70.9  $\pm$  0.1 eV (spectra (b) and (c) of Fig. 9) is observed. By comparison with the Pt4f spectrum of pure metallic platinum (spectrum (d) of Fig. 9) and with the literature [41-43], this can be assigned to metallic platinum (Pt°) with a Pt/Ti ratio of 0.12. Thus the non-metallic platinum is obtained for lower Pt/Ti ratio (Pt/Ti = 0.02) as evidenced by the only presence of  $Pt^{2+}$  which is essential for catalytic activity of the doped TiO<sub>2</sub> [44]. Metallic platinum is observed for higher Pt/Ti ratio, which would be interesting for an enhancement of the photocatalytic activity of anatase TiO2. For example, Vorontsov and Dubovitskaya evidenced that the addition of metallic platinum to TiO<sub>2</sub> led to optimum photocatalytic performance with Pt/Ti = 1.1 [20]. The metallic Pt NPs are very effective traps for the electrons due to the formation of a Schottky barrier at the metalsemiconductor contact [5,39,43].

The Pt4f<sub>5/2</sub> line in the spectrum of the films deposited with  $F_{Pt} = 0.5 \text{ g} \cdot \text{min}^{-1}$  exhibits a kind of shoulder on higher binding energy (spectrum (a) of Fig. 9). The shape of Pt4f lines can seem strange, which is composed of 3 components. It is impossible for f lines, i.e. for a core level composed of doublets. Actually, the third line located at ~78.7 eV is probably rather an effect of the huge background resulting from the encapsulation of platinum atoms by TiO<sub>2</sub>. This phenomenon increases the number of scattered electrons having lost kinetic energy. Same kind of shape is also recorded in the XPS spectrum of the film elaborated with  $F_{Pt} = 1 \text{ g} \cdot \text{min}^{-1}$  (spectrum (b) of Fig. 9)



**Fig. 7.** (a) TEM cross-section image of nanostructured Pt–TiO<sub>2</sub> composite films elaborated at 400 °C with a platinum precursor flow rate of 1 g  $\cdot$  min<sup>-1</sup>. (b) HRTEM image shows the crystallized TiO<sub>2</sub> film together with a platinum nanoparticle oriented along {111} planes with interplanar distances d = 0.228 nm. (c) Size distribution of platinum nanoparticles.

#### Table 2

Binding energies and atomic Pt/Ti ratios of nanostructured  $Pt-TiO_2$  composite thin films versus platinum precursor flow rate  $(F_{Pe}).$ 

$F_{Pt}(g \cdot min^{-1})$	Pt4f <sub>7/2</sub> (eV)	Ti2p <sub>3/2</sub> (eV)	01s (eV)	Pt/Ti
0.5	$72.7\pm0.1$	$459.0 \pm 0.1$	$529.6 \pm 0.1$	0.02
1	$70.9 \pm 0.1$	$459.0\pm0.1$	$529.5 \pm 0.1$	0.03
2	$70.9 \pm 0.1$	$459.0\pm0.1$	$529.7\pm0.1$	0.12

even though in this case the process is not characterized by a phantom peak.

The Pt–TiO<sub>2</sub> films prepared with  $F_{Pt} = 0.5$  and 1 g·min<sup>-1</sup> were annealed at 500 °C and 600 °C in order to study the behavior of Pt chemical state at high temperatures. After annealing, the Pt–TiO<sub>2</sub> film elaborated with  $F_{Pt} = 1$  g·min<sup>-1</sup> shows that the Pt4f<sub>7/2</sub> peak position is at higher binding energy than that of the as-deposited film. It is around 71.5  $\pm$  0.1 eV (spectra (b) and (c) of Fig. 10). It seems that the



Fig. 8. Ti2p and O1s XPS spectra of nanostructured Pt–TiO2 composite films elaborated at 400 °C with a platinum precursor flow rate of (a) 0.5, (b) 1 and (c) 2 g·min<sup>-1</sup>.



Fig. 9. Pt4f XPS spectra of nanostructured Pt–TiO<sub>2</sub> composite films elaborated at 400 °C with a platinum precursor flow rate of (a) 0.5, (b) 1 and (c) 2 g·min<sup>-1</sup>. (d) XPS spectrum of metallic platinum (Pt°) reference.

metallic platinum would tend towards oxidized species but less pronounced than  $Pt^{2+}$  species upon annealing. In the case of the  $Pt-TiO_2$  film prepared with  $F_{Pt} = 0.5 \text{ g}\cdot\text{min}^{-1}$  (Fig. 11), the annealing at 500 °C does not change the chemical state of platinum which is still  $Pt^{2+}$  (spectrum (b) of Fig. 11), while transformation of  $Pt^{2+}$  to metallic platinum is observed after heat treatment at 600 °C (spectrum (c) of Fig. 11). Thus the annealing conditions allow controlling the platinum chemical state.

#### 4. Conclusions

Nanocomposite Pt–TiO<sub>2</sub> films have been prepared by DLI-MOCVD, using TTIP and MeCpPtMe<sub>3</sub> as precursors. The morphology, the crystalline structure and the chemical state of platinum in the TiO<sub>2</sub> film were investigated versus the Pt content by SEM, XRD and XPS.

SEM and TEM observations exhibit that the Pt nanoparticles are dispersed all along the  $TiO_2$  films. XRD patterns show the face-centered cubic structure of platinum into the anatase  $TiO_2$  phase. Moreover XPS analysis reveals that the presence of  $Pt^{2+}$  and  $Pt^0$  varies as a function of platinum flow rate. When decreasing the platinum precursor flow rate,  $Pt^{2+}$  is mostly observed while the opposite occurs for the higher platinum precursor flow rate. Pt nanoparticles elaborated by DLI-CVD



**Fig. 10.** Pt4f XPS spectra of (a) nanostructured Pt–TiO<sub>2</sub> composite film elaborated at 400 °C with a platinum precursor flow rate of 1 g·min<sup>-1</sup>. The nanocomposite was annealed at (b) 500 °C and (c) 600 °C. (d) XPS spectrum of metallic platinum (Pt°) reference.



Fig. 11. Pt4f XPS spectra of (a) nanostructured Pt–TiO<sub>2</sub> composite film elaborated at 400 °C with a platinum precursor flow rate of 0.5 g·min<sup>-1</sup>. The nanocomposite was annealed at (b) 500 °C and (c) 600 °C. (d) XPS spectrum of metallic platinum (Pt°) reference.

possess small particle sizes with a low degree of agglomeration. In addition the chemical state of platinum present in the form of Pt<sup>2+</sup> or Pt<sup>°</sup> nanoparticles can be controlled by the relative Pt content of the film and by the temperature.

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## 5.3 Conclusion

La DLI-CVD a permis de synthétiser du dioxyde de titane dopé au platine en une seule étape de synthèse. La morphologie des dépôts se caractérise par une croissance colonnaire avec une distribution homogène des particules de platine. Le débit de la solution de précurseur de platine permet de modifier l'état d'oxydation du platine. Un faible débit (0.5 g.min<sup>-1</sup>) permet d'obtenir du platine non métallique Pt<sup>2+</sup> alors qu'un débit plus important (2 g.min<sup>-1</sup>) ne permet d'obtenir que du platine métallique. Le platine non métallique Pt<sup>2+</sup> n'est présent que pour les dépôts dont le débit en platine est très faible contrairement aux dépôts d'oxyde de cérium dopé où le platine non métallique est présent quel que soit le débit de la solution de précurseur en platine.

# 6 Films d'oxycarbure de tungstène

Afin de réduire les coûts de production et de limiter l'utilisation du platine dans le but d'améliorer la gestion de l'épuisement des ressources naturelles, de nombreuses alternatives aux catalyseurs contenant du platine ont été développées<sup>71,72,73,74</sup>.

Ce chapitre se concentre sur la synthèse d'oxycarbure de tungstène, matériaux prometteur de par ses propriétés catalytiques proche de celles du platine.

### 6.1 Choix du précurseur

Les précurseurs pour la synthèse CVD de matériaux à base de tungstène sont nombreux (Tableau 6.1-1) mais certaines contraintes techniques ont proscrit l'utilisation de certains d'entre eux. Le précurseur ne devait pas contenir de composés halogénés pour ne pas endommager le dispositif de dépôt et l'utilisation de dihydrogène était exclue pour des raisons de sécurité. Un des précurseurs envisagés a été l'hexacarbonyle de tungstène, il s'agit d'un précurseur largement utilisé en CVD mais son utilisation en DLI-CVD est limitée par sa faible réaction avec l'oxygène.

Précurseurs	Gaz réactifs	Inconvénients
W(CO) <sub>6</sub> <sup>75</sup>	O <sub>2</sub>	Peu réactif avec l'oxygène
$WX_6^{76}$	O <sub>2</sub> , H <sub>2</sub> , CH <sub>4</sub>	Sous-produits corrosifs
W(OPh) <sub>6</sub> <sup>77</sup>	$O_2$	Non commercialisé

Tableau 6.1-1 : précurseurs pour la synthèse CVD de matériaux à base de tungstène

Par ailleurs, il existe différents précurseurs organométalliques (Tableau 6.1-2). Le choix du précurseur s'est porté sur un composé pouvant réagir avec le dioxygène, ne rejetant pas de

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sous-produits corrosif, ayant une température de dépôt faible ( $300 \text{ }^\circ\text{C} - 800 \text{ }^\circ\text{C}$ ) et étant peu onéreux. Il s'agit du dihydrure biscyclopentadiényle de tungstène IV (Cp<sub>2</sub>WH<sub>2</sub>) (Figure 6.1-1).

Précurseurs			
W(Cl) <sub>2</sub>	Bis(cyclopentadienyl)tungsten(IV) dichloride		
$H_{3C} \xrightarrow{H-W-H} CH_{3}$	Bis(isopropylcyclopentadienyl)tungsten(IV) dihydride		
$H_{3C}$ $CH_{3}$ $H_{3C}$ $CH_{3}$ $H_{3C}$ $CH_{3}$ $H_{3C}$ $CH_{3}$ $H_{3C}$ $CH_{3}$ $H_{3C}$ $CH_{3}$ $H_{3C}$ $CH_{3}$ $CH_{3}$ $CH_{3}$	Bis(t-butylimido)bis(dimethylamino)tungsten(VI)		
t-Bu NH t-Bu−N=W=N−t-Bu NH t-Bu	Bis(tert-butylimino)bis(tert-butylamino)tungsten		
$H_{3}C_{N}^{C}H_{3}$ t-Bu-N=W=N-t-Bu $H_{3}C^{N}CH_{3}$	Bis(tert-butylimino)bis(dimethylamino)tungsten(VI)		

Tableau 6.1-2 : précurseurs organométalliques à base de tungstène



Figure 6.1-1 : molécule de Cp<sub>2</sub>WH<sub>2</sub>

# 6.2 Synthèse d'oxycarbure de tungstène par DLI-CVD

Dans cette étude des couches minces d'oxycarbure de tungstène ont été obtenus sur substrats de silicium et sur grilles MET. Les résultats font l'objet d'une publication en cours de publication.
Direct liquid injection chemical vapor deposition of porous tungsten oxycarbide thin films

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#### Abstract

Thin films of tungsten oxycarbide were grown by direct liquid injection chemical vapor deposition on silicon wafer covered by native oxide using tungsten hydride as precursor. A two steps process has been developed by depositing a dense tungsten oxycarbide layer on a porous tungsten oxide layer. Surface and cross-sectional morphologies obtained by scanning electron microscopy evidenced that porosity of the tungsten oxide layer is temperature dependent. However, oxycarbide deposits obtained at higher temperature on the oxide do not modify the porosity character. X-ray photoelectron spectra evidenced that oxycarbide deposit completely covers the tungsten oxide.

Keywords: platinum alternative, tungsten oxycarbide thin films, chemical vapor deposition, X-ray photoelectron spectroscopy

#### **1. Introduction**

In recent years fuel cells became one of the most attractive technology for energy conversion devices [1-3]. The use of catalyst and more specifically platinum allows to increase the

conversion rate [4-7]. With the growing interest for these technologies the price of platinum increased dramatically and the resource depletion constrained to find an alternative way. One possibility is to develop a non-platinum material as catalyst. It has been shown that tungsten carbide presents the same electronic behavior as platinum but in the last decades only few studies focused on this compound [8-12]. Due to their ability to react with oxygen in air, carbides are easily oxidized. Several studies reported that the reactivity of these modified carbides are changed [13]. Depending on kind of synthesis methods and kind of oxygen occupied sites, catalyst effect on rates of reaction increases or decreases [13-15]. It has been demonstrated that when oxygen atoms replace carbon atoms, that is upon the formation of tungsten oxycarbide, the catalytic activity is enhanced [16].

To increase the surface reactivity and keep the device as compact as possible, the catalyst material has to present a high surface to volume ratio and thus to be porous. Moreover, it is very important to prepare in a controlled way nanostructured tungsten oxycarbide. Different methods have been proposed such as physical vapour deposition or chemical vapour deposition allowing a good control of the physical and chemical properties [10,17,18].

Direct liquid injection chemical vapor deposition (DLICVD) has been chosen in this work for its capacity to produce conform coverage on a large area and porous layers [19-21]. It also allows depositing layers with good thickness controls and using a wide range of precursor. Moreover, to our knowledge, there are no works dealing with tungsten oxycarbide obtained by DLICVD.

Bis(cyclopentadienyl)tungsten(IV) dihydride [Cp<sub>2</sub>WH<sub>2</sub>] has been chosen as tungsten precursor. This compound presents a low deposition temperature  $(300^{\circ}C - 800^{\circ}C)$  with a high chemical stability and non-corrosive by-products [22].

Hence, this study presents different routes to obtain porous tungsten oxycarbide thin films by DLICVD with oxygen and methane as reactive gas. Three different protocols were necessary

to obtain an oxycarbide porous layer. First, thin porous oxide layers were synthesized to control the availability of depositing tungsten with the chosen precursor and control the porosity. Then deposition of oxycarbides was studied. Finally, the combination of the two previous processes was chosen to obtain tungsten oxycarbides with control of the porosity. A two steps deposition route was thus chosen: tungsten oxycarbide was deposited on a previously grown porous tungsten oxide layer. This deposition route was done is a previous work [20] and allows to deposit two different phases from two precursors or two reactive gas different. In this case, to synthesize tungsten oxide, precursor reacted with oxygen. Once the deposit obtained, the reaction chamber was purged to remove residual oxygen. Then, the precursor was injected with methane to obtain oxycarbide.

The morphology and the chemical properties of the films deposited using the different routes were studied by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

#### 2. Experimental

DLICVD experiments were carried out with an Annealsys MC-050 system equipped with a tubular cold wall reactor, a direct liquid injection system Kemstream and infrared lamps for rapid thermal heating of substrates [23]. Tungsten compounds were deposited using a reactor pressure of 10 hPa with  $5.10^{-3}$  mol.L<sup>-1</sup> solution of [Cp<sub>2</sub>WH<sub>2</sub>] (Sigma-Aldrich) diluted in anhydrous cyclohexane (C<sub>6</sub>H<sub>12</sub>, Sigma Aldrich 99.99%).

The layers were elaborated on silicon Si(100) substrates (Si-Mat Silicon Materials, 99.99%) covered by native oxide, at deposition temperatures of 300-800°C. Oxygen and methane were used as reactive gas. The oxygen flow rates (10 -1000 sccm) and methane flow rates (200 or 380 sccm) were tuned in order to obtain tungsten oxides or tungsten oxycarbides. The tungsten precursor solution flow rate was 1 g.min<sup>-1</sup>.

SEM was used to estimate the film thickness and porosity through cross section images and to observe the surface morphology and determinate the grain size of the material. A JEOL 7600F microscope was used, working at 15kV. Transmission Electron Microscopy (TEM) experiments were performed on a JEOL 2100 FEG microscope working at 200 kV. The samples were directly grown on TEM carbon coated copper grids for (EMS CF300-Cu) for direct observation of the morphologies: this avoids long preparations inducing potential sample perturbations

Chemical information was obtained with X ray photoelectron spectroscopy characterizations using an Al K $\alpha$  X-ray source (hv = 1486.6 eV). Electron detection was provided by a hemispheric analyzer CLAM 4 MCD (Thermo VG Scientific). The spectra were referenced to the C1s line of the residual carbon at ca. 285 eV. Photoelectrons were collected with pass energy of 100 eV for survey spectra and 20 eV for more precise acquisition of W4f, O1s and C1s. Photoemission peak areas were determined after background subtraction using a Shirley routine. Decompositions of tungsten and oxygen core level lines were done by fitting the peaks with Gaussian (70%)–Lorentzian (30%) shapes in order to determine the stoichiometry and the oxidation states of the different deposits.

#### 3. Results and discussion

#### 3.1. Deposition of tungsten oxide

In order to determine the parameters allowing obtaining a layer as porous as possible, thin oxide films were deposited at different temperatures (400-600°C) during 15 minutes. The oxygen flow rate was 500 sccm and the precursor solution flow rate was 1.0 g.min<sup>-1</sup>. Those values have been chosen because they allowed obtaining the most porous layers for all deposition temperatures. They also presented a fast growth rate close to 5 nm.min<sup>-1</sup> at 400 °C. Moreover, the low oxygen flow rate has been chosen to prevent a to high oxygen implantation

in the deposits. The SEM observations of the film obtained at 400°C show cauliflower shape microstructure with particles smaller than 10 nm (Fig.1(a)). The deposit obtained at 600°C reveals the presence of nanorods with an average diameter of 50 nm (Fig.1(c)). The thicknesses of the films grown at 400°C and 600°C were respectively 70 nm and 50 nm as determined through SEM cross section experiments (Fig.1(b), (d)). Moreover, it can be noticed that the density of the layer increases with the temperature.



Fig. 6.2.1 - Secondary electron SEM images of tungsten oxide deposited on Si substrates with an oxygen flow rate of 500 sccm. (a) surface and (b) cross section at 400°C and (c) surface and (d) cross section at 600°C.

Concerning the oxidation state of the elements constituting deposits, XPS analyses were performed. Fig.2 presents XPS spectra showing a W4f core level exhibiting one doublet at ca. 35.4 eV for the W4f<sub>7/2</sub> and 37.4 eV for the W4f<sub>5/2</sub> [24]. These binding energy values correspond to W<sup>6+</sup> oxidation state i.e. to tungsten in an oxide such as WO<sub>3</sub>.



Fig. 6.2.2 - W4f X-ray photoelectron spectra for tungsten oxide thin films obtained at 400°C, 500°C and 600°C on Si substrates.

Decompositions of the O1s core levels (not presented here), reveal two components, the first one corresponding to W-O bond at ca. 530.1 eV and the second one to hydroxide or hydrated oxide at ca. 531.5 eV [25]. This study has shown that tungsten trioxide is present in the bulk and the hydrated oxide is on the surface. It was not possible to discriminate the presence of adsorbed hydroxide or the presence of W-OH bond. The hydrated oxide or hydroxide component is explained by the presence of residual pressure of water vapor in the reaction chamber. Oxygen to tungsten ratios were calculated by correcting peak areas by the photoionization cross sections [26] as well as inelastic mean free path according to the following equation (1):

$$\frac{[O]}{[W]} = \frac{A_O \times \sigma_W \times \lambda_W}{A_W \times \sigma_O \times \lambda_O} \tag{1}$$

Where  $A_W$  is the area of the W4f doublet,  $A_O$  is the area of the O1s peak corresponding to oxygen linked to tungsten (the second component in the higher binding energy is not considered here),  $\sigma_W$  and  $\sigma_O$  correspond to the photoionization cross sections and  $\lambda_W$  and  $\lambda_O$ 

correspond to the inelastic mean free paths. The photoionization cross sections of transitions W4f and O1s were taken equal to 0.1449 and 0.04 respectively. The inelastic mean free paths of photoelectrons W4f and O1s are proportional to the square root of the kinetic energy. For each temperature, [O]/[W] ratio is close to 3, confirming the presence of WO<sub>3</sub>. Hence, the modification of the deposition temperature does not change drastically the tungsten chemistry.



Fig. 6.2.3 – (a) High resolution TEM image on one tungsten oxide needle with carbon envelope, (b) corresponding C1s X-ray photoelectron spectrum

Furthermore, Fig. 3 (b) shows a C1s core level spectrum exhibiting two components at ca. 285 eV and at ca. 286.1 eV corresponding respectively to C-C or C-H bond and C-O bond. It reveals a high amount of carbon in the layer. TEM experiments were performed in order to localize the carbon. Fig.3 (a) shows a high resolution TEM image of a WO<sub>3</sub> particle with a needle shape deposited directly on a carbon coated TEM grid. It should be noticed that after deposition, the carbon membrane of the grid is not degraded. The needle length is around 20-30 nm and the diameter is around 5-7 nm. An envelope around the needle is visible as a light grey contour. The contrast and XPS analysis of the sample deposited on silicon substrate suggest that the envelope consists of amorphous carbon.



Fig. 6.2.4 - W4f X-ray photoelectron spectra for tungsten oxide thin films obtained with different oxygen flow rates on Si substrates.

In Fig. 4 are presented W4f core level spectra for samples obtained with different oxygen flow rates. All the layers show one doublet at ca. 35.3 eV for the W4f<sub>7</sub>/2 corresponding to  $W^{6+}$ . The spectrum for the layer obtained without oxygen show two additional doublets at ca. 33.2eV and 34.2eV corresponding respectively to  $W^{4+}$  and  $W^{5+}$  [27]. The presence of tungsten in an oxidized state even in absence of oxygen as reactive gas could be explained by the residual oxygen in the reactor chamber or due to an oxidation in air when going from the growth chamber to the XPS analysis chamber, this analysis being carried out ex-situ.

#### 3.2. Deposition of tungsten oxycarbide

In order to deposit carbides, a preliminary work was done to know what would be the ideal deposition temperature. It has been observed that for a temperature lowest than 600°C no carbide layers were observed. The best growth rate was reached with a deposition temperature of 800°C. Thin carbides films were grown with a deposition temperature of 800°C during 10

minutes using a precursor solution flow rate of 1.0 g.min<sup>-1</sup>. Methane was used as reactive gas with a flow rate of 200 sccm.

SEM observations were not possible on these samples. This is due to the fact that the growth rate was very low without oxygen. With an average detection limit of 10 nm, thin film thicknesses were estimated between 10 and 15 nm.



Fig. 6.2.5 - W4f X-ray photoelectron spectra for tungsten carbide thin film obtained with a methane flow rates of 200 sccm on Si substrates at 800°C. Thin lines correspond to the different components used to obtain the best fit.

Fig.5 presents XPS analysis showing W4f core level exhibiting a main doublet at ca. 31.8 eV and 34.0 eV respectively for the W4f<sub>7/2</sub> and W4f<sub>5/2</sub> lines [10,28]. These components are related to tungsten carbide. An additional doublet is also present at ca. 35.5 eV and 37.9 eV. This doublet shows the presence of an oxidized form of tungsten, WO<sub>3</sub>.

The presence of the oxidized form could be explained by the diffusion of the oxygen atoms from the native oxide of the silicon to the deposit. It should be noticed that no Si2p peaks are evidenced through XPS analyses (not shown here). Moreover, the system works under primary vacuum, the residual oxygen and methane could both react with the precursor to form tungsten oxycarbide. 3.3 Deposition of tungsten oxycarbide on WO<sub>3</sub> porous layer

First, WO<sub>3</sub> thin porous layer was deposited at 400°C during 15 minutes with an oxygen flow rate of 800 sccm and a precursor solution flow rate of 1 g.min<sup>-1</sup>. Then oxycarbide layer was deposited on top of the porous layer at 600°C during 10 minutes with a methane flow rate of 200 sccm and the same precursor solution flow rate. In this case, 600°C was preferred in order to do not affect the porosity of the oxide layer.



Fig. 6.2.6 - Secondary electron SEM images of tungsten oxycarbide deposited at 600°C with a methane flow rate of 200 sccm on porous tungsten oxide obtained at 400°C with an oxygen flow rate of 800 sccm. (a) surface and (b) side view.

Fig. 6 shows surface and cross-section SEM images of a covering oxycarbide tungsten layer on a porous tungsten oxide layer. Fig. 6(a) shows the morphology of the layer with a cauliflower shape with agglomerate particles with a size equal to 15 nm. The thickness of the films is 150 nm as determined through SEM cross section experiments (Fig.6(b)). Compare to the tungsten oxide layer obtain at 400 °C, the morphology of the layer is not modified. The second part of the deposit, obtained at 600 °C, allows conserving the porosity character.



Fig. 6.2.7 - W4f X-ray photoelectron spectra. (a) oxycarbide thin film directly grown on silicon and (b) oxycarbide thin film deposited on WO<sub>3</sub> thin film.

Fig. 7 presents XPS analyses showing a comparison between the W4f core level obtained on anoxycarbide layer directly grown on the Si substrate (Fig.6(a)) and on WO<sub>3</sub> thin film (Fig.6(b)). The XPS analysis revealed for both layers a main doublet at ca. 31.8 eV and 34.0 eV respectively for the W4f<sub>7/2</sub> and W4f<sub>5/2</sub> lines corresponding to the carbide form of the tungsten. Moreover, an additional doublet is also present corresponding to the oxide form. It is clear that the deposition on top of the oxide layer do not change the chemistry of the oxycarbide. The chosen depositing route is an ideal way to obtain a tungsten oxycarbide with a high porous character.

#### 4. Conclusion

Tungsten oxycarbide thin films were obtained using direct liquid injection chemical vapour deposition, [Cp<sub>2</sub>WH<sub>2</sub>] being used as precursor. SEM and TEM have been performed to study the influence of the growth parameters and allow obtaining porous layers. Moreover, thanks to the XPS results a two-step route has been chosen. By using oxygen as reactive gas at

deposition temperature of 400°C, WO<sub>3</sub> porous layers are obtained. At 800°C and if methane is used as reactive gas, a dense oxycarbide layer is obtained. By depositing an oxycarbide layer on top of a porous tungsten oxide, the deposit is perfectly porous. This way seems to be perfect in order to perform the growth of films porous enough to have a high reactive surface for catalytic purpose.

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#### 6.3 Conclusion

La DLI-CVD a permis d'obtenir des couches extrêmement poreuses d'oxycarbure de tungstène à partir d'un protocole en deux étapes successives, la vitesse de croissance des dépôts d'oxyde de carbure étant trop faible pour les obtenir en une étape. Un premier dépôt d'oxyde de tungstène présentant une morphologie en aiguille doit ainsi être réalisé avant d'initier un second dépôt permettant de recouvrir l'oxyde de tungstène par de l'oxycarbure de tungstène.

### **Conclusion générale**

L'objectif de ce travail était de développer des protocoles d'élaboration de matériaux catalytiques susceptibles d'être intégrés dans des micro-piles à combustible de type PEMFC. Dans ce contexte, il s'agissait également de diminuer au maximum la charge en platine. La technique d'élaboration retenue pour cette étude a été la DLI-CVD puisque cette technique permet de réaliser des dépôts homogènes sur une grande surface (à l'échelle des µ-PEMFC) tout en contrôlant parfaitement l'épaisseur, la composition voire la morphologie des films élaborés. L'étude de la littérature a alors permis de dégager deux axes de travail.

Le premier portait sur la substitution de la majorité du platine à partir de sa promotion par un oxyde ayant lui-même des propriétés catalytiques : l'oxyde de cérium. Des paramètres de croissance permettant de contrôler et d'optimiser la porosité des échantillons ont tout d'abord été déterminés à partir de la croissance de films d'oxyde de cérium de type CeO<sub>2</sub>. A partir de ces paramètres, des films d'oxyde de cérium dopé au platine ont été élaborés. Différents modes de synthèse ont été testés afin d'obtenir une charge en platine ionique (Pt<sup>2+</sup>) à la surface des particules composant les films la plus importante possible. Un protocole de type « séquentiel » a alors permis d'obtenir des couches poreuses avec près de 5% de platine ionique à l'extrême surface des particules. Par ailleurs, il a été montré que l'état d'oxydation du platine dépend de la quantité de précurseur injectée : plus cette quantité injectée est faible plus la charge en platine ionique est importante tout en diminuant fortement la charge totale en métal noble de l'échantillon. Ce résultat a été étayé par une étude parallèle menée sur le système Pt-TiO<sub>2</sub> où il a été clairement mis en évidence la possibilité de modifier l'état d'oxydation du platine en fonction du flux de précurseur de platine.

Le second axe de travail a consisté à tenter de synthétiser un matériau aux propriétés catalytiques ne contenant pas de platine. Le choix s'est porté sur l'oxycarbure de tungstène. Pour ce type de composé, il a été possible d'obtenir des couches très poreuses, encore une fois à partir de dépôts de type « séquentiel ». Dans ce cas, un film poreux d'oxyde de tungstène WO<sub>3</sub> est élaboré à 400 °C sur lequel peut ensuite être déposé, à 600 °C, une couche conforme d'oxycarbure de tungstène, la porosité initiale de la couche d'oxyde étant alors conservée.

D'une manière générale, ces travaux ont démontré l'intérêt que peut présenter la DLI-CVD pour l'élaboration de matériaux très poreux, de grande surface spécifique et donc potentiellement très actifs en tant que catalyseurs. L'étude de l'activité catalytique des matériaux élaborés lors de ce travail se doit maintenant d'être menée.

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