

Electrical energy storage materials and devices for zero net energy buildings and clean transportation

Etienne Le Calvez

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Etienne LE CALVEZ

Electric energy storage materials and devices for zero net energy buildings and clean transportation

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Rapporteurs avant soutenance :

Liliane Guerlou-Demourgues		Professeur, CNRS – ICMCB, UMR 5026 Université de Bordeaux			
Sophie Cassaignon		Professeur, CNRS – LCMCP, UMR 7574 Sorbonne Université			
Compositio	on du Jury :				
Président :	sident : Rita Baddour-Hadjean		Directrice de recherche, CNRS – ICMPE, UMR 718 Université Paris-Est		
Examinateurs : Christian Masquelier		quelier	Professeur, CNRS – UPJV, UMR 7314 Université de Picardie Jules Verne		
Dir. de thèse : Thierry Brousse		e	Professeur, IMN, UMR 5026 Université de Nantes		
Co-encadrant de thèse : Olivier Crosnier			Maître de conférences, IMN, UMR 5026 Université de Nantes		
Co-encadrant de thèse : Bruce Dunn			Professeur, University of California at Los Angeles		
Invités					
Margaud Lecu	iyer		Docteur, Blue Solutions		
Cécile Tessier			Docteur, SAFT		
Jérémy Pruvost			Professeur, GEPEA UCMR 6144		
			Université de Nantes		

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Introduction générale

Publié en 1972, *The limits to growth* (les limites de la croissance) est l'un des premiers rapports à suggérer des problèmes futurs concernant le mode de vie de l'humanité.¹ Cette simulation informatique du Club de Rome a montré que l'augmentation constante de la population humaine et de la consommation qui lui est associée entraîneront une insuffisance des ressources planétaires.

Depuis cette date, les humains n'ont manifestement pas prêté suffisamment attention aux limites énoncées par cette simulation alarmante ainsi qu'aux innombrables rapports qui l'ont suivie.² D'une part, la population mondiale a largement augmenté depuis 1900. Les rapports les plus récents estiment que nous compterons 10 milliards d'humains en 2100. La demande énergétique mondiale augmentera en raison de cette croissance démographique. D'autre part, la croissance économique constante (intrinsèque à nos modèles économiques actuels) et la nécessité pour les populations pauvres d'améliorer leur niveau de vie (l'histoire montrant que la consommation d'énergie est finement liée à la qualité de vie (IDH)³) forment d'autres raisons à la croissance de la demande énergétique mondiale. Ces facteurs ont déjà et vont continuer à entraîner une augmentation drastique des besoins énergétiques globaux dans les décennies à venir.

Avant la première révolution industrielle vers 1850, la majorité de l'énergie utilisée par l'homme pour transformer son environnement provient du bois, cette source d'énergie est un combustible permettant la formation de chaleur. Dans ce monde alors, toute l'énergie peut être considérée comme renouvelable. Les moulins à vent et les moulins à eau ayant également joué un rôle important dans la transformation de l'énergie. Une crise du bois va apparaître d'abord

¹ Meadows, D. H.; Meadows, D. H.; Randers, J.; Behrens III, W. W. The Limits to Growth: A Report to the Club of Rome (1972). *Google Sch.* **1972**, *91*.

² IPCC, 2018: Global Warming of 1.5°C. IPCC, 2019: Climate Change and Land

³ Recchia, S. On 'Cultural Liberty' and Its Self-Defeating Implications: A Critique of the UNDP Human Development Report 2004. *Ethnopolitics* **2006**, *5* (2), 183–190.

en Angleterre et en France à la fin du 18ème siècle.⁴ Le bois devenant rare et la taille des forêts européennes diminuant, le charbon va se substituer à cette source d'énergie. Avec le développement des chemins de fer et de la navigation commerciale, le charbon prend une place majeure comme source d'énergie pour les mobilités. Le vingtième siècle verra l'apparition simultanée du pétrole et du gaz.⁵ La première goutte de pétrole est extraite aux États-Unis par Edwin Drake en 1859. L'essor de la voiture équipée d'un moteur à combustion interne comme la Ford T permettra le développement du pétrole dans le monde entier en 1908.¹⁰ Le charbon est désormais surtout utilisé pour la production d'électricité. En deux siècles, l'homme a augmenté de façon exponentielle sa consommation d'énergie grâce au charbon, au pétrole et au gaz et par la même occasion son niveau de vie. Les centrales nucléaires se développent quelques temps après la fin de la Seconde Guerre mondiale. La première étant construite en 1954 à Obninsk (URSS).

La relation entre les émissions de CO₂ et la consommation dépend de la source d'énergie. L'utilisation du charbon comme combustible produit plus de 800 eq-CO₂/kWh, quand le pétrole émet plus de 700 eq-CO₂/kWh. Bien qu'il soit impossible de ne pas émettre d'eq-CO₂ en transformant de l'énergie, certaines sources sont largement moins consommatrices de gaz à effet de serre. Par exemple, le nucléaire, les centrales géothermiques ou les panneaux photovoltaïques transforment l'énergie avec de relativement faibles émissions de CO₂. Selon le rapport du GIEC (Groupe Intergouvernemental sur l'Evolution du Climat), un mix énergétique composé d'énergie nucléaire et d'énergies renouvelables (photovoltaïque, hydroélectrique, éolienne, ...) semble être le moyen le plus durable et le plus rapide pour réduire nos émissions de CO₂.⁶ Lorsque la centrale nucléaire profite d'une production d'électricité maitrisable dans le temps, les énergies renouvelables ont une production d'énergie intermittente qui dépend de la présence du vent, du soleil, etc. Le stockage de l'énergie est alors un moyen efficace de pallier cet inconvénient. Cela justifie en partie le développement récent de nombreux dispositifs de stockage d'énergie.

⁴ Warde, P. Fear of Wood Shortage and the Reality of the Woodland in Europe, c. 1450–1850. In *History Workshop Journal*; Oxford University Press, **2006**; Vol. 62, pp 28–57.

⁵ Buell, F. A Short History of Oil Cultures: Or, the Marriage of Catastrophe and Exuberance. *J. Am. Stud.* **2012**, *46* (2), 273–293.

⁶ IPCC, 2018: Global Warming of 1.5°C. IPCC, 2019: Climate Change and Land

Dans ce contexte, les chercheurs et les industriels progressent encore dans différents domaines (volant d'inertie, sel thermique, hydroélectricité...). Classiquement, les dispositifs de stockage d'énergie sont classés en fonction de leur densité énergétique, qui correspond à la quantité d'énergie qu'ils peuvent fournir par unité de masse ou de volume (Wh/g ou Wh/L) et de leur densité de puissance, qui correspond à la vitesse de libération de l'énergie par unité de masse ou de volume (W/g ou W/L). Le diagramme de Ragone est utile pour représenter tous les dispositifs de stockage d'énergie. Si les supercondensateurs et les volants d'inertie sont très puissants, les batteries et les piles à combustible présentent une densité énergétique élevée. De fait, grâce à leurs diversités et leurs flexibilités, les dispositifs électrochimiques sont l'une des voies les plus prometteuses pour le stockage futur des énergies renouvelables.

Le sujet général des travaux de la thèse présentée ici est le développement de matériaux et de systèmes électrochimiques permettant de combler l'écart entre les batteries Li-ion et les supercondensateurs et donc, d'obtenir des densités d'énergie et de puissance intermédiaires. Ainsi, différentes approches ont été pensées dans le but de proposer une large variété de solutions à cette problématique. Il s'inscrit dans le projet DISCUS (Developing Innovative Integrated Solutions for Sustainable Communities and Urban Systems) initié par le Prof. Jérémy Pruvost du laboratoire GEPEA. Ce projet a été labélisé par l'ISITE NExT dans le cadre de l'appel à projet International Research Partnerships. Les contours du projet sont indiqués cidessous.

La population mondiale évolue rapidement vers une urbanisation accrue, ce qui pose de graves problèmes et préoccupations en matière de durabilité de l'environnement. Par exemple, l'agglomération de Los Angeles est la deuxième plus grande ville des États-Unis avec une population croissante de 10 millions d'habitants. Nantes, est la cinquième ville de France et se développe de façon importante. Les deux villes sont situées près d'un grand océan où se concentrent de nombreuses activités industrielles et commerciales et des ports de commerce. Elles ont une densité de population similaire variant entre 3 000 (Los Angeles) et 4 500 (Nantes) personnes/km². Les deux ont également une forte présence d'établissements d'enseignement supérieur et de recherche bien établis. Le projet DISCUS⁷ (Développement de solutions intégrées innovantes pour des collectivités et des systèmes urbains durables) vise à développer

⁷ https://next-isite.fr/partenariats-internationaux-de-recherche/

des solutions innovantes, intégrées et durables répondant à l'interdépendance critique des aliments, de l'énergie et de l'eau dans les systèmes urbains. Pour ce faire, il réunira des équipes pluridisciplinaires basées à l'Université de Nantes et à l'Université de Californie à Los Angeles, reconnues internationalement dans leurs domaines respectifs, pour former un centre d'excellence international.

L'utilisation de dispositifs de stockage de l'énergie électrique pouvant être mis en œuvre au niveau des bâtiments est l'un des principaux problèmes à résoudre pour atteindre l'objectif d'un bâtiment à consommation énergétique nette zéro. Cela suppose que de nouveaux matériaux/nouveaux dispositifs soient développés pour être couplés à des systèmes de récupération d'énergie tels que des panneaux photovoltaïques couvrant la façade du bâtiment. De tels dispositifs de stockage d'énergie doivent répondre aux critères de durée de vie, de durabilité des composants et de facilité de mise en œuvre dans un bâtiment sans impacter le volume intérieur. Seules les approches innovantes en matière de nouveaux matériaux et de nouvelles conceptions des dispositifs de stockage d'énergie peuvent apporter une avancée majeure dans ce domaine. Les batteries de puissance sont particulièrement intéressantes en raison du caractère intermittent des systèmes de récupération d'énergie envisagés.

Ainsi, le premier chapitre de cette thèse s'attachera à proposer un état de l'art du paysage scientifique actuel vis-à-vis des batteries Li-ion et des supercondensateurs. Dans un second temps, les matériaux pouvant fonctionner en tant qu'électrode négative et présentant des capacités spécifiques intéressantes à courant élevé seront détaillés. Une attention particulière sera portée aux oxydes multicationiques à base de niobium, de titane, de vanadium et de tungstène et les structures cristallographiques communément associées à ces derniers.

Le second chapitre présentera un nouveau concept permettant de faire fonctionner un matériau non lithié en tant qu'électrode positive pour des systèmes électrochimiques de puissance. Pour cela, l'oxyde $Ag_2V_4O_{11}$ sera associé à un sel de lithium sacrificiel qui fournira au système les ions alcalins nécessaires à son bon fonctionnement. Cette électrode composite sera étudiée dans un premier temps en demi-cellule (en face d'une électrode de lithium), puis en cellule complète (en face d'une électrode de graphite). Aussi, une étude des propriétés électrochimiques d' $Ag_2V_4O_{11}$ en fonction de la taille et de la morphologie des particules sera réalisée dans le but de mieux comprendre les mécanismes de stockage de charge de cette phase.

Dans le chapitre III, la substitution du site A de la pérovskite AgNbO₃ par du lanthane sera étudié dans le but de créer des lacunes cationiques permettant l'insertion par voie électrochimiques des ions lithium. Cette substitution permet la formation des phases Ag_{1-3x}La_{x□2x}NbO₃ avec □ correspondant aux lacunes et 0<x<0.20. Une étude des propriétés d'insertion de ces différents matériaux est proposée, démontrant leur intérêt comme matériau modèle pour l'étude de l'insertion rapide d'ions lithium dans des structures pérovskites.

Tandis que le chapitre III démontrera la possibilité d'insérer des ions grâce à la substitution cationique, le chapitre IV présentera lui la formation de sites d'insertion par échange ionique. La famille composée de KTiNbO₅, HTiNbO₅ et Ti₂Nb₂O₉ sera synthétisée par deux voies de synthèse différentes permettant d'obtenir des morphologies différentes. L'influence des ions potassium et des protons dans ces structures lamellaires sera étudiée. Aussi, les mécanismes de charge permettant à ces oxydes de se charger rapidement seront élucidés.

Enfin, dans le chapitre V, deux matériaux proposant des structures cristallographiques intéressantes vis-à-vis de l'insertion du lithium, Rb₂TiNb₆O₁₈ et Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄, subiront eux aussi un échange ionique dans le but de remplacer leurs ions alcalins par des protons. Une comparaison des propriétés de ces matériaux et des caractéristiques électrochimiques avant et après échanges ioniques sera réalisée.

Une conclusion générale résumera les principaux résultats obtenus dans cette thèse tandis que les dernières lignes de cette thèse établiront quelques perspectives ainsi qu'un point de vue critique et personnel sur ces travaux de thèse.

Chapitre I. Revue de la littérature

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L'objectif principal de ce chapitre est dans un premier temps d'exposer les principes fondamentaux qui régissent le fonctionnement ainsi que les grandeurs physico-chimiques les plus importantes des dispositifs électrochimiques et tout particulièrement des batteries Li-ion (LIB). Ensuite, les matériaux utilisés comme électrode négative pour des applications dans les batteries de puissance seront détaillés afin de comprendre les connaissances actuelles sur le sujet et plus particulièrement au regard de la chimie des matériaux associés.

I. Généralités sur les batteries Li-ion.

1. Historique et applications des batteries

L'Histoire nous montre l'importance croissante des dispositifs électrochimiques dans nos vies depuis l'invention de la première pile par Alejandro Volta en 1800.^{1,2} De l'alimentation du télégraphe au développement des appareils électroniques portables, le développement de la technologie des batteries est désormais essentiel pour faire converger nos sociétés vers un modèle plus durable en transformant d'une part les véhicules à moteur à combustion interne en véhicules électriques et d'autre part en stockant l'énergie produite par les énergies renouvelables. Ce sont aujourd'hui les deux objectifs principaux des scientifiques qui développent des batteries plus efficaces et plus durables. La technologie Li-ion est actuellement la plus prometteuse en matière de densité énergétique pour ces applications. Dans les années 90, Toyota, General Motors ou Renault commencent à travailler sur des véhicules hybrides qui combinent moteurs thermiques et électriques. Aujourd'hui, les véhicules électriques sont une réalité. De nombreux constructeurs de voitures électriques et hybrides utilisent les technologies développées autour du lithium pour produire des véhicules plus propres. D'autres applications peuvent être envisagées. Par exemple, l'alimentation de l'Internet des objets (IoT) par des micro-batteries ou des micro-supercondensateurs est un moyen d'améliorer notre qualité de vie.^{3,4}

2. Pourquoi le lithium ?

Le lithium a été découvert en 1800 par Johann August Arfvedson. Le mot "lithium" vient du grec "*lithos*" qui signifie pierre. On le trouve naturellement sur la Terre sous forme de minéral ou dissous dans l'eau de mer. Actuellement, ce métal est extrait sous forme de carbonate de lithium (Li₂CO₃), principalement en Amérique du Sud. La demande actuelle

augmente de 10% chaque année et 25% du lithium extrait est utilisé pour les batteries.⁵ Le lithium a d'autres applications que les batteries : médicament régulateur de l'humeur avec du carbonate de lithium pur (Li_2CO_3) en médecine^{6,7}, matériau pour l'optique non linéaire (perovskite LiNbO₃)⁸, nucléophiles et bases en chimie organique ou encore comme réactif en science nucléaire.

Dans la science des matériaux pour les batteries, le lithium est très intéressant car il est le métal le plus léger (d = 0.53 g.cm^{-3}) et le couple Li⁺/Li a le potentiel le plus faible (-3.04V par rapport à une électrode standard à hydrogène à 25° C).⁵ Grâce à ces avantages, les batteries à base de lithium peuvent avoir, respectivement, une grande capacité ainsi qu'une tension de cellule élevée. La capacité spécifique du lithium métal est de 3 860 mAh.g⁻¹. Pour toutes ces raisons, la batterie au lithium a été proposée comme l'avenir des technologies de stockage de l'énergie dans les années 70.

Dans les balbutiements des premières années, toutes les LIB étaient des batteries primaires (ou piles) n'étaient donc pas rechargeables.^{9–11} Elles ont permis une amélioration significative de la densité énergétique des batteries primaires et ont été utilisées dans les stimulateurs cardiaques ou dans le domaine militaire. Dans ces batteries primaires, l'électrode positive (la cathode) était composée majoritairement d'un vanadate d'argent (Ag₂V₄O₁₁) ou bien d'un matériau carboné (CF_x),^{12–14} l'anode étant une électrode de lithium métallique.

En 1977, les premières batteries rechargeables au lithium sont inventées par Whittingham et son équipe qui utilisent le TiS₂ comme matériau cathodique d'intercalation.^{15,16} Associé à une électrode négative de lithium, la formation de dendrites à la surface de cette électrode pose un problème de sécurité et peut conduire à des court-circuit et une explosion. Le remplacement de l'électrode négative en lithium métal est envisagé et sera le graphite qui prendra sa place, assurant un potentiel de fonctionnement relativement haut.^{17,18} De plus, en 1980, les équipes de Goodenough proposent une solution pour augmenter la tension de cellule et fournir au système une source de lithium: LiCoO₂.¹⁹ Cet oxyde, qui est un matériau d'intercalation, servira d'électrode positive et de source de lithium pour le système. La *rocking chair battery* basée sur l'intercalation réversible d'ions lithium est née. Pour la première fois, en 1991, Sony mettra sur le marché la batterie graphite/LiCoO₂ qui envahira le monde.⁹ Aujourd'hui, presque tous les appareils portables sont équipés d'une batterie lithium-ion (LIB).

Le prix Nobel de chimie a été décerné en 2019 à 3 scientifiques pour leurs travaux sur le développement de ces batteries : John B. Goodenough, Stanley Whittingham et Akira Yoshino.²⁰ Cela montre l'importance de cette technologie dans le monde d'aujourd'hui. Cependant, de nombreuses améliorations sont encore espérées pour pouvoir permettre un déploiement plus large des véhicules électriques ainsi que le stockage des énergies renouvelables et intermittentes. Parmi celles-ci, l'augmentation de la cyclabilité, l'amélioration de la densité de puissance et de la densité d'énergie ainsi que la sécurité et le recyclage sont des aspects primordiaux pour un développement durable de la technologie.

3. Principe de fonctionnement générale

Une LIB est composée de deux électrodes différentes, une électrode positive et une électrode négative (Figure.I.1). Un électrolyte est placé entre ces deux électrodes afin de permettre le flux ionique tout en empêchant le flux électronique. Le collecteur de courant permet de récolter les électrons échangés d'une électrode à une autre lors des différentes réactions d'oxydation et de réduction afin de les sortir du système électrochimique.^{9,21,22}

Pour transformer de l'énergie électrique en énergie chimique, l'électrode positive (ici LiCoO₂) est oxydée, comme exprimé dans l'Equation.I. 1, et libère ainsi des électrons et des ions lithium. Les électrons vont vers l'électrode négative par un circuit externe. Les ions lithium traversent alors l'électrolyte conducteur pour venir s'intercaler entre les feuillets du graphique, comme l'explique l'Equation.I. 2. On parle alors de charge car la différence de potentiel entre les deux électrodes (équivalent à la tension de cellule) augmente.

$$\text{LiCo}^{\text{III}}\text{O}_2 \rightleftharpoons \text{Li}_{1-x}\text{Co}^{\text{IV}}\text{O}_2 + x\text{Li}^+ + xe^-$$
 Equation.I. 1

$$C_6 + xLi^+ + xe^- \rightleftharpoons Li_xC_6$$
 Equation.1.2

Dans les LIB dites secondaires, ce processus est réversible. L'étape inverse est un processus spontané qui va permettre de générer un courant. Thermodynamiquement, cela signifie que l'énergie libre de Gibbs (ΔG) va diminuer dans le système pour atteindre un état plus stable. Ici, l'énergie libre de Gibbs est calculée grâce à l'Equation.I. 3

$$\Delta G_{\text{cell}} = -nFE^0$$

Où, n, est le nombre de charges élémentaires transférées, F, la constante de Faraday, E^0 , le potentiel entre l'électrode positive et la négative (tension de cellule).



Figure.I.1 Schéma d'une batterie Li-ion. Ici, l'électrode négative est représentée par du graphite tandis que la positive est un oxyde de cobalt (LiCoO₂)

4. Grandeurs caractéristiques

Différentes grandeurs physiques sont d'importance pour permettre de caractériser une batteries Li-ion. On présentera ici, les grandeurs physiques les plus étudiées par les chercheurs.

Le potentiel : Chaque couple redox possède son propre potentiel. L'énergie nécessaire à un transfert d'électrons dépend largement de l'atome qui lui est associé et de la structure cristallographique autour de ce dernier. Exprimée en Volt, la tension de cellule est la différence entre le potentiel de l'électrode positive et celui de l'électrode négative.

La capacité : Exprimée en Ampère-seconde (ou Coulomb), la capacité est le nombre de charges élémentaires que peut stocker un matériau. Dans le domaine de la recherche, afin de comparer différents matériaux, la capacité est normalisée par la masse et exprimée en mAh.g⁻¹ ou en C.g⁻¹ On parle alors de capacité spécifique. Une capacité théorique peut être déterminée par l'Equation.I. 4. Elle dépend de la masse molaire du matériau utilisé.

$$Capacit\acute{e} = \frac{F.n_e^{-}}{M} (en C.g^{-1})$$

Equation.I. 4

Où n_{e^-} , est le nombre de charges élémentaires échangées, F, la constante de Faraday en C.mol⁻¹, M, la masse molaire en g.mol⁻¹.

Il est important de noter que chaque matériau a sa propre capacité spécifique (qui dépend de la vitesse de charge/et du courant imposé) mais dans une batterie complète le système est optimisé pour que la capacité de l'électrode positive soit égale à celle de l'électrode négative (en mAh).

L'énergie : Selon les conventions du système international, l'énergie est exprimée en Joule. Dans le domaine des batteries, l'énergie est le plus souvent exprimée en Wh. C'est une caractéristique importante pour exprimer la qualité d'un dispositif complet. Comme exprimée dans l'Equation.I. 5., l'énergie d'une batterie est le produit de la capacité par le potentiel opérationnel de la cellule. Ainsi, une augmentation de la tension de cellule et/ou de la capacité permet d'augmenter l'énergie stockée dans le système. Afin de normaliser la valeur, ce produit est divisé par la masse (ou le volume) donnant lieu à des capacités gravimétriques ou volumiques.

$$Energie = \frac{Capacité \Delta E}{m}$$
(En Wh) Equation.I. 5

La puissance : Exprimée en W, la puissance est une énergie par unité de temps, comme indiqué dans l'Equation.I. 6. La puissance permet d'exprimer l'aptitude que peut avoir une batterie à rapidement restituer son énergie.

$$Puissance = \frac{Energie}{t} = i.V (En W)$$
Equation.I. 6

II. Les différents mécanismes de stockage de charge

Toutes les caractéristiques de la partie précédente dépendent largement des propriétés physico-chimiques, cristallographiques ainsi qu'électrochimiques des matériaux utilisé en tant

qu'électrodes positives et négatives. Ici, vont être décris les différents mécanismes mis en jeu dans les matériaux pour batteries, supercondensateurs et dispositifs hybrides.

1. L'intercalation

Notamment grâce aux travaux de chercheurs français comme Jean Rouxel dans notre laboratoire nantais puis au Collège de France, la chimie d'intercalation naît dans les années 70.^{16,23–26} Au début, principalement dans des chalcogénures ou dans des oxydes lamellaires, les chimistes du solide montrent que l'intercalation d'ions alcalins (Li⁺, Na⁺, K⁺...) *via* des méthodes de chimie douce ou par électrochimie est possible. De plus, l'intercalation dans ces matériaux est démontrée comme étant réversible impliquant ainsi une desintercalation des ions présents dans l'interfeuillet de TiS₂.^{16,23} À un potentiel donné, il est désormais possible d'intercaler et desintercaler des ions alcalins, comme exprimé ici dans le cas de l'oxyde de cobalt (Equation.I. 1)

Deux types de phénomènes peuvent accompagner et expliquer cette intercalation. Soit une transition de phase apparaît lors du départ et/ou de l'arrivée des ions lithium, comme dans le cas de l'olivine LiFePO₄. On parle alors d'une réaction biphasique car deux structures cristallines bien distinctes coexistent (LiFePO₄ et FePO₄).^{27–29} Ce phénomène est décrit par l'Equation.I. 7. Soit on parle de solution-solide, c'est-à-dire d'une modification progressive de la structure cristalline du matériau comme dans le cas de TiS₂ comme exprimée grâce à l'Equation.I. 8.³⁰ Dans certains cas plus complexes il est possible que le matériau intercale des ions lithium sans changement de phase dans un premier temps, puis après une certaine quantité de lithium une seconde phase apparait elle-même réagissant selon un mécanisme dit de solution solide.³¹

$$LiFePO_4 \rightleftharpoons FePO_4 + Li^+ + e^-$$
 Equation.1. 7

$$Li_xTiS_2 \rightleftharpoons TiS_2 + xLi^+ + xe^-$$

2. Le stockage pseudocapacif

Contrairement aux matériaux d'intercalation classiques, les matériaux dits « pseudocapacitifs » stockent des charges électriques grâce à des réactions faradiques de

Equation.I. 8

surface ou de proche surface.^{41–44} Ainsi, le stockage de charge n'est limité ni par la diffusion ni par un changement de phase progressif des particules. Dans ce cas, les réactions d'oxydoréduction sont essentiellement limitées par le transfert de charge et/ou la conductivité électronique de l'électrode. D'un point de vue électrochimique, cela implique qu'il existe une relation linéaire entre le potentiel du matériau pseudocapacitif et le temps de charge et/ou de décharge. Comme illustré Figure.I. 2A, RuO₂.xH₂O ^{32,33} et MnO₂ ^{34–36} présentent des comportements de type « pseudocapacitif » avec une voltammétrie cyclique quasi rectangulaire, proche des matériaux adsorbant des charges de manière électrostatiques (EDLC).³⁷ Ces matériaux présentent une faible densité d'énergie mais une densité de puissance très élevée comparé à leurs analogues pour batteries.

3. L'intercalation pseudocapacitive.

Plus récemment. une nouvelle classe matériaux présentant de une «intercalation pseudocapacitive» a été introduite.^{37–40} Ces matériaux montrent une voltammétrie cyclique proche des matériaux « pseudocapacitifs » avec un courant quasi constant sur une certaine plage de potentiel (Exemple du Nb₂O₅, Figure.I. 2B). Cependant, l'origine du stockage de charge n'est pas la même que dans les matériaux « pseudocapacitifs » classiques. Une intercalation réversible sans changement de phase et avec une cinétique rapide (faible limitation par la diffusion) est à l'origine du processus de charge/décharge. Grâce à cette intercalation, une plus grande quantité de charges peut être stockée car les réactions ont lieu dans tout le volume des particules.

Il est à souligner que cette intercalation pseudocapacitive peut être intrinsèque ou extrinsèque. T-Nb₂O₅ présente ainsi une pseudocapacité intrinsèque car ces particules ne doivent pas nécessairement être de taille nanométrique pour présenter un tel comportement.^{39,41} A l'inverse, l'insertion d'ions lithium dans MoS₂ présente une voltammétrie cyclique proche des matériaux capacitifs uniquement quand les particules sont nanométriques mais pas dans le cas de particules micrométriques.^{42,43} On retrouve alors une voltammétrie cyclique présentant des pics redox définis, caractéristiques des matériaux soumis aux lois de la diffusion de Randles-Ševčík (Figure.I. 2.C-D).^{44,45} Ainsi pour MoS₂, on parle alors de pseudocapacité extrinsèque.

Ces matériaux intéressent les chercheurs et les industriels car ils permettent d'augmenter la densité d'énergie des supercondensateurs et la densité de puissance des batteries. Ils sont également d'intérêt pour comprendre le lien étroit entre tous ces mécanismes.⁴⁶



Figure.I. 2 (A-B-C-D) Différents mécanismes de stockage de charge présents dans les matériaux d'électrodes. A. Matériaux pseudocapacifs fonctionnant grâce à des réactions redox de surface ou de proche surface. B. Matériaux présentant une signature pseudocapacitive grâce à une insertion des ions lithium sans limitation due à la diffusion. C. Matériaux présentant des particules nanométriques permettant une diminution drastique de la limitation cinétique liée à la diffusion des ions dans la structure cristallographique. D. Matériau présentant une intercalation d'ions alcalins typique des matériaux de batteries.⁴⁶

- III. Les batteries de puissance
- 1. Pourquoi pas le graphite ?

Dans les batteries à charge rapide, le choix du graphite comme électrode négative, qui insère le lithium à un potentiel moyen proche de celui du Li⁺/Li (0,1 V), peut conduire à la formation de dendrites de lithium entraînant d'éventuels court-circuit et des surchauffes quand le potentiel descend en dessous 0V vs Li⁺/Li. De plus, la capacité spécifique du graphite, qui est théoriquement de 372 mAh.g⁻¹, est largement réduite à fort courant en raison de la mobilité

limitée des ions entre les couches de graphène. Dans la plupart des matériaux que l'on trouve dans les batteries actuelles, la diffusion des ions dans le matériau est un facteur limitant la recharge rapide. Dès lors que le courant imposé est trop grand, la diffusion des ions dans la structure cristallographique est trop lente pour permettre une bonne (dé)lithiation du matériau et limite la capacité mesurée.

Ainsi et dans le but de remplacer le graphite pour obtenir des charges en quelques minutes, la recherche de matériaux alternatifs a significativement augmenté au cours de la dernière décennie. Les principales caractéristiques que doivent proposer ces futures batteries sont leur haute densité de puissance, leur longue durée de vie ainsi qu'une sécurité accrue et un faible coût. L'un des matériaux d'électrode négative les plus connus pour les applications à haut débit est le Li₄Ti₅O₁₂ (LTO). Plusieurs compagnies comme Altarinano ou encore Toshiba proposent des batteries fonctionnant avec cet oxyde de titane. Elles permettent d'obtenir une charge de 90% en 10 minutes.⁴⁷ Les caractéristiques cristallographiques et électrochimiques de ce matériau seront détaillées dans les prochaines parties de cette thèse.

Néanmoins, de nouveaux moyens ont été proposés dans le but d'offrir un plus grand choix pour le remplacement du graphite. Entre autres, des matériaux à « structure partagée » (*crystallographic shear structure*), notamment TiNb₂O₇ ou Nb₁₆W₁₈O₉₃, offrent des valeurs de capacité gravimétrique et volumétrique relativement élevées à fort courant. Des faibles changements de volume lors de l'insertion du lithium et un potentiel de fonctionnement permettent d'éviter la formation d'une interphase d'électrolyte solide (SEI) consommatrice de lithium et limitante vis-à-vis de la diffusion des ions dans l'électrode.

Des approches alternatives dans la synthèse de nouveaux matériaux sont nécessaires pour découvrir différents matériaux à charge rapide et comprendre leurs mécanismes de charges associés.⁴⁸ Le travail de cette thèse est en partie de mieux comprendre la chimie des matériaux associée aux batteries de puissance pour découvrir ou redécouvrir des oxydes de métaux de transition d'intérêt pour ce type de système de stockage.

2. Récent développement de matériau d'électrode négative

Dans cette sous-partie, une attention particulière va être donnée au développement d'électrodes négatives de puissance à base de métaux de transition (Nb, Ti, Mo, W...). Un bref historique de la chimie des matériaux ainsi que la description des structures permettront une compréhension des liens entre la cristallographie de ces métaux de transition et leurs comportements électrochimiques associés. Les premières sous-parties développeront l'intérêt d'oxydes monocationiques à base de titane et de niobium (TiO₂ et Nb₂O₅). Puis, une seconde sous-partie se proposera d'expliquer les phases à structure partagée et leurs analogues lamellaires tant d'un point de vue de la chimie des matériaux que de l'électrochimie. KTiNbO₅ et ses composés associés seront étudiés plus en détail comme exemple de phases lamellaires présentant une structure partagée. En fin de sous partie, une ouverture sur différentes phases potentiellement intéressantes sera également développée. En commençant par des structures à intercroissance (Rb₂TiNb₆O₁₈, Rb₁₂W₃Nb₃₀O₉₀...), puis en passant par des bronzes tétragonaux (TTB) et hexagonaux (HTB) ainsi que des pérovskites lamellaires (KLaNb₂O₇...), cette ouverture nous permettra d'expliciter l'extraordinaire diversité cristallographique qu'offrent les métaux de transition comme le niobium, le titane, le tungstène ou encore le molybdène.

a. Les oxydes de niobium (T-Nb₂O₅ et autres polymorphes)

Dans son état métallique, le niobium (ou columbium aux Etats-Unis, Cb) a été découvert en 1801 par Hatchett dans un minéral appelé columbite. Le niobium est classé au 33^{eme} rang des éléments les plus abondants dans la croute terrestre ($24 \mu g/g$).⁴⁹ Sa production était de 69.100t en 2017. Le Brésil et le Canada sont les leaders mondiaux dans l'extraction des minerais à base de niobium. Au Brésil, le minerai extrait est un pyrochlore, (Ca,Na)_{2-m}Nb₂O₆(O,OH,F)_{1-n}.xH₂O.⁵⁰

Location	Capacity 10 ⁶ kg Nb ₂ O5	Ore grade	Reserves, 10 ⁶ t Nb ₂ O5	Production, 10 ⁶ kg Nb ₂ O5
Araxa, Brazil	24.75	3.0	500+	9.45
St. Honore, Quebec	3.15	0.7	11	3.15
Catalao, Brazil	2.48	1.5	50	2.48
Nigeria	0.9			
Thailand	0.45-0.9			
Zaire	pilot scale	2-3	extensive	0.23

Tableau.I.1. Site d'extraction de niobium avec la capacité de production ainsi que les réserves estimées.⁴⁹

Le deuxième minéral à base de niobium le plus important est le coltan (columbiumtantalite), il est largement présent en République Démocratique du Congo ainsi qu'en Tanzanie. Cependant, l'extraction et la vente illégale de coltan en Afrique Centrale est l'une des raisons ayant entrainé la guerre civile faisant plus de 6 millions de morts.^{51,52} Actuellement, le niobium est majoritairement utilisé dans l'industrie pour la fabrication d'alliages Fe/Nb. Le Tableau I.1 récapitule les principaux sites d'extraction ainsi que les réserves et leurs productions annuelles.

Au début des années 2010, l'équipe de Bruce Dunn remet sur le devant de la scène l'oxyde de niobium (Nb₂O₅) pour des applications dans le stockage de l'énergie. Sous sa forme orthorhombique, T-Nb₂O₅ cristallise dans le groupe d'espace Pbam et présente une structure proche des bronzes de tungstène comme illustré Figure.I. 3A. Les octaèdres (NbO₆) sont très déformés et partagent entre eux leur sommet. Un autre environnement non octaédrique est présent dans cette oxyde, des sites où se forment des pentagones bipyramidaux partiellement occupé (NbO₇).⁵³ En somme, les octaèdres de (NbO₆) forment des couches selon l'axe c qui sont reliés par des pentagones bipyramidaux aléatoirement répartis dans tous les sites disponibles.

$$Nb_2O_5 + xLi^+ + xe^- \leftrightarrow Li_xNb_2O_5$$
 Equation.1.9

D'un point de vue électrochimique, la capacité théorique de Nb₂O₅ est de 200 mAh.g⁻¹ pour 2e⁻/Nb₂O₅. L'insertion du lithium est décrite par l'Equation.I. 9. Il est possible d'insérer 1,45 Li⁺/T-Nb₂O₅ (145 mAh.g⁻¹) lors d'une charge durant une heure grâce à la réduction réversible du couple Nb⁵⁺/Nb⁴⁺. Comme illustré par la Figure.I. 3.B., l'intérêt de cet oxyde réside principalement dans son excellent comportement à haute vitesse de charge-décharge. En effet, lors d'une charge de 6 minutes (10 C), le matériau conserve une capacité d'environ 140 mAh.g⁻¹ faisant de T-Nb₂O₅ une référence dans le domaine de la charge rapide. De tous les matériaux qui vont être présentés dans cette partie, le T-Nb₂O₅ semble être l'oxyde conservant le plus de capacité entre 1C et 10C. Cependant, le potentiel moyen de T-Nb₂O₅ est relativement élevé (1,65V) réduisant ainsi la densité d'énergie des dispositifs associés.

Le mécanisme d'insertion du lithium dans T-Nb₂O₅ a été décrit comme étant pseudocapacitif ³⁹. En effet, comme illustrée Figure.I. 3B, entre 2,0V et 1,2V vs Li/Li⁺, la pente de la courbe capacité/potentiel en charge et en décharge est constante ce qui correspond à la définition d'un matériau (pseudo)capacitif. Différentes techniques ont permis l'identification de cette « intercalation pseudocapacitive ». Des mesures de diffraction des rayons X *in situ* montrent que l'oxyde présente un mécanisme de charge de type solution solide sans changement de phase où le paramètre de maille *c* varie très peu. L'étude de Jérémy Come *et al.*⁵⁴ montre qu'une augmentation du paramètre *c* de seulement 0,09 Å est observable après l'insertion de 1,8 Li⁺/T-Nb₂O₅. L'étude par XAS/EXAFS *in situ* montre une réduction du Nb⁵⁺ en Nb⁴⁺ et une évolution de la longueur des liaisons Nb-O au cours du cyclage, confirmant l'insertion des ions lithium³⁹. Finalement, une analyse cinétique par l'application de la loi de puissance et calcul de la « *b*-value », détaillée par l'Equation.I. 10, montre que l'insertion n'est pas limitée par la diffusion des ions lithium à l'intérieur du matériau. La valeur de *b* est alors proche de 1, impliquant une relation linéaire entre le courant et la vitesse de balayage (typique des matériaux pseudocapacitifs).

 $i = a.v^b$

Equation.I. 10



Figure.I. 3 (A) Structure cristallographique selon le plan (ac) de T-Nb₂O₅. (B) Courbe de charge décharge à 10C entre 1V et 3V vs Li/Li ainsi que la capacité en fonction de la vitesse de charge et décharge pour Nb₂O₅ et Li₄Ti₅O₁₂.

Une étude plus récente de Kent J. Griffith *et al.*⁴¹ explique que la structure de T-Nb₂O₅ est intéressante car les atomes de niobium occupant les sites pentagonaux peuvent être considérés comme des piliers stabilisant la structure tandis que l'organisation des octaèdres (NbO₆) permet une voie de diffusion facilitée pour les ions lithium.

Dans cette même étude,⁴¹ leurs auteurs étudient d'un point de vue électrochimique différents polymorphes de Nb₂O₅ (T-Nb₂O₅, B-Nb₂O₅, H-Nb₂O₅ et TT-Nb₂O₅). Ce travail met en lumière les relations entre structure cristalline et performances électrochimiques dans le cas du pentoxyde de niobium. Les structures cristallines des polymorphes de Nb₂O₅ sont exposées Figure.I. 4A. Ce papier démontre que H-Nb₂O₅ possède les meilleures performances à faible courant (C/10). Cependant, T-Nb₂O₅ et TT-Nb₂O₅ (deux polymorphes très similaires) conservent de bonnes capacités à haut courant (>C) (Figure.I. 4B). Des analyses par « Bond valence Sum maps » (BVS) démontrent une faible barrière d'activation pour T-Nb₂O₅ comparativement aux autres polymorphes.



Figure.I. 4 (a) Structure cristallographique des différents polymorphes de Nb₂O₅. (b) Courbe de charge décharge à 10C entre 1V et 3V vs Li/Li⁺ pour 5 oxydes de niobium. Rétention de capacité vis-à-vis des cycles et dérivé selon le potentiel des courbes de charge et décharge de ces mêmes oxydes de niobium.

Dans les parties qui vont suivre, d'autres oxydes de niobium (multicationiques) seront présentés démontrant l'attrait de ce métal de transition pour des applications dans les batteries de puissance.

b. Les oxydes de titane (TiO_2 , $Li_4Ti_5O_{12}$, $H_2Ti_3O_7$...)

Du fait de la faible masse molaire du titane ainsi que de la possible réaction d'oxydoréduction du couple Ti^{4+}/Ti^{3+} , les oxydes de titane représentent un intérêt particulier dans le domaine du stockage électrochimique de l'énergie. Ici, plusieurs exemples permettront de corroborer cette assertion.

i. Le cas de $Li_4Ti_5O_{12}$:

Comme discuté précédemment, l'un des matériaux d'électrode négative le plus répandu pour des applications de batteries de puissance est l'oxyde $\text{Li}_4\text{Ti}_5\text{O}_{12}^{55,56}$. Cristallisant dans une structure spinelle, ce matériau offre une alternative de choix pour le développement de batteries à charge rapide avec une capacité spécifique relativement élevée (160 mAh.g⁻¹ pour une charge d'une heure). Cette capacité correspond à une insertion d'environ 3 Li⁺/ Li₄Ti₅O₁₂ (Figure.I. 5A).

$$Li_4Ti_5O_{12} + 3xLi^+ + 3xe^- \leftrightarrow (1-x)Li_4Ti_5O_{12} + xLi_7Ti_5O_{12}$$
 Equation.1. 11

La réaction est décrite par l'Equation.I. 11. Pour un matériau synthétisé par voie solide qui présente des particules de taille micrométrique, la capacité diminue rapidement pour des vitesses de charge plus rapides. Ainsi, une capacité de 50 mAh.g⁻¹ à 10C est observée pour ce type de matériau comme l'illustre la Figure.I. 5B. Cependant des synthèses par chimie douce entraînent une nanostructuration des particules et permettent d'obtenir une meilleure capacité spécifique à plus haut courant (Figure.I. 5B).



Figure.I. 5 (A) Courbe de charge et décharge de $Li_4Ti_5O_{12}$ entre 2V et 1.2V vs Li/Li^+ (B) Courbe de décharge pour différents courants. $Li_4Ti_5O_{12}$ nano versus $Li_4Ti_5O_{12}$ synthétisé par voie céramique en inset.

Par exemple, dans le cas d'une synthèse par auto combustion⁵⁷, la capacité spécifique à 10C est de 140 mAh.g⁻¹. De plus, Li₄Ti₅O₁₂ est décrit dans la littérature comme « zero-strain » ce qui implique que la variation volumique durant la lithiation/delithiation est négligeable⁵⁵. Ainsi, il est possible d'imaginer que ce type de matériau représente un atout majeur dans le développement de batterie tout-solide nécessitant une faible variation volumique à l'électrode positive comme à l'électrode négative.

ii. Le cas de TiO_2 :

En plus de présenter une capacité théorique relativement élevée de 358 mAh.g⁻¹, la grande diversité des polymorphes de TiO₂ offre un large panel aux chercheurs pour investiguer les formes cristallographiques les plus intéressantes. La forme appelée « TiO₂ (B) » est le titanate le plus étudié des 20 dernières années.⁵⁸ Dans ce polymorphe, des octaèdres de (TiO₆) partagent entre eux leurs arêtes pour former des unités 2x2. Ces unités partagent entre elles

leurs sommets. Ceci permet de former une structure tridimensionnelle où l'on peut trouver selon l'axe (010) des tunnels.

Cette phase offre, entre 1V et 3V *vs* Li/Li⁺, une capacité spécifique pouvant aller à faible courant jusqu'à 200 mAh.g⁻¹ lorsque les particules sont sous forme nanométrique. Cette capacité résulte de la réduction du couple Ti⁴⁺/Ti⁺³, comme explicité par l'Equation.I. 12. Le matériau présente également une bonne rétention de capacité à courant élevé. Comme pour un TiO₂ sous sa forme anatase ou sous forme de nano feuillets réempilés ^{59,60}, il a été démontré qu'une relation linéaire existait entre la vitesse de balayage et l'intensité des pics d'oxydoréduction dans TiO₂ (B) ⁶¹. Une intercalation pseudocapacitive est donc une nouvelle fois à souligner.

$$TiO_2(B) + xLi^+ + xe^- \leftrightarrow Li_xTiO_2$$
 Equation.1. 12

iii. Le cas du système H-Ti-O :

Pour synthétiser du TiO₂ (B), une des voies les plus utilisées est de passer par la synthèse haute température de K₂Ti₄O₉. Dans un second temps, il est possible d'échanger les ions potassium par des protons en plongeant le matériau dans une solution d'acide concentrée (typiquement 3M HNO₃). En résulte la phase protonée H₂Ti₄O₉. La déshydratation topotactique de cet oxyde à 500°C permet l'obtention de TiO₂ (B). Un schéma récapitulatif est présenté Figure.I. 6A.^{62–64}

Dans une plus récente étude, Fleichmann et al.^{65,66} étudient les caractéristiques électrochimiques des différents oxydes intermédiaires durant la déshydratation de $H_2Ti_4O_9$ permettant l'obtention de TiO₂ (B). Ils démontrent que l'oxyde présentant une déprotonation partielle propose les capacités les plus élevées pour tous les courants testés (Figure.I. 6.B-C-D). Ce travail permet aussi de mettre en lumière l'impact des protons et des molécules d'eau situés entre les feuillets dans les mécanismes de charge des oxydes de titane. Ainsi, une légère différence de protonation de l'interfeuillet peut amener à des courbes de charge-décharge très différentes impliquant une insertion des ions lithium selon des mécanismes distincts. Ceci est expliqué par le rôle prédominant que jouent les protons dans la diffusion des ions lithium de l'interfeuillet.



Figure.I. 6 (A) Evolution de la structure cristallographique du système H-Ti-O en fonction de la température. (B) Courbe de charge décharge des différents oxydes du système H-Ti-O ainsi que leurs capacités en fonction du courant appliqué (C) et des cycles (D).

c. Les oxydes dit de Wadsley-Roth : l'apogée des oxydes multi cationiques.

Dans l'objectif de comprendre les oxydes multicationiques à base de titane et de niobium, il est primordial d'introduire la structure de l'oxyde de rhénium, ReO₃ ainsi que d'intégrer l'effet de l'insertion de lithium dans ce dernier. Dans la phase cubique Pm $\overline{3}$ m du ReO₃, les octaèdres de (ReO₆) partagent exclusivement leurs sommets comme exposé sur la Figure.I. 7A.^{67–69} Lors de l'insertion du lithium, différents changements de phase apparaissent. Dans un premier temps, entre 0 < x < 0.35, Li_xReO₃ se trouve décrit par une maille cubique et un groupe d'espace Im3.⁶⁸ Une distorsion des octaèdres (ReO₆) apparaît et le lithium est décrit comme étant situé dans des « plans carrés ». Ensuite, le composé défini, LiReO₃, peut être décrit par une phase hexagonale comportant une large distorsion des octaèdres. Les ions lithium étant trop petits pour s'insérer dans la structure hôte, une diminution de 5% du volume de la maille est observée.^{68,70} Puis, jusqu'à x=2, la structure reste décrite par une maille hexagonale présentant un volume supérieur pour pouvoir accommoder l'insertion de 2 ions lithium par

cage. De nouveau, les octaèdres (ReO₆) se trouvent très distordus (Figure.I. 7B). Ces changements cristallographiques engendrent de forte contrainte et une large variation volumique et donc une faible réversibilité et une médiocre rétention de capacité sont observées après quelques cycles (Figure.I. 7C).⁶⁸



Figure.I. 7 (A-B) Structure cristallographique du ReO₃ et Li₂ReO₃ (c) et leurs propriétés électrochimiques associées. Le violet correspond à x_{Li} = 0.35, le vert à x_{Li} = 2. ⁶⁸

En 1948, A. Magnéli propose la structure de deux nouveaux oxydes de molybdène $(Mo_9O_{26} \text{ et } Mo_8O_{23})$.⁷¹ Dans ces oxydes réduits, on constate que le degré d'oxydation total des molybdène est en moyenne de 5.77 et 5.75 pour Mo₉O₂₆ et Mo₈O₂₃ respectivement. Il est donc impossible pour les octaèdres (MoO₆) de s'organiser sous une forme cristallographique de type ReO₃. A. Magnéli comprend que le surplus de cations molybdène est compensé par une augmentation du nombre de liaisons moyennes entre les cations et les oxygènes et non par une déficience en oxygène. D'un point de vue cristallographique, cela se traduit par un changement d'organisation des octaèdres (MoO₆) qui partagent entre eux non seulement leurs sommets comme dans ReO₃ mais également leurs arêtes, comme illustrée Figure.I. 8(A-C). En d'autres termes, la structure se condense permettant la création d'octaèdres partageant leurs arêtes. Ces particularités cristallographiques sont appelées « défauts de Wadsley ».

De fait, dans les années 50, Wadsley remarque que l'organisation des « défauts de Wadsley » permet la formation de matériaux de composition M_nO_{3n-a} . Il introduit alors le concept qu'il nomme « *crystallographic shear* » (CS) tout en l'étendant à divers oxydes réduit à base de tungstène (WO_{3-x}) mais également à des matériaux complètement oxydés (H-Nb₂O₅ ou TiNb₂O₇) comme illustré Figure.I. 9. Dans le cas de ces derniers, les octaèdres (MO₆)
forment des blocs ou des colonnes selon un plan donné. n et m représentent le nombre d'enchainements d'octaèdres (MO₆) dans ce plan. Les blocs s'organisent comme l'oxyde de rhénium avec un partage de sommets entre octaèdres.



Figure.I. 8 (A) Structure de Mo₉O₂₆ décrit pour la première fois en 1948 par Magnéli. (B-C) Principe des défauts de Wadsley montrant le passage des structures de type ReO₃ (B) aux matériaux dit de « Wadsley-Roth » (C).⁷²



Figure.I. 9 Mécanisme de création des défauts de Wadsley entrainant la formation d'octaèdres partageant leurs arêtes.⁷³

i. Le cas de $TiNb_2O_7$:

TiNb₂O₇ est un exemple de matériau ayant une structure de type Wadsley-Roth. Il est composé de blocs $(3x3)_{\infty}$ d'octaèdres partageant leurs sommets illustrant la formation de « blocs ReO₃ » comme le montre la Figure.I. 10A. Le degré d'oxydation moyen des cations métalliques est de +4,66, loin des +6 nécessaires pour obtenir une structure de type ReO₃. Ce degré d'oxydation implique un partage élevé des atomes d'oxygène entre les métaux de transition et de fait un grand nombre d'octaèdres se liant par leurs arêtes.⁷⁴

 $TiNb_2O_7 + xLi^+ + xe^- \leftrightarrow Li_xTiNb_2O_7 \qquad Equation.I. 13$

De nombreuses études montrent l'intérêt de TiNb2O7 comme électrode négative pour les batteries Li-ion dites de puissance. En effet, ce matériau développe une capacité spécifique de 300 mAh.g⁻¹ à faible courant et présente une capacité de 175 mAh.g⁻¹ pour une charge à 10C (6 min de charge) comme illustré Figure.I. 10B. De nouveau, la réduction réversible des couples Ti⁴⁺/Ti³⁺ et Nb⁵⁺/Nb⁴⁺ permet d'obtenir des capacités relativement élevées. (Equation.I. 13) Il a été observé que la bonne rétention de capacité observée était due à une conductivité ionique élevée permise par les couloirs créés dans le matériau. Ces tunnels qui permettent une bonne diffusion des ions lithium sont formés grâce au partage des arêtes par les octaèdres de (Nb/TiO₆) typique des matériaux de type Wadsley-Roth.⁷⁵ Par l'utilisation de méthode RMN, une conductivité de 10⁻¹¹ m².s⁻¹ est reportée. De plus, dans TiNb₂O₇ la lithiation du matériau engendre une augmentation singulière de la conductivité électrique. Une bonne cyclabilité est expliquée par la rigidité des structures à CS permettant une faible distorsion de la structure pendant l'insertion et la désinsertion du lithium. L'ajout de nanotubes de carbone, la nanostructuration ou le coating de carbone conducteur à la surface de ce matériau semble permettre une meilleure rétention de capacité à fort courant même si les caractéristiques électrochimiques du matériau « bulk » sont déjà remarquables.⁷⁶⁻⁷⁹



Figure.I. 10 (A) Structure cristallographique du TiNb₂O₇ (B) et ses propriétés électrochimiques associées.⁷⁵

ii. Le cas de PNb_9O_{25} :

Décrit pour la première fois par Wadsley et Roth⁸⁰, PNb₉O₂₅ est un autre oxyde CS possédant une activité électrochimique particulièrement intéressante pour des applications dans les batteries à charge rapide. Bien qu'il soit également composé de blocs $(3x3)_{\infty}$ (Figure.I. 11A), sa structure diffère de TiNb₂O₇ car le degré d'oxydation moyen des métaux de transition est égal à 5 dans PNb₉O₂₅. Ainsi, moins de partage des oxygènes est nécessaire et donc moins d'octaèdres se liant par leurs arêtes. On remarque également la présence de tétraèdres (PO₄) entre 4 blocs 3x3 d'octaèdre (NbO₆). Les connexions entre les tétraèdres (PO₄) et les octaèdres (NbO₆) se font par partage de sommets.^{80–82}

En 2002, Patoux *et al.* étudient PNb_9O_{25} comme matériau d'électrode. ⁸² A faible courant (C/10), ils remarquent l'insertion de 13.5 Li⁺ dans la structure permettant la réduction partielle des ions Nb⁵⁺ jusqu'à un degré d'oxydation Nb³⁺ (Equation.I. 14). Cette insertion d'un grand nombre d'ions alcalins ne se fait pas sans changement de phase. Une étude par diffraction des rayons X *in situ* révèle l'apparition de trois phases différentes pendant l'insertion.

Cependant, aucun test à plus haut courant n'a été réalisé dans cette étude. O.A. Drozhzhin *et al.* montrent également que le coefficient de diffusion des ions lithium se situe entre 10^{-9} et 10^{-11} cm².s⁻¹, révélant l'intérêt de cette phase à structure partagée pour une diffusion facilitée des ions lithium.

$$PNb_9O_{25} + xLi^+ + xe^- \leftarrow \rightarrow Li_xPNb_9O_{25}$$

Equation.I. 14



Figure.I. 11 (A) Structure cristallographique du PNb₉O₂₅ (B) et ses propriétés électrochimiques associées.⁸³

C'est plus récemment que le groupe du Pr. Bruce Dunn revisite PNb_9O_{25} en tant qu'électrode pour batterie de puissance.^{83–85} Les auteurs démontrent une capacité de 150 mAh.g⁻¹ pour une charge à 10C (6 minutes de charge) (Figure.I. 11B). Différents arguments sont donnés afin d'expliquer les capacités de cette phase à fort courant. Premièrement, des mesures de susceptibilité magnétique *ex situ* sur des électrodes ainsi que des calculs par DFT montrent une transition isolant – conducteur métallique ce qui permet un transfert de charge rapide. Cette transition est due au recouvrement orbitalaire de la couche électronique externe (4d) du Nb³⁺ dont les octaèdres (NbO₆) partagent leurs arêtes.^{83,84} Des mesures d'entropie semblent également confirmer cette transition.⁸⁵ Une étude par calorimétrie faite dans des conditions *operando* semble démontrer que la partie majoritaire des pertes se produit par effet Joule (chaleur) et qu'une faible enthalpie de mélange permet à ce matériau d'être adapté pour fonctionner à haut courant.⁸⁵ De plus, cette étude très complète montre l'importance des méthodes *in situ/operando* (DRX, XAS, calorimétrie, *etc.*) ainsi que l'utilisation du calcul pour mieux comprendre l'implication des ions lithium dans la structure cristalline et plus largement les propriétés physico-chimiques des oxydes à structure partagée.

iii. Le cas de Nb₁₈ $W_{16}O_{93}$:

En 1965, Wadsley et Roth décrivent conjointement une partie des oxydes du système W-Nb-O présentant des caractéristiques de type CS.^{86–88} Ainsi, dans la même mouvance que les oxydes précédents, de nombreuses études ont démontré l'intérêt du système W-Nb-O en tant que potentiels matériaux d'électrode négative. Les travaux du Prof. R.J. Cava dans les années 1980 ont montré la voie.⁸⁹ Il prouve la possibilité d'insérer 1 lithium par métal de transition dans WNb₁₂O₃₃, W₃Nb₁₄O₄₄ et W₈Nb₁₈O₆₉ à faible courant tout en montrant une faible variation volumique pendant la lithiation de ces oxydes. Plus tard, D. Saritha *et al.* étudient plus en détail WNb₁₂O₃₃ synthétisé par voie céramique et par voie sol-gel.⁹⁰ La synthèse sol-gel démontre une capacité de 142 mAh.g⁻¹ à 20C (charge en 3 minutes). Cette capacité est attribuée à la réduction réversible des couples W⁶⁺/W⁵⁺ et Nb^{5+/}Nb⁴⁺ ainsi que la réduction partielle du couple Nb⁴⁺/Nb³⁺ et W⁵⁺/W⁴⁺ démontrant un redox multiélectronique.

Plus tard, d'autres oxydes du système W-Nb-O formant des matériaux dits de Wadsley-Roth ont été étudiés par le groupe de la Prof. Clare P. Grey.^{91–95} Un exemple est l'oxyde Nb₁₆W₅O₅₅ qui est formé d'unité (5x4) $_{\infty}$ d'octaèdres (MO₆) comme illustré Figure.I. 12A. Le degré d'oxydation moyen des cations métalliques étant plus élevé (5,47), un plus faible partage des arêtes est nécessaire ce qui entraine des blocs d'octaèdres plus étendus. Les caractéristiques électrochimiques décrites sont très intéressantes. Comme illustré Figure.I. 12B, ce matériau propose une capacité de 145 mAh.g⁻¹ à 10C (charge en 6 minutes). Une nouvelle fois, cette capacité à 10C est expliquée par une bonne diffusion des ions lithium dans les tunnels du matériau (D_{Li+} = 10⁻¹³ cm².s⁻¹ calculé par « pulsed field gradient » RMN). Les bonnes rétentions de capacité sont aussi expliquées par la faible énergie d'activation des sites de lithiation présent dans la structure (0.27-0.30 eV). D'autres oxydes du système W-Nb-O ont également été étudiés et montrent des comportements électrochimiques très similaires.^{91,92,94,96} Une des spécificités de ses travaux est l'utilisation de la RMN du solide *ex situ/in situ* pour décrire les sites de lithiation, mesurer les coefficients de diffusion du lithium ainsi que calculer les énergies d'activation de ses oxydes lors de la lithiation. Une nouvelle fois l'aide du calcul (DFT, méthode de Monte Carlo...) a également été primordiale pour la compréhension des phénomènes mis en jeu dans ces matériaux.^{91,92,94,96}



Figure.I. 12 (A) Structure cristallographique de Nb₁₆W₅O₅₅ (B) et ses propriétés électrochimiques associées.⁹¹

Ainsi, l'étude bibliographique des phases dites de WR nous a montré que le partage des octaèdres (MO₆) montre plusieurs avantages. Contrairement à ReO₃, ces oxydes démontrent une meilleure rigidité et un maintien de la structure durant la lithiation/delithiation. De plus, ces structures forment des tunnels (ou « couloirs ») donc l'énergie d'activation est dans certains cas très faibles et le coefficient de diffusion des ions élevé (de l'ordre de 10⁻¹¹ - 10⁻¹² cm².s⁻¹). De récentes publications semblent également montrer qu'une transition isolant-conducteur lors de la réduction du Nb⁴⁺ en Nb³⁺ par délocalisation des électrons ainsi qu'une faible perte d'énergie par effet Joule entre la charge et la décharge permet d'obtenir de très bonnes performances à haute vitesse de charge/décharge. Dernièrement, la densité volumique relativement élevée de ses matériaux permet d'obtenir des capacités volumiques (mAh.cm⁻³) plus élevées que le graphite.

Cependant, certains oxydes de type WR fonctionnent relativement mal en tant qu'électrode négative pour batterie de puissance. On peut donner l'exemple de H-Nb₂O₅ qui présente une bonne capacité à faible courant (225 mAh.g⁻¹ à C/10 pour une charge en 10 heures) mais une capacité spécifique presque nulle à haut courant (25 mAh.g⁻¹ à 3C pour une charge en 20 minutes).⁴¹ H- Nb₂O₅ étant formé de deux blocs $(3x4)_{\infty}$ et $(3x5)_{\infty}$ d'octaèdres (NbO₆). Griffith *et al.* expliquent que malgré le grand nombre de sites de lithiation disponibles, une mauvaise connexion entre ces sites ne permet pas aux ions lithium de correctement diffuser au sein de la structure. Ceci entraine l'obtention de faibles capacités à haut courant. Un autre exemple est VNb₉O₂₅ qui est isostructural à PNb₉O₂₅. Lors de la lithiation, le couple V⁵⁺/V⁴⁺ va également rentrer en jeu offrant une capacité plus élevée lors du premier cycle. Cependant, le processus n'étant pas réversible une perte de capacité ainsi qu'une plus faible stabilité structurale sont observées entrainant un comportement à haut courant plus faible que pour son analogue PNb₉O₂₅.⁸³ De plus, une faible stabilité est observée lors des tests de cyclabilité. Ainsi, il est important de comprendre le rôle de la structure cristallographique et des cations métalliques mis en jeu pour designer des oxydes à CS performant.

d. Les structures lamellaires dérivées des oxydes de Wadsley-Roth.

En 1987, B. Raveau publie une revue de la littérature intitulée, *structural relationships in lamellar oxide built up from edge-sharing octahedra.*⁹⁷ Dans cette article, il développe l'idée que certains oxydes lamellaires, qui ont dans leurs couches des octaèdres partageant leurs arêtes, peuvent être décris de manière très similaire aux matériaux dit de Wadsley-Roth. Il explique l'origine du partage des arêtes de la manière suivante: *"The number of octahedral oxides with a layer structure is limited owing to the fact that it is rather difficult to ensure the rigidity of layers which are only built up from octahedra. When the octahedra share only their corners, the sheets must generally be thick in order to avoid a collapse of the layer as shown for the titanates and titanoniobates* $A_nM_nO_{3n+2}$, for which the smallest member, represented by $Ca_2Nb_2O_7$, is formed of four octahedra thick ReO_3 -type layers. Then it appears that the connection of the octahedra through their edges will be necessary to generate thin layers, *i.e.* to increase the lamellar character of octahedral oxides."⁹⁷

Il propose deux motifs pour la création de ses couches comme illustré Figure.I. 13. Ils seront respectivement appelés mode I (Figure.I. 13A) et mode II (Figure.I. 13B). Dans le mode

I, chaque octaèdre partage deux arêtes avec les octaèdres adjacents. Dans le second mode (mode II), chaque octaèdre partage trois arêtes avec les octaèdres adjacents permettant une plus grande compacité des couches.

i. Les matériaux lamellaires présentant uniquement un partage d'arête :

Des couches présentant uniquement un partage d'arête sont formées par une répétition de ces deux différents modes. Par exemple, comme illustré Figure.I. 14A, la succession de mode I permet la formation de l'oxyde ThTi₂O₆.⁹⁸ De manière plus complexe, la succession du mode I puis du mode II conduit à la formation des couches de Ag_xV₂O₅ comme illustré Figure.I. 14B.^{99,100} Bien d'autres oxydes peuvent être formés par ce principe (Ag_{1+x}V₃O₈, K_xMn₂O₄ ou encore LiMnO₂)



Figure.I. 13 (A-B) Motifs élémentaires permettant la création de couche d'oxyde lamellaire *via* un partage partiel des arêtes.



Figure.I. 14 Structures des oxydes (A) ThTi₂O₆ et (B) Ag_xV₂O₅.⁹⁷

ii. Les matériaux lamellaires présentant un partage d'arêtes et de sommets :

Au contraire, certaines couches présentent des octaèdres ne partageant pas seulement leurs arêtes mais également leurs sommets. La famille des titanates/titanoniobates $A_nM_{2n}O_{4n+2}$ (A=K, Rb, Cs, Tl & M=Ti, Nb) est représentative de ce type de phase. Ces oxydes peuvent être décrits comme *n* successions du mode II suivi par un partage des octaèdres aux extrémités *via* leurs sommets. Ainsi, si n = 3, des couches (M₃O₇) vont être formées comme illustré dans la Figure.I. 15A. Pour un n donné, différentes structures peuvent être formées en fonction de la disposition des couches entre elles. Dans le cas de Na₂Ti₃O₇, la position d'une couche par rapport à une autre peut être décrite par simple translation.^{101,102} Dans d'autres cas comme celui de A₃Ti₅NbO₁₄ (Figure.I. 15A), une rotation de 90° est nécessaire selon l'axe (010) entre chaque couche.



Figure.I. 15 Structure de l'oxyde (A) A₃Ti₅NbO₁₄ et de (B) KTiNbO₅.⁹⁷

Un des membres de la série n = 2 est ATiNbO₅ avec A = K, Rb, Tl et peut-être décrit comme l'association d'un partage des arêtes selon le mode II suivi d'un partage des sommets. Cette série permet la création d'unités (2x2) d'octaèdres partageant leurs arêtes (Figure.I. 15B). De la même manière que A₃Ti₅NbO₁₄ une rotation de 90° est nécessaire selon l'axe (010) pour décrire l'enchainement des couches.^{97,103–105}

e. Étude de cas : KTiNbO₅, HTiNbO₅ et Ti₂Nb₂O₉

i. KTiNbO₅, HTiNbO₅ et Ti₂Nb₂O₉ : Propriétés d'échanges ioniques

Une partie des travaux de thèse présentée dans les chapitres suivants s'intéressera à la famille des titanoniobates dérivant de KTiNbO₅ ainsi que des oxydes proches. Ainsi, une étude bibliographique précise de ces oxydes semble primordiale dans le but de comprendre l'histoire, la complexité ainsi que la grande diversité de phases et de morphologies que propose cette famille de matériau. Comme décrit ci-dessus, KTiNbO₅ est un oxyde lamellaire présentant des unités 2x2 d'octaèdres partageant leurs arêtes. Ces blocs forment des couches (TiNbO₅⁻)_n par partage de sommets. Entre ces couches se trouvent des ions potassium. Décrit pour la première fois par Wadsley¹⁰³, KTiNbO₅ cristallise dans une maille orthorhombique et un groupe d'espace Pnma. Le matériau est alors décrit comme étant lamellaire selon c avec des paramètres de maille valant : a = 6.459 Å, b = 3.792 Å, c = 18.742 Å (Figure I.16.A). Les ions titane sont majoritairement sur les octaèdres externes aux couches car ces derniers sont moins distordus.¹⁰⁶



Figure.I. 16 Structure cristallographique du (A) KTiNbO₅ (B) HTiNbO₅ (C) Ti₂Nb₂O₉.

Raveau *et al.* remarquent que KTiNbO₅ possède des propriétés d'échange cationiques (Equation.I. 15). En plongeant l'oxyde KTiNbO₅ dans une solution d'acide concentré, il est possible d'obtenir la phase protonée HTiNbO₅.¹⁰⁷ Des analyses par ATG montre que la réaction d'échange se fait sans insertion de molécules d'eau dans la structure du fait du rôle primordiale du proton dans le maintien de la structure lamellaire de HTiNbO₅. Du fait d'un rayon ionique plus faible et d'une charge électrique plus concentrée, la distance interlamellaire dans HTiNbO₅ est plus faible que son analogue KTiNbO₅. HTiNbO₅ cristallise également dans une maille orthorhombique et un groupe d'espace Pnma avec a = 6.531 Å, b = 3.781 Å, c = 16.704 Å (Figure.I. 16).

Une autre phase peut être synthétisée *via* HTiNbO₅. En effet, un recuit à 400°C entraine une réaction transformant HTiNbO₅ en Ti₂Nb₂O₉ *via* la perte d'une molécule d'eau (Equation.I. 16). Cette transformation topotactique entraine une diminution significative du paramètre c ainsi que le passage d'un matériau lamellaire en un autre présentant des tunnels pentagonaux comme illustré Figure.I. 16C. Ti₂Nb₂O₉ cristallise dans une maille orthorhombique et un groupe d'espace Pnmm avec a = 6.4 Å b = 3.8 Å c = 14.9 Å.¹⁰⁸

$KTiNbO_5 + H^+ \rightarrow HTiNbO_5 + K^+$	Equation.I. 15
$2 \text{ HTiNbO}_5 \rightarrow \text{Ti}_2\text{Nb}_2\text{O}_9 + \text{H}_2\text{O}$	Equation.I. 16

La versatilité de ce matériau permet grâce à différents traitements par voie aqueuse ou solide l'obtention de diverses autres phases telles que TlTiNbO₅¹⁰⁷, LiTiNbO₅¹⁰⁹, NaTiNbO₅¹⁰⁷, NH₄TiNbO₅¹⁰⁷, Mn(Sr)²⁺_{0.5}TiNbO₅¹¹⁰, *etc.* Il a été également reporté l'insertion de molécules organiques dans l'espace interfeuillets tel que des alkylamines et/ou des alcools alkyliques.^{111–115}

Dernièrement, la réaction acido-basique de l'acide $HTiNbO_5$ avec du tetrabutylammonium (TBAOH) en solution aqueuse permet l'exfoliation des feuillets $TiNbO_5^-$ se retrouvant alors en suspension. Une solution colloïdale est formée. Les nanofeuillets peuvent être réempilés par un ajout progressif d'acide dans la solution (typiquement HCl ou HNO₃).



Figure.I. 17 Images MEB (A) de HTiNbO₅ (B) de feuillets de HTiNbO₅ réempilés.¹¹⁶ (C) Photographie par AFM et le profilomètre associé démontrant qu'il s'agit de monofeuillets de HTiNbO5.¹¹⁷

Les images MEB de la Figure.I. 17(A-B) illustrent la différence de morphologie observée entre les particules de HTiNbO₅ avant (A) et après (B) le processus d'exfoliation réempilement. On remarque une organisation aléatoire et désordonnée des feuillets entre eux, permettant d'augmenter significativement la surface spécifique comparativement aux particules avant exfoliation. La littérature reporte des surfaces spécifiques supérieures à 100 m².g⁻¹ pour des nanofeuillets réempilés quand le précurseur possèdent des particules micrométriques avec une surface spécifique d'environ 5 m².g⁻¹.¹¹⁸ La photographie et le profilomètre de la Figure.I. 17C illustre également la possibilité d'obtenir des monofeuillets d'HTiNbO₅. Ces derniers ont été largement étudiés pour leurs performances en catalyse.

Dans la littérature, KTiNbO₅ a été majoritairement synthétisé *via* voie céramique. Un recuit entre 1000°C et 1150°C des précurseurs K₂CO₃, Nb₂O₅ et TiO₂ permet l'obtention de particules micrométriques.^{103,104,119,120} Ces particules présentent une croissance préférentielle selon la direction \vec{c} comme illustrée Figure.I. 18A.



Figure.I. 18 (A-D) Images MET de particules de KTiNbO₅ pour différentes méthodes de synthèse.^{118,121-123}

Cependant, de nombreuses études proposent la synthèse de KTiNbO₅ par chimie douce.^{121–126} Ainsi comme illustré Figure.I. 18B-D, il est possible d'obtenir des nanoparticules. H. Park *et al.* proposent une synthèse par voie solvothermale à 200° par dissolution des ions K/Ti/Nb dans une solution basique d'alcool isopropylique. Un recuit entre 500° et 1100° permet l'obtention de nanoparticules. Les auteurs remarquent que les particules montrent une croissance préférentielle selon l'axe \vec{c} avec l'augmentation de la température de cristallisation jusqu'à prendre la forme de nano plaquettes à 1100°C (Figure.I. 18*B*).¹²¹ Dans une autre étude, N. Wang *et al.* proposent une synthèse sol-gel de KTiNbO₅ permettant une nouvelle fois d'obtenir des nanoparticules (Figure.I. 18*D*).¹²³ Dernièrement, B. Li *et al.* démontrent l'intérêt du post-traitement solvothermal pour obtenir des particules de plus petite taille que dans le cadre d'une simple réaction sol-gel (Figure.I. 18*C*).¹²²

ii. KTiNbO₅, HTiNbO₅ et Ti₂Nb₂O₉ : Un matériau d'électrode prometteur

La famille de matériaux dérivant de KTiNbO₅ a permis d'explorer plusieurs domaines d'application. Parmi ceux-ci, la catalyse, l'élaboration de matériaux hybrides organique-

inorganique pour améliorer les propriétés thermomécaniques de ces oxydes ou encore la séparation de molécules organiques de leurs solvants.^{111–115} Ici nous nous intéresseront à ces oxydes comme de potentielles électrodes négatives pour batterie Li-ion. Il n'existe qu'une poignée de publications scientifiques exposant le comportement de KTiNbO₅, HTiNbO₅ et Ti₂Nb₂O₉ comme matériaux d'électrode. La Tableau 2. est une liste non exhaustive de ces matériaux et permet de récapituler les principales caractéristiques électrochimiques de KTiNbO₅, HTiNbO₅ et Ti₂Nb₂O₉.

	Potential range	Capacity at 1C / mAh.g ⁻¹	Capacity at 10C / mAh.g ⁻¹	Capacity retention	Reference
HTiNbO₅ bulk	1V-3V vs Li/Li ⁺	~ 150	Not reported	83 % (50 cycles)	127
HTiNbO ₅ nanowire	1V-3V vs Li/Li ⁺	~ 169	< 90	85.84 % (150 cycles)	31
HTiNbO ₅ nanosheet	1V-3V vs Li/Li ⁺	~ 100	Not reported	Not reported	128
HTiNbO5 nanosheet/ MXenes	1V-3V vs Li/Li ⁺	~ 221	< 110	86.4 % (1000 cycles)	128
Ti ₂ Nb ₂ O ₉ bulk	1V-3V vs Li/Li ⁺	~ 114 (C/5)	Not reported	83 % (30 cycles)	129
Ti ₂ Nb ₂ O ₉ bulk	1V-3V vs Li/Li ⁺	~ 160	~ 50	> 80% (500 cycles)	106
Ti ₂ Nb ₂ O ₉ NS	Not reported in literature				

Tableau.I. 2 Comparaison de KTiNbO₅, HTiNbO₅ et Ti₂Nb₂O₉ décris pour matériau d'électrode négative pour batteries.

Premièrement, KTiNbO₅ présente une insertion des ions lithium relativement limitée entre 1V et 3V *vs* Li/Li⁺. En 2019, Yu *et al.* ont montré que des nanofils de KTiNbO₅ ne proposaient une capacité spécifique que de 20 mAh.g⁻¹ à 0.5C comme illustré Figure.I. 19A.³¹ Cette faible capacité est expliquée par la gêne stérique qu'entraine la présence d'ions potassium entre les couches de (TiNbO₅)_n. Cette capacité de 20 mAh.g⁻¹ était probablement d'origine surfacique (stockage capacitif et/ou pseudocapacitif).



Figure.I. 19 Comportement électrochimique de KTiNbO₅ et HTiNbO₅. (A) Courbe de charge décharge de mesure de cyclabilité ainsi que test de charge décharge à différent courant de KTiNbO₅ et HTiNbO₅ (B) Expérience de DRX *in situ* durant les 2 premiers cycles de HTiNbO₅.³¹

Cependant, lors du remplacement des cations présents dans l'espace interfeuillets par des protons, l'insertion de Li⁺ augmente significativement. J.F Colin et al démontre une capacité de 150 mAh.g⁻¹ (à C) pour des particules micrométriques de HTiNbO₅.¹²⁷ Les performances à plus fort courant ne sont pas présentées dans cette étude. Plus récemment, des capacités de 169.5 mAh.g⁻¹ pour une charge à 1C et < 90 mAh.g⁻¹ pour une charge à 10C ont été reportées pour H_{0.92}K_{0.08}TiNbO₅ sous forme de nanofils (Figure.I. 19A). De plus, des études en cyclage démontrent une rétention de capacité de l'ordre de 85% après 150 cycles. Une étude par DRX *in situ* (Figure.I. 19B) met en évidence un changement de phase initiale menant à l'oxyde Li_{0.4}H_{0.92}K_{0.08}TiNbO₅ puis un mécanisme de charge de type solution solide. Le stockage de charges de type solution solide est un atout dans les applications de puissance car les changements de phase sont cinétiquement limitants. Des résultats intéressants sont donc

démontrés pour la phase HTiNbO₅. De manière remarquable, de faibles différences de capacité sont observées à 1C entre les deux types de morphologies (particules micrométriques et nanofils).

HTiNbO₅ a également été étudié après exfoliation c'est-à-dire sous forme de nanofeuillets rempilés.¹²⁸ Dans cette étude récente, une floculation de nanofeuillets de MXene et de HTiNbO₅ est mise en œuvre. Les MXenes sont de bons conducteurs électriques ^{130–132} mais également des matériaux d'électrode négative de choix pour des applications de puissance.^{40,133} Ainsi, pour un ratio HTiNbO₅ : MXene de 3 pour 1, des capacités de 221 mAh.g⁻¹ pour une charge à 1C et < 110 mAh.g⁻¹ pour une charge à 10C sont reportées. Quand les nanofeuillets ré-empilés de HTiNbO₅ sont testés sans ajout de MXene, une faible capacité est reportée (inférieure à 100 mAh.g⁻¹ à C/10) dû à une faible réversibilité lors du premier cycle ainsi qu'à un transfert de charge lent à cause de la faible conductivité intrinsèque de ce titanate de niobium. Il est important de signaler que malgré le possible intérêt du proton dans cet oxyde, aucune publication n'étudie son rôle précis dans le mécanisme de charge.

Le dernier oxyde de cette famille, Ti₂Nb₂O₉, a également été étudié en tant que matériau d'électrode dans la littérature. En 2008, J-F Colin *et al.* étudient des particules micrométriques de Ti₂Nb₂O₉ synthétisées par voie céramique. Ils remarquent la création de nanoporosité dans le matériau résultant de la déshydratation de HTiNbO₅. Une insertion favorisée des ions lithium et une capacité de 114 mAh.g⁻¹ à C/5 sont reportées dans cette publication. De plus, une bonne rétention de capacité est observée (83% après 30 cycles). Plus récemment, Drozhzhin *et al.* revisitent Ti₂Nb₂O₉ comme matériau d'électrode négative. Dans cette étude, Ti₂Nb₂O₉ est une nouvelle fois synthétisé par voie céramique entrainant la formation de particules micrométriques. Ils démontrent une capacité d'environ 160 mAh.g⁻¹ à C et de 50 mA mAh.g⁻¹ à 10 C (Figure.I. 20A-B). Une bonne cyclabilité est observée, comme illustré Figure.I. 20C, avec une rétention de capacité de 80% après 500 cycles. Grâce à l'utilisation de la DRX et de spectrométrie d'absorption des rayons X dans des conditions *operando*, les auteurs mettent en évidence d'une part que le mécanisme de charge est de type solution solide (Figure.I. 20D) et que les couples Ti⁴⁺/Ti³⁺ et Nb⁵⁺/Nb⁴⁺ sont à l'origine du transfert de charge.



Figure.I. 20 (A-B) Courbe de charge décharge de $Ti_2Nb_2O_9$ à courant de charge constant (A) ou courant de décharge constant (C) Mesure de cyclabilité de $Ti_2Nb_2O_{9.}$ (D) Expérience de DRX *in situ* durant 2 cycles de $Ti_2Nb_2O_{9.}$

Ti₂Nb₂O₉ et HTiNbO₅ n'ont jamais été étudiés dans le cadre d'une même publication scientifique. Il est donc compliqué de faire des conclusions quant aux rôles du proton ainsi que l'influence entre une structure lamellaire et tunnellaire sur le stockage de charge. Les chapitres expérimentaux qui vont suivre s'attacheront à décrire plus en détail le lien entre les propriétés cristallographiques et électrochimiques de ces oxydes.

D'autres phases intéressantes dont la composition est basée sur les métaux de transition préalablement explorés (Nb, W, Ti...) ont été décrits dans la littérature. Les chimistes des matériaux ont développé un important panel de phases dans les systèmes A-Nb-W-O ou A-Nb-Ti-O ou A-M-Nb-O ou A est un alcalin et M = (La, Sr, Ca). Dans la plupart des cas, ces phases présentent des propriétés d'échange ionique similaires à KTiNbO₅. Cependant, peu d'entre elles ont été étudiées pour leurs propriétés électrochimiques. Elles feront l'objet d'une étude dans le Chapitre V de cette thèse.

IV. Conclusion

Ce chapitre a permis d'exposer les principes généraux des systèmes électrochimiques comme les batteries Li-ion ou les supercondensateurs. Une attention particulière a été portée aux oxydes de niobium et de titane pour remplacer l'électrode de graphite dans l'idée de produire des batteries se chargeant plus rapidement. Enfin, nous nous sommes attachés dans une dernière partie à mettre en évidence l'intérêt des structures possédant des partages d'octaèdres par leurs arêtes comme les oxydes de Wadsley-Roth ou encore le matériau lamellaire KTiNbO₅.

Avant que le chapitre III et les suivants s'intéressent aux oxydes à base de niobium, cette thèse commence par l'utilisation de l'oxyde $Ag_2V_4O_{11}$ possédant, comme décrit précédemment, une structure lamellaire avec un partage des octaèdres par leurs arêtes. Cette oxyde est historiquement utilisé comme cathode dans les piles pour les défibrillateurs implantés car il permet de fournir une quantité significative d'énergie en très peu de temps et démontre une faible autodécharge. L'utilisation de ce matériau pour des batteries Li-ion rechargeables est exposée dans le Chapitre II.

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Chapitre II. Etude de l'applicabilité d'Ag₂V₄O₁₁ comme électrode positive dans des systèmes rechargeables.

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I. Introduction

1. Les sels de lithium sacrificiel dans les *Li-ion capacitors*.

Au début de cette thèse, une partie de l'équipe de recherche travaillait sur les *Li-ion capacitors*. Ces derniers sont des dispositifs de stockage électrochimique combinant une électrode de supercondensateur et une électrode de batterie.^{1–4} L'objectif de tels systèmes est de trouver un compromis entre la densité de puissance élevée du supercondensateur et la grande densité d'énergie d'une batterie Li-ion. Ainsi, dans la plupart des cas, le graphite fonctionne en tant qu'électrode négative quand du charbon actif agit à l'électrode positive.⁵ Des *Li-ion capacitors* sont, par exemple, commercialisés par JM Energy offrant une densité d'énergie de 20 Wh.kg⁻¹ et une densité de puissance de 10kW.kg⁻¹ pour une capacité de 3300 F.^{6,7}

Contrairement aux batteries Li-ion traditionnelles, l'un des désavantages des Li-ion capacitors réside dans l'absence de matériau d'électrode contenant du lithium. Ainsi, lors de la première charge, le graphite va insérer le lithium provenant de l'électrolyte et non de l'électrode positive. Cette déplétion d'ions lithium dans l'électrolyte va diminuer la conductivité ionique entre les deux électrodes et donc limiter la densité de puissance du système. Notre groupe en collaboration avec celui du Pr. François Béguin ont étudié différentes solutions pour contrer ce problème.^{8,9} La voie la plus prometteuse semble être l'utilisation d'un composé lithié et sacrificiel placé dans l'électrode positive. Ainsi, pendant sa thèse, Pawel Jezowski a travaillé sur des oxydes et des sels sacrificiels dans le but d'apporter du lithium de manière in situ au système. Li_{0.65}Ni_{1.35}O₂ ainsi que Li₅ReO₆ ont été étudiés en tant que matériaux sacrificiels pour la prélithiation des *Li-ion capacitors*.^{8,9} Ces oxydes proposent respectivement une capacité irréversible de 125 et 410 mAh.g⁻¹ lors de la première charge et ne fournissent pas de capacités aux cycles suivants. Le coût et l'empreinte environnementale élevés de ces matériaux ainsi que la complexité que représente le recyclage des métaux contenus dans ces oxydes ont amené notre groupe à proposer une solution alternative. Cette alternative réside dans l'utilisation d'une molécule organique lithiée, le 3,4-dihydroxybenzonitrile dilithium salt (Li2DHBN). Elle présente une capacité théorique irréversible de 365 mAh.g⁻¹ et un potentiel de délithiation proche de 3.3V vs Li⁺/Li assurant la non-oxydation de l'électrolyte.⁷ De plus, cette molécule possède l'intérêt de rendre le système plus simplement recyclable (car organique) et de réduire son empreinte carbone. D'autres molécules organiques servant de sources de lithium pour les *Li-ion capacitors* ont depuis été développées par différents groupes de recherche. ^{10–13}

Dans la continuité de ce travail, la première partie de mes travaux de thèse avait pour ambition de développer des batteries rechargeables utilisant une cathode non lithiée grâce à l'ajout de Li₂DHBN au sein de l'électrode positive. Ag₂V₄O₁₁, un matériau que l'on retrouve dans les batteries primaires de puissance, a été utilisé pour établir une preuve de concept du fonctionnement d'un tel système électrochimique.

2. L'oxyde $Ag_2V_4O_{11}$ comme cathode dans les batteries primaires

 $Ag_2V_4O_{11}$ est un oxyde cristallisant dans une structure monoclinique (C2/m). C'est un matériau lamellaire dont la formation des couches peut être décrite grâce à la nomenclature décrite par B. Raveau et explicitée dans le Chapitre I.¹⁴ L'association d'un partage des arêtes selon le mode II, créent des unités 2x2 d'octaèdres (VO₆). Celles-ci forment une couche (V₄O₁₁)_n grâce à un partage du sommet des octaèdres externes. Les couches de (V₄O₁₁)_n sont séparées par des ions argent (Ag⁺). La structure est très proche de Cu_{1.8}V₄O₁₁ comme indiqué par Rozier et al.¹⁵

Ce matériau a été largement utilisé dans les dispositifs électrochimiques non rechargeables (piles) nécessitant de la puissance. Ainsi, en 1993, tous les défibrillateurs implantables utilisaient une pile avec comme matériau de cathode $Ag_2V_4O_{11}$.¹⁶ On estime que plus de 80 000 « piles $Ag_2V_4O_{11}$ » ont été implantées chez l'homme. Le groupe de la Pr. Esther Takeuchi a largement contribué à la compréhension du mécanisme de décharge de ces matériaux.^{17–22} De plus, le groupe du Pr. Jean-Marie Tarascon a également prouvé la partielle réversibilité du processus de stockage de charge de ce matériau.^{23,24} Les mécanismes mis en jeu seront largement explicités dans la publication associée à ce chapitre.

3. Stratégie pour l'utilisation d'Ag₂V₄O₁₁ dans les batteries secondaires

Pour résumer, l'originalité de ce travail réside dans l'utilisation d'un sel sacrificiel (Li₂DHBN) en association avec un matériau d'électrode de puissance utilisé dans les batteries primaires ($Ag_2V_4O_{11}$) pour créer une électrode fonctionnant dans une cellule complète et rechargeable. Dans un premier temps, nous avons revisité le mécanisme de stockage de charge complexe dans $Ag_2V_4O_{11}$. Une électrode composite associant $Ag_2V_4O_{11}$ et Li₂DHBN a été

testée ensuite en face d'une électrode de lithium puis en cellule complète en association avec du graphite. Les résultats sont résumés dans la publication ci-après.

II. La publication

Ag₂V₄O₁₁: from primary to secondary battery

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ORIGINAL PAPER



$Ag_2V_4O_{11}$: from primary to secondary battery

Etienne Le Calvez^{1,2} · Olivier Crosnier^{1,2} · Thierry Brousse^{1,2}

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Abstract

 $Ag_2V_4O_{11}$ (silver vanadium oxide, SVO) is the positive electrode in primary lithium/SVO batteries that had known an extraordinary success as a power source in implantable cardiac defibrillators (ICD). However, its use in rechargeable batteries is questioned due to the need of the negative lithium metal electrode that acts as the lithium source and that cannot be safely recharged in standard liquid electrolytes. In this study, a proof of concept of rechargeable graphite/SVO battery is demonstrated. The introduction of 3,4-dihydroxybenzonitrile dilithium salt (Li₂DHBN) as a sacrificial lithium source in the positive electrode allows in situ lithiation of the graphite electrode. The cell can further be cycled as a secondary battery. Different parameters have been investigated such as the particle size of $Ag_2V_4O_{11}$ synthesized by solid state and hydrothermal processes, especially with regard to peak power delivery. In situ XRD was used to investigate the link between irreversible silver reduction, which allows high electronic conductivity, and amorphization of the SVO structure.

Keywords $Ag_2V_4O_{11}$ · Prelithiation · Primary battery · Rechargeable Li-ion battery · Sacrificial lithium salt

Introduction

Lithium/silver vanadium oxide $(Ag_2V_4O_{11}, SVO)$ primary batteries have been developed from 1979 [1]. Since then, they have met an outstanding commercial success mainly due to their ability to power implantable cardiac defibrillator (ICD) while meeting all the requirements of such peculiar application [2]. To summarize the major requirements expected for such batteries, it can be emphasized that an ICD continuously monitors heart function and on demand delivers a high-energy shock to the heart to treat arrhythmias. Practically, this means that apart from the continuous delivered current (10 to 50 µA) required to power the monitoring circuitry, there is a need to sustain high power pulses, in the range of 1 to 4 A, to rapidly charge the high

Dedicated to Prof. Doron Aurbach, a researcher who genuinely investigated so many battery chemistries, providing major findings to our community.

Thierry Brousse

thierry.brousse@univ-nantes.fr

- ¹ Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, 44000 Nantes, France
- ² Réseau Sur Le Stockage Electrochimique de L'Energie (RS2E), CNRS FR 3459, 33 rue Saint Leu, 80039 Amiens Cedex, France

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voltage capacitors whose discharge to the heart interrupts the ventricular fibrillation. The Li/SVO battery is also able to be operated at 37 °C (human body temperature) with less than 2% self-discharge per year on open-circuit storage or under low current drain. Long shell life is also depicted [2]. Moreover, a practical energy density close to 1000 Wh/L makes the Li/SVO system attractive for applications where battery size is of concern.

 $Ag_2V_4O_{11}$ cathode of this primary battery and more largely the Li/SVO battery itself has been extensively studied by the team of Prof. Esther Takeuchi in numerous papers tackling all aspects of this energy storage device [2–7]. SVO cathode belongs to the class of vanadium bronzes and possesses semiconducting properties. Its electrochemical reduction is depicted as a multistep process taking place between 3.2 and 1.5 V vs Li⁺/Li, leading to the overall reaction:

$$Ag_2V_4O_{11} + 7Li^+ + 7e^- \rightarrow Li_7Ag_2V_4O_{11}$$
 (1)

This results in a theoretical capacity of 315 mAh g⁻¹ within this potential window. The irreversible reduction of silver occurring at the highest potential of the electrochemical window provides electronic conductivity to the surface of the SVO particles, which further enhances the high rate capability of this electrode. The growth of silver nanoparticles or nanowires upon the first stage of reduction has been evidenced by different teams [8–10].

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Although Li/SVO batteries have been practically cycled over tenth of charge/discharge cycles, the use of the metallic lithium anode is detrimental to the safety of a practical use as rechargeable power source for ICD. This is indeed mainly related to the growth of lithium dendrites upon cycling at such temperatures, which can shortly lead to internal shortcircuiting the battery [11]. However, with the growing interest in inductively rechargeable batteries, it can be interesting to design a SVO-based battery which keeps the advantages of this cathode material. This supposes that a lithium source can be implemented in the battery and that this lithium reservoir is not supplied by a metallic lithium foil.

It can be noted that such a problematic is quite similar to that encountered by lithium-ion capacitors that are using a graphite-based negative electrode and an activated carbon positive electrode [12–14]. The lack of a lithium source is detrimental to the operation of such devices and practical solutions have been proposed to prelithiate the graphite anode during a preliminary charging step. These solutions are of three kinds: the use of a metallic lithium sacrificial electrode [12], the use of the electrolyte as a lithium ions provider (at the expense of a decrease in ionic conductivity) [15], and the use of a lithium-rich sacrificial compound that can irreversibly provide lithium cations before becoming a dead weight in the battery [16–18]. This later solution has found some practical interest especially when molecules with high capacities are targeted [19–23].

In this study, we propose to couple both approaches and provide a proof of concept of a graphite/Ag₂V₄O₁₁ secondary battery. This will be achieved by mixing a lithiated organic material, namely 3,4-dihydroxybenzonitrile dilithium salt (Li₂DHBN) to $Ag_2V_4O_{11}$ positive electrode. This molecule will irreversibly provide lithium cations to a graphite electrode during an initial in situ charging step, while the graphite/ $Ag_2V_4O_{11}$ cell can be further cycled. Indeed, Li2DHBN salt exhibits very interesting characteristics as a sacrificial lithium source in a Li-ion capacitor, with a high irreversible capacity (365 mAh g^{-1}) which is delivered at a moderate potential (<4.5 V vs Li⁺/Li) which prevents electrolyte decomposition. After delithiation, it dissolves in the electrolyte without gas formation, thus not altering the pressure in the cell. Moreover, the delithiated form of Li₂DHBN seems to be electrochemically inactive within a large potential window as demonstrated in our previous study [23].

Experimental section

Synthesis of Ag₂V₄O₁₁ and Li₂DHBN

 $Ag_2V_4O_{11}$ powders have been prepared by two distinct procedures. A solid-state synthesis method was used to

synthesize $Ag_2V_4O_{11}$, further depicted as $Ag_2V_4O_{11}$ SS. Stoichiometric amounts of V_2O_5 (Alfa Aesar, 99.9% metal basis) and Ag_2O (ACROS Organics 99%) were thoroughly mixed using an agate mortar and pestle. The powdered mixture was heated at 550 °C for 12 h in air using an alumina crucible. A hydrothermal method was also used to synthesize $Ag_2V_4O_{11}$ H. Stoichiometric amounts of V_2O_5 (Alfa Aesar, 99.9% metal basis) and AgNO₃ (ACROS Organics 99%) were introduced into a Teflon-lined vessel containing 15 mL of water. Then, 200 µL of ethylenediamine (Alfa Aesar) was added dropwise under stirring. After 2 h, the vessel was introduced into its autoclave and put in an oven at 180 °C for 48 h.

3,4-Dihydroxybenzonitrile dilithium salt (Li₂DHBN) has been synthesized in a similar way to our previous report [23]. Briefly, 3,4-dihydroxybenzonitrile (Sigma-Aldrich) was introduced in a beaker which contained 14 mL of tetrahydrofuran in an oxygen free glove box. Then, LiH (Sigma-Aldrich) was also introduced in order to start the ionic exchange between protons and lithium. After 15 h of stirring, Li₂DHBN had totally precipitated and the powder was recovered by filtration and then dried under vacuum at 150 °C.

Characterization

Powder X-ray diffraction

Powder XRD data were collected using a PANalytical X'Pert Pro diffractometer with a Cu source ($K_{\alpha 1} = 1.5406$ Å, $K_{\alpha 2} = 1.5444$ Å) and K_{α} filter (Nickel) in the Bragg–Brentano reflection geometry. Data were collected from 10 to 90° 20. In situ electrochemical cycling XRD patterns were obtained using a lab-produced cell, close to "Leriche cell" using a Beryllium window and by cycling the cell at 0.02 A g⁻¹ with 30 min at open circuit voltage for XRD pattern acquisition [24]. All XRD were collected with ~0.008° 20 steps.

SEM

SEM micrographs were obtained using a Zeiss MERLIN Instrument operated at 20 kV using in-lens annular detector. Samples were prepared by dispersing a small fraction of the powder on a piece of conducting carbon tape. EDX spectra were collected at 8.0 mm working distance using an X-Max 50 mm² OXFORD Instruments detector.

Electrochemistry

To balance the mass ratio between $Ag_2V_4O_{11}$, Li_2DHBN , and graphite, the electrode composition has been determined considering both the irreversible capacity of Li_2DHBN (365 mAh g⁻¹) as well as the reversible capacity of graphite (around 370 mAh g⁻¹) and $Ag_2V_4O_{11}$ (150 mAh g⁻¹)

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which represents the capacity of $Ag_2V_4O_{11}$ -H at 0.02 A g^{-1} as shown later). Then, mass ratio between Li_2DHBN and graphite was calculated to be 1.01. Mass ratio between $Ag_2V_4O_{11}$ and graphite was chosen as 2.46 in order to get the same capacity on the positive and negative electrodes once the first lithiation has been performed. For these reasons, $Li_2DHBN/Ag_2V_4O_{11}$ electrode was fabricated with the ratio 1 Li_2DHBN : 2.50 $Ag_2V_4O_{11}$. The different freestanding electrodes were prepared following these compositions:

- 1. Li₂DHBN-based electrode consisted of 45% of Li₂DHBN, 45% of conductive carbon, and 10% of PTFE.
- Positive electrode (Li₂DHBN with Ag₂V₄O₁₁ composite electrode) was fabricated following these proportions: 62.50% of Ag₂V₄O₁₁, 25.00% of Li₂DHBN, 6.25% of conducting carbon, and 6.25% of polyvinylidene fluoride (PTFE) binder.
- 3. 89.00% of graphite, 1.00% of conducting carbon, and 10.00% of PTFE were used for the fabrication of the freestanding negative electrode.

First, electrodes were prepared by thoroughly grinding the active material, conducting carbon (Superior graphite) and polyvinylidene fluoride (PTFE) binder (Sigma-Aldrich, 60 wt.% dispersion in H₂O) in a 75:15:10 wt. ratio, with about 2 mL of ethanol, until a homogeneous paste was obtained. Then, the paste was dried at 70 °C overnight before introducing in glove box for incorporation of Li₂DHBN, as reported in our previous paper [23]. The latter was rolled out to a thickness of ~150 µm using a glass cylinder. Then, electrodes were cut into 12-mm diameter disks using a manual electrode puncher.

All the resulting electrode weights ranged between 5 and 10 mg cm⁻², consistent with reasonable mass loading [25]. Electrochemical experiments were performed using Swagelok®-type cells in a 2-electrode configuration. Cells were mounted inside an argon-filled glovebox (<0.1 ppm O_2 , H_2O) using a single Lithium (Li) foil as both the reference and counter electrode (99.9%, Sigma Aldrich). A

Fig. 1 Crystal structure of

Ag₂V₄O₁₁

glass fiber separator (Whatman) and 200 μ L of 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC) 1:1 v/v (Solvionic, 99.9% purity, electrochemistry grade) were used as the separator and electrolyte, respectively. All electrochemical studies were performed using a MPG2 BioLogic Potentiostat/Galvanostat controlled by EC-Lab Software. Galvanostatic cycling with potential limitation (GCPL) was performed in a series of 5 cycles at 0.02, 0.05, 0.10, 0.20, 0.50, 1.00, and 2.00 A g⁻¹ (considering mass of active materials) between 1.5 V and 3.2 V vs Li⁺/Li. The charge–discharge plots shown in the related figures always correspond to the third charge/discharge cycle.

Results and discussion

In this work, we revisited the electrochemistry of $Ag_2V_4O_{11}$ not only as primary lithium-ion battery cathode materials but also as active materials in positive electrodes for rechargeable batteries. For these reasons, two different syntheses have been performed to compare the influence of particle size on lithium ions intercalation.

 $Ag_2V_4O_{11}$ has a monoclinic structure (space group C2/m) with cell parameters close to a = 15.48 Å, b = 3.58 Å, c = 9.58 Å, and $\beta = 128.74$ Å [26]. The layered structure of this oxide is formed by 2×2 edge-sharing highly distorted octahedra that are linked together by corner-sharing, as presented in Fig. 1. These layers are formed along the a axis. Between these $(V_4O_{12})_n$ layers, silver cations (Ag^+) are coordinated with 7 oxygen atoms. In fact, the stability of these layers seems to be possible thanks to the sharing of some octahedral by their edges [27]. The structure is very close to $Cu_{1.8}V_4O_{11}$ as pointed out by West et al. [9]. $Ag_2V_4O_{11}$ has been considered in the past as a possible electrode material for high power primary lithium ions batteries due to its layered structure as well as the possible reduction of both silver and vanadium cations during the discharge as previously explained. Indeed, silver nanoparticles help to increase the electronic conductivity of the electrode.



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As presented in Fig. 2A, XRD patterns show that a pure phase is obtained with both syntheses. All the main reflection peaks of the phase are visible between 20 and 60°. Furthermore, a large difference in terms of crystallite size is observed, as it can be seen with the much broader peaks observed in the case of $Ag_2V_4O_{11}$ H. In fact, the average crystallite size is found to be > 1 µm in the case of solid-state synthesis and ~250 nm in the case of hydrothermal synthesis. These results are found by applying the Scherrer equation on (110) and (003) peaks.

SEM images at different magnifications are presented in Fig. 2B–E. Both types of particles presented preferential growth along $[30\ \overline{2}]$ with rods like shape [28, 29]. Nevertheless, particles size is found to be much smaller in the case of Ag₂V₄O₁₁-H as expected from XRD patterns: particles synthesized using solid-state synthesis exhibit a size of a few tens of micrometers, while hydrothermal particles are nanorods of about 500 nm long with a diameter of 50 nm. Moreover, these nanorods are agglomerated and form micrometer size secondary particles.



Fig. 2 A Diffractograms of $Ag_2V_4O_{11}$ synthesized by solid state and hydrothermal method. B, C SEM images of $Ag_2V_4O_{11}$ synthesized by solid-state method. D, E SEM images of $Ag_2V_4O_{11}$ synthesized by hydrothermal method

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Fig.3 A, B Charge-discharge experiments at different current densities for $Ag_2V_4O_{11}$ synthesized by hydrothermal method. C Specific capacity vs cycle number at different current densities for both

solid state and hydrothermal powders. D Cycling stability of both $Ag_2V_4O_{11}$ synthesized by solid state and hydrothermal methods



Fig.4 In situ XRD experiment of $Ag_2V_4O_{11}$ synthesized by hydrothermal method. **A** First discharge curve at 0.05 A g.⁻¹. **B**, **C** Associated diffractograms of $Ag_2V_4O_{11}$ at different states of discharge




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<Fig. 5 A Scheme of the proposed transition from a primary battery to a secondary and therefore rechargeable battery using a sacrificial salt and $Ag_2V_4O_{11}$. **B** Electrochemical delithiation of Li₂DHBN associated or not with $Ag_2V_4O_{11}$ at a charging rate of C/10 (considering the theoretical capacity of Li₂DHBN). **C** Charge and discharge plots of $Ag_2V_4O_{11}$ with Li₂DHBN at different current densities vs metallic lithium. **D** First cycle of $Ag_2V_4O_{11}$ with Li₂DHBN associated with a graphite electrode at C/5 (considering the mass of graphite). **E** Second cycle of $Ag_2V_4O_{11}$ with Li₂DHBN associated with a graphite electrode at C/5 (considering mass of graphite)

Thanks to the large difference in terms of crystallite and particle size between hydrothermal and solid-state reactions, it is of interest to compare the respective electrochemical responses of both materials vs a lithium metal electrode. For this reason, charge-discharge cycles at different current densities have been performed. The results are presented in Fig. 3A, B. To avoid the re-oxidation of Ag^0 to Ag^+ , the potential should not exceed 3.2 V upon oxidation sweep [6, 7]. Thus, the selected potential range of the experiment has been set up between 1.5 V and 3.2 V vs Li⁺/Li. During the first reduction, capacities are 277 mAh g⁻¹ and 292 mAh g⁻¹ for respectively solid-state and hydrothermal Ag₂V₄O₁₁ electrodes. These values correspond to the insertion of respectively 6.1 and 6.5 $\text{Li}^+/\text{Ag}_2\text{V}_4\text{O}_{11}$. This large capacity during the first reduction is assigned to both silver reduction which allows Ag⁺/Li⁺ displacement reaction (Eq. 2) and V⁵⁺/V⁴⁺ reduction followed by the partial reduction of V^{4+} into V^{3+} (Eq. 3). The charge storage mechanism of this first reduction will be discussed later. The low coulombic efficiency of the first cycle is also explained by the irreversible reduction of Ag⁺ to metallic silver and then part of the Li⁺ needs to remain in the interlayer to prevent the collapsing of the pristine layered structure.

$$Ag_2V_4O_{11} + xLi^+ + 2e^- \rightarrow Li_xV_4O_{11} + 2Ag^0$$
 with x < 2
(2)

$$Li_xV_4O_{11} + yLi^+ + ye \rightarrow Li_{x+y}V_4O_{11}$$
 with y < 5 (3)

After this first cycle, both materials presented a relatively high reversible capacity between 1.5 V-3.2 V vs Li⁺/ Li. At a current density of 0.02 A g⁻¹, a capacity of around 150 mAh g⁻¹ is observed for the electrodes prepared using both Ag₂V₄O₁₁ powders. This capacity represented 3.3 Li⁺/Ag₂V₄O₁₁. However, when the current density increases, a faster decrease in the capacity retention is observed for Ag₂V₄O₁₁-SS sample compared to Ag₂V₄O₁₁-H. For example, at 0.10 A g⁻¹ and 0.50 A g⁻¹, Ag₂V₄O₁₁-SS exhibits respectively 78 and 14 mAh g⁻¹ while Ag₂V₄O₁₁-H shows 109 and 73 mAh g⁻¹. A smaller lithium diffusion pathway that limits the intrinsic kinetic limitations of this phase can explain this better capacity retention. In fact, Fick's first law concerning diffusion explained that diffusion length has a strong impact on diffusion time ($L \propto \sqrt{D.t}$ where L is the diffusion length, D is the diffusion coefficient, and t is the diffusion time).

Figure 3D shows the cyclability of both powders at 0.2 A g^{-1} upon cycling. After 250 cycles and considering the second cycle as the reference, capacity retentions of about 75% and 110% are observed for solid-state and hydrothermal Ag₂V₄O₁₁, respectively. It can be noticed that the capacity increases after few cycles in the case of Ag₂V₄O₁₁-H₂ which can be due to a continuous change of the structure during these first cycles allowing a greater insertion of the lith-ium ions. From our understanding, nanomaterials undergo lower stress which leads to a better capacity retention upon cycling.

To understand more in-depth the charge storage mechanism occurring in Ag₂V₄O₁₁-H, in situ XRD experiments were performed at 0.02 A g^{-1} between 1.5 and 3.2 V vs Li⁺/Li during the first reduction. In 2010, Sauvage et al. carried out in situ XRD characterizations on micrometric $Ag_2V_4O_{11}$ [30]. They found that at the early stage of the lithiation, Li⁺ insertion occurs without Ag⁺ displacement and/or reduction. For this reason, no amorphization takes place. However, after the insertion of around one lithium per chemical formula, a progressive loss of crystallinity occurs in parallel to silver reduction until full amorphization at 2.2 Li⁺ per chemical formula. Then, steady reduction of silver continues until reaching a fully metallic silver state. In situ XRD experiment of Ag₂V₄O₁₁-H is represented in Fig. 4A-C. It is found that both amorphization and silver reduction take place at the beginning of the lithiation. In the case of Ag₂V₄O₁₁-H, Li⁺/Ag⁺ displacement reaction occurs at the first stage of the reduction process and not V^{5+}/V^{4+} reduction. The reaction is in this sense dependent of particle size, which is in agreement with literature data [10]. The collapse of the structure can be explained by the bigger ionic radii of silver cations (1.22 Å) compared to Li⁺ ions (0.76 Å) which does not allow the layer architecture to be stable [31, 32]. Furthermore, the reduction of silver creates nanoparticles of metallic silver at the surface of $Li_x Ag_{2-y} V_4 O_{11}$ (x < y) particles. This "coating" has been reported to increase the electronic conductivity and then allows its use as high power primary cathode material [33-35].

Then, after the characterization of $Ag_2V_4O_{11}$ with two different morphologies, the next step was to show that this lithium-free oxide could be used in association with a sacrificial lithium source in a secondary lithium-ion battery setup. In other words, the idea of the present paper is summarized in Fig. 5A. Here, $Ag_2V_4O_{11}$ -H will be used as efficient negative electrode materials. Moreover, Li_2DHBN was considered as a source of lithium as it shows a relevant behavior in Li-ion capacitor [23].

First, two different electrodes have been prepared, one serving as the reference with only 3,4-dihydroxybenzonitrile dilithium salt (Li₂DHBN) and a second one which is a composite of Ag₂V₄O₁₁ and Li₂DHBN. Details on the mass ratio between $Ag_2V_4O_{11}$ and Li_2DHBN can be found in the "Experimental section". To provide lithium to the system, the irreversible delithiation of Li2DHBN occurs between 3.0 V and 4.0 V vs Li⁺/Li. This delithiation has been performed using a charging rate of C/10 considering the mass of Li₂DHBN. As shown in Fig. 5B, the delithiation behavior of the pristine Li2DHBN and the composite positive electrodes is similar with a capacity of about 300 mAh g^{-1} (per g of Li₂DHBN). This capacity translates in a release of 1.7 Li⁺/ Li₂DHBN. The difference in terms of delithiation potential is due to the larger open circuit potential of the composite electrode containing Ag₂V₄O₁₁-H and Li₂DHBN. We can then conclude that delithiation of Li2DHBN occurs in a similar manner with or without the presence of $Ag_2V_4O_{11}$ -H.

After this irreversible delithiation of the Li₂DHBN organic molecule, DHBN is dissolved in electrolyte and not present anymore in the positive electrode as explained by P. Jezowski et al. [23] Figure 5.C reports on the following cycles at different current densities when metallic lithium is used as the negative electrode. As observed, $Ag_2V_4O_{11}$ -H presents a discharge capacity on the third cycle of 120 mAh.g⁻¹ at 0.02 A.g⁻¹ between 3.2V and 1.5V vs Li⁺/Li. Compared to the Li₂DHBN-free Ag₂V₄O₁₁-H electrode 248 (Fig. 3B), we observed a decrease of 40 mAh.g⁻¹, which is mainly due to vanadium dissolution during first Li₂DHBN delithiation [36]. In fact, the separator is found to be greenish, which is characteristic of $V5^+$ species in solution. The following cycles show good capacity retention indicating that Ag₂V₄O₁₁-H dissolution only occurs concomitantly with this initial delithiation. At 0.05 and 0.1 A.g⁻¹, the values of capacity are equal to 63 and 33 mAh.g⁻¹ respectively (Fig. 5C). These lower capacities compared to the pristine Li₂DHBN-free $Ag_2V_4O_{11}$ -H electrode (Fig. 3B) can be explained by several reasons. First, the ratio between Ag₂V₄O₁₁ and conductive carbon has not been optimized in Li₂DHBN Ag₂V₄O₁₁-H electrode with a low amount of conductive carbon (6.25%). In fact, adding more conductive carbon can increase the electronic conductivity of the electrode and then improve the capacity at higher current densities. Furthermore, the electronic percolation can be deteriorated by the dissolution of Li2DHBN in the electrode. Nevertheless, we note that the electrode works relatively well at moderate current densities. For this reason, the $Li_2DHBN Ag_2V_4O_{11}$ -H composite electrode has been further associated with a graphite negative electrode in a full device assembly.

The two first cycles of the $Li_2DHBN Ag_2V_4O_{11}$ -H electrode vs a graphite electrode are presented Fig. 5D, E. A thick lithium wire has been used to monitor the evolution of both

electrode potentials. During the first charge, at the positive electrode, Li2DHBN effectively releases its lithium cations (around 1.8 Li⁺/Li₂DHBN), thus evidencing the effectiveness of in situ lithiation of the cell. In the negative electrode, graphite inserts lithium cations until reaching ~0.1 V vs Li⁺/Li as typically observed for this negative electrode material that has been deeply investigated by Prof. Doron Aurbach and his team [37–39]. The observed capacity is about 350 mAh g^{-1} which is very close to its theoretical capacity of 372 mAh g^{-1} . Moreover, the plateau observed at ~ 0.8 V vs Li⁺/Li represents the formation of the solid electrolyte interphase (SEI). During the second discharge, the cell shows a relatively poor coulombic efficiency with less than 40%. In fact, the graphite electrode only partially releases the inserted lithium. Several explanations can support this poor coulombic efficiency. First of all, the vanadium which is liberated and dissolved during the Li₂DHBN delithiation can further react during the SEI formation and/or migrate to the anode and simply be deposited on the surface of the graphite electrode as observed by Takeuchi [40]. This has been largely commented in literature concerning Mn^{2+} dissolution in LiMn₂O₄ and is responsible for similar issues [41-43]. As well, silver metal and/or silver ions can also be dissolved, and migrate to the graphite electrode giving rise to this poor coulombic efficiency [38, 39]. Lastly, it is also possible that the delithiated DHBN molecules are involved in the complexation of vanadium species in solution, thus disturbing the formation of the SEI on the surface of graphite, and then partially preventing the lithium ions from leaving the graphite upon subsequent discharge of the cell. As observed in Fig. 5E, the coulombic efficiency is still poor for the following cycle. Based on the literature data, different solutions can be used to increase the coulombic efficiency. Among them, using high concentrated salt and/or adding additives in the electrolyte can reduce vanadium dissolution [42, 44, 45]. Carbon-coated Ag₂V₄O₁₁ particles can also allow to cancel this drawback [46]. These solutions are currently under investigation to obtain a better coulombic efficiency. Nevertheless, this first insight of how to turn Ag₂V₄O₁₁/Li primary battery into Ag₂V₄O₁₁/graphite secondary (rechargeable) battery has been demonstrated, thanks to in situ lithiation of this system using Li₂DHBN sacrificial molecules. This work provides new guidelines to use non-lithiated positive electrodes in rechargeable lithium ion-batteries.

Conclusion

This work presents the characterization of two $Ag_2V_4O_{11}$ powders synthesized by solid-state and hydrothermal processes. Hydrothermal $Ag_2V_4O_{11}$ exhibits superior electrochemical behavior with a capacity of 150 mAh g⁻¹ at a moderate current density (0.02 A g⁻¹) between 1.5 and

3.0 V vs Li⁺/Li after an initial capacity of 300 mAh.g⁻¹. In situ XRD has shown the irreversible reduction of silver during the first cycle concomitantly to the amorphization of the structure. Moreover, $Ag_2V_4O_{11}$ -H was associated to a sacrificial organic lithium salt at the positive electrode and the related composite electrode was tested against graphite as negative electrodes in rechargeable batteries. This is a first report of such a proof of concept of how to turn a performing positive electrode for primary batteries into a rechargeable cathode for a lithium-ion cell. In this study, we highlighted the possibility of using such a device even if coulombic efficiency is still modest for this first insight. Finally, several other possibilities exist for improving the system and potentially achieve better coulombic efficiency, especially with the use of other sacrificial salts (Li₃N, Li₂C₄O₄...) [19–22, 47, 48].

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Author contribution All authors contributed to the study conception and design. Conceptualization and methodology were managed by T. Brousse and O. Crosnier. Material preparation, data collection, and analyses were performed by E. Le Calvez and O. Crosnier. The first draft of the manuscript was written by E. Le Calvez and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Declarations

Conflict of interest The authors declare no competing interests.

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III. Conclusion et perspectives

Dans cet article, la possibilité d'associer un sel de lithium sacrificiel avec un matériau possédant des propriétés redox réversibles et ne contenant pas de lithium a été démontré. Il a été choisi d'utiliser $Ag_2V_4O_{11}$ et Li₂DHBN à l'électrode positive ainsi que du graphite à l'électrode négative dans le but d'apporter une preuve de concept du système étudié.

Malgré les résultats prometteurs obtenus, une bonne cyclabilité de la cellule complète n'a pas été démontrée lors de cette étude. En effet, une faible efficacité coulombique au niveau de l'électrode de graphite est observée limitant considérablement l'applicabilité d'un tel système. Plusieurs possibilités d'améliorations ont été discutées mais n'ont pas été étudiées dans le cadre de cette thèse. Pour mieux comprendre les déficiences de l'électrode de graphite, il aurait été nécessaire de caractériser la cellule *post-mortem* en analysant la surface de l'électrode et la SEI formée au niveau des particules du graphite. Des méthodes d'analyses comme l'EDX, la RMN ou encore la microscopie électronique auraient pu nous donner des informations utiles pour mieux comprendre l'origine des dysfonctionnements. Aussi, une étude plus aboutie vis-à-vis de la dissolution du vanadium en solution ainsi que la diffusion de ce vanadium vers l'électrode de graphite est nécessaire pour corroborer nos assertions.

Nous avons décidé, avec mes encadrants de thèse, de ne pas aller plus loin dans ce projet tout en continuant à étudier des matériaux contenant des ions argent (Ag^+) pour permettre d'augmenter la conductivité électronique lors de la réduction irréversible de ce cation comme dans le cas de $Ag_2V_4O_{11}$. En effet, la conductivité ionique et électronique sont deux facteurs essentiels pour permettre d'obtenir une charge rapide des batteries Li-ion.²⁵

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Chapitre III. Etude de la pérovskite Ag₁-3xLax□2xNbO3 comme électrode négative dans des systèmes de stockage.

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I. Introduction

1. Réduction des ions argent pour augmenter la conductivité électrique

Comme décrit dans le chapitre bibliographique, ReO₃ est une phase pouvant insérer 2 Li⁺ par métal de transition.¹ Ainsi, une capacité relativement élevée est observée (~228 mAh.g⁻¹). Cependant, la forte distorsion des octaèdres (ReO₆) lors de la lithiation et la délithiation entraine une faible cyclabilité.¹ Cette capacité élevée ainsi que la forte distorsion des octaèdres sont dues à la faible compacité de la structure qui permet de trouver dans cet oxyde un grand nombre de sites vacants pour l'insertion d'ions lithium. A l'inverse, bien que quelques publications présentent l'insertion d'ions lithium dans des pérovskites^{2–4}, le faible nombre de site d'insertion dû à la compacité élevée de la structure ne permet pas, à première vue, l'insertion d'ions lithium. Il existe un lien étroit entre la structure ReO₃ et les pérovskites (ABO₃) car ReO₃ peut être décrit comme une pérovskite sans cation dans les sites A (BO₃).⁵

Ce chapitre présente la synthèse d'un matériau de type pérovskite (ABO₃) avec $A = Ag^+$. L'hypothétique extraction irréversible des ions argent du site A lors de la première réduction (similairement à $Ag_2V_4O_{11}$) permettrait la formation de sites vacants et ainsi l'insertion des ions lithium. Le niobium semblant être un élément de choix pour les batteries Li-ion dans les applications de puissance^{6–8}, notre intérêt s'est porté sur $Ag^INb^VO_3$. Cette pérovskite a été étudiée comme matériau anti ferroélectrique mais jamais comme matériau actif pour le stockage électrochimique de l'énergie.^{9–12}

2. La création de lacune pour l'insertion des ions.

Synthétisé par voie sol-gel dans le cadre de ce travail, le niobate d'argent cristallise dans une maille orthorhombique. Les particules d'AgNbO₃ sont nanométriques et agglomérées. Plus d'informations vis-à-vis de la caractérisation du matériau sont présentes dans la publication associée à ce chapitre.

Comme illustré Figure.III 1, un pic de très faible intensité correspondant à réduction de l'argent est observé lors du premier cycle (environ à 2.9V vs Li⁺/Li). Ce pic correspond à une capacité de 0.5 mAh.g⁻¹ tandis que la réduction totale des ions argent correspondrait théoriquement à 107 mAh.g⁻¹. Ainsi, environ 0.25% des ions argent sont réduits, probablement des ions se trouvant à la surface ou à proximité de la surface des particules. Cette absence de réduction irréversible d'ions argent de la structure n'entraine donc pas la création de lacunes



qui auraient permis l'insertion d'ion lithium. Ainsi, aucune capacité due à l'insertion est observée dans ce matériau.

Figure.III 1 Voltammétrie cyclique représentant le premier cycle d'une électrode composée de 75% d'AgNbO₃ synthétisé par voie sol-gel entre 3V et 1V vs Li⁺/Li dans 1M LiPF₆ EC/DMC 1 :1. La vitesse de cyclage est de 0.1 mV.s⁻¹.

Fort de ce constat, une nouvelle stratégie a été mise en place pour permettre l'insertion d'ions alcalins dans cette structure. L'idée est de substituer l'ion argent monovalent par un cation multivalent, ayant un rayon ionique proche (Sr^{2+} , La^{3+} , ...), entrainant ainsi la formation de lacunes sur le site A de la pérovskite. Les rayons ioniques des ions Ag⁺, Sr^{2+} , La^{3+} pour une coordinance de 12 sont égaux à 1.54 Å, 1.44 Å et 1.36 Å.^{14,15} respectivement. Ainsi, la substitution d'une partie des Ag⁺ par des La^{3+} a été réalisée entrainant la création de 2 lacunes pour chaque substitution. La formule chimique est exprimée comme étant : Ag_{1-3x}La_x $\Box_{2x}NbO_3$ avec \Box correspondant aux lacunes. Divers taux de substitution ont été réalisés allant de x=0 jusqu'à x=0.20 (AgNbO_3, Ag_{0.85}La_{0.05}\Box_{0.10}NbO_3, Ag_{0.70}La_{0.10}\Box_{0.20}NbO_3, Ag_{0.55}La_{0.15}\Box_{0.30}NbO_3, Ag_{0.40}La_{0.20}\Box_{0.40}NbO_3).

L'évaluation des propriétés physico-chimiques et électrochimiques des différents matériaux ont donné lieu à la publication présentée ci-dessous.

II. La publication

Investigating the Perovskite $Ag_{1-3x}La_x \square_{2x}NbO_3$ as High-Rate Negative Electrode for Li-ion Batteries.

Etienne Le Calvez, Julio César Espinosa-Angeles, Grace J. Ghang, Nicolas Dupré, Bruce S. Dunn, Olivier Crosnier, Thierry Brousse, Frontiers in Chemistry (2022).

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University College London,

Graz University of Technology, Austria

Qingdao University of Science and

thierry.brousse@univ-nantes.fr

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Investigating the Perovskite Ag_{1-3x}La_xNbO₃ as a High-Rate Negative Electrode for Li-Ion Batteries

Etienne Le Calvez^{1,2}, Julio César Espinosa-Angeles^{1,2}, Grace J. Whang³, Nicolas Dupré¹, Bruce S. Dunn³, Olivier Crosnier^{1,2} and Thierry Brousse^{1,2}*

¹Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, Nantes, France, ²Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR 3459, Amiens Cedex, France, ³Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, CA, United States

The broader development of the electric car for tomorrow's mobility requires the emergence of new fast-charging negative electrode materials to replace graphite in Liion batteries. In this area, the design of new compounds using innovative approaches could be the key to discovering new negative electrode materials that allow for faster charging and discharging processes. Here, we present a partially substituted AgNbO3 perovskite material by introducing lanthanum in the A-site. By creating two vacancies for every lanthanum introduced in the structure, the resulting general formula becomes $Ag_{1-3x}La_x \square_{2x}NbO_3$ (with x \leq 0.20 and where \square is a A-site vacancy), allowing the insertion of lithium ions. The highly substituted Ag_{0.40}La_{0.20} - 0.40 NbO₃ oxide shows a specific capacity of 40 mAh.g⁻¹ at a low sweep rate (0.1 mV s⁻¹). Interestingly, Ag_{0.70}La_{0.10}D_{0.20}NbO₃ retains 64% of its capacity at a very high sweep rate (50 mV s⁻¹) and about 95% after 800 cycles. Ex situ ⁷Li MAS NMR experiments confirmed the insertion of lithium ions in these materials. A kinetic analysis of Ag1-3xLax22xNbO3 underlines the ability to store charge without solid-state ion-diffusion limitations. Furthermore, in situ XRD indicates no structural modification of the compound when accommodating lithium ions, which can be considered as zero-strain material. This finding explains the interesting capacity retention observed after 800 cycles. This paper thus demonstrates an alternative approach to traditional insertion materials and identifies a different way to explore notso common electrode materials for fast energy storage application.

Keywords: silver niobate, lithium-ion battery, high rate anode material, fast charging, innovative oxide

INTRODUCTION

To eliminate our dependence on carbon-based energy production, specifically in the field of mobility, it is essential to develop energy storage devices able to store the intermittent energy harvested by renewable energy sources (Armand and Tarascon 2008). A key to the deployment of electric vehicles is the ability of batteries to charge quickly while ensuring long cycle life, and optimized safety (Burnham et al., 2017; Li et al., 2020). The current use of graphite as a negative electrode only partially satisfies these needs (Choi et al., 2020). In fast-charging batteries, graphite enables the insertion of lithium at an average potential close to that of Li⁺/Li (0.1 V vs. Li⁺/Li), which can lead to the formation of lithium plating followed by dendrite growth, resulting in possible short circuits and thermal runaway. Moreover, the specific capacity of graphite is drastically reduced at high current

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densities due to kinetic limitations on ion mobility between graphene layers (Sivakkumar et al., 2010).

For these reasons, alternative negative electrode materials have attracted increased attention over the past decade One of the best known negative electrode materials for high-rate applications is Li₄Ti₅O₁₂ (LTO) (Prakash et al., 2010; Song et al., 2014; Thackeray and Amine 2021). Crystallizing in a spinel structure, this zero strain material offers an alternative route towards designing fast charging batteries with a relatively high specific capacity. Moreover, new approaches have been proposed to offer more options for the replacement of graphite electrode. Among others, shear-structure materials including TiNb₂O₇ (Griffith et al., 2019) or Nb₁₆W₁₈O₉₃ (Griffith et al., 2018) offer relatively large capacity values at high rate between 1V and 3V vs. Li⁺/Li. Low volume changes upon lithium insertion and an operating potential that avoids the formation of lithium-consuming solid electrolyte interphase (SEI) are the main advantages offered by these materials. In addition, a new approach has recently been proposed to transform a material traditionally used as an ionic conductor into a material for high-rate Na-ion batteries. Partial substitution of Al by Fe in B"-Al2O3 offers both ionic and electronic conduction, allowing fast and reversible Na⁺ intercalation (Butts et al., 2021). This material displays cyclic voltammogram with broad peaks attributed to a surface-controlled charge storage mechanism. Similar approaches are needed to unravel different fast charging materials and their associated mechanisms.

In this work, we propose an alternative way to produce materials that can insert alkali cations with minor diffusion limitation, thus allowing high current density operation. More precisely, the A-site of AgNbO₃ perovskite synthesized by sol-gel process has been partially substituted by lanthanum (La³⁺), allowing the creation of vacancies in this crystallographic site. Insertion of Li ions is observed in every substituted Ag_{1-3x}La_x \Box_{2x} NbO₃ compound (with x > 0), thus leading to experimental specific capacities close to the theoretical values. Calculation of *b*-value shows a non-diffusion-controlled mechanism and *in situ* XRD shows negligible volume expansion (zero strain electrode) during the insertion/deinsertion mechanism for this new family of materials, therefore explaining the cycling stability of Ag_{1-3x}La_x \Box_{2x} NbO₃.

EXPERIMENTAL SECTION

Synthesis of Ag_{1-3x}La_x^D_{2x}NbO₃

 $Ag_{1-3x}La_x\square_{2x}NbO_3$ powders were synthesized by a sol-gel route (SG) based on a previous report (Wu et al., 2013). Briefly, a

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stoichiometric mixture of NbCl₅ (99%, Sigma Aldrich), La(NO₃)₃ (99.9%, Alfa Aesar), AgNO₃ (99.9%, Alfa Aesar), and citric acid in excess (99+%, Alfa Aesar) was dissolved in 30% (w/w) H₂O₂ in H₂O (Sigma Aldrich). Upon complete dissolution of the species, the solution turned to a dark yellow color. At this point, the solution was heated at 120°C until the formation of a dark brown gel. The latter was heated to 300°C overnight to remove organic moieties and dehydrate the gel. The resulting powder is ground in an agate mortar and then annealed at 650°C for 6 h in an alumina crucible to crystallize the material. Depending on the degree of substitution, the resulting powder ranges from dark grey for AgNbO₃ to whitish powder in the case of Ag_{0.40}La_{0.20} $\Box_{0.40}$ NbO₃.

Characterization

Powder X-Ray Diffraction

X-ray diffraction (XRD) patterns were collected using a PANalytical X'Pert Pro diffractometer (Malvern Panalytical, Almelo, Netherlands). An X'Celerator detector with Cu-Ka1-Ka2 ($\lambda = 1.54060$, 1.54439 Å) radiation was used with acceleration voltage and current of 40 kV and 40 mA, respectively. With a step scan of 0.0167°, diffraction patterns have been collected between 20° and 80° (20). Using pseudo-Voigt functions, Le Bail refinement was performed using FullProf Suite. Preliminary lattice parameter values have been taken from the literature (Sciau et al., 2004). For *in situ* XRD measurements, patterns were collected using a homemade "Leriche-like" cell (Leriche et al., 2010). During charge-discharge experiment, a current of 0.005 A g⁻¹ was applied for 20 min and stopped during 30 min for XRD pattern acquisition.

Electron Microscopy and Energy Dispersive X-Ray Analyses

The morphology and particle size were studied with a transmission electron microscope ThermoFisher S/TEM Themis G3 at 300 kV (Breda) point to point resolution: 0.18 nm. SEM micrographs were obtained at 20 kV using a Zeiss MERLIN Instrument using in-Lens annular detector. Samples were prepared by dispersing a small fraction of the powder on a piece of conducting carbon tape. EDX was collected at 8.0 mm working distance using an X-Max 50 mm² OXFORD Instruments detector. The measurements were performed on at least two samples per synthesis and for each sample at least 10 acquisitions were performed. The atomic percentage of each cation was determined with an accuracy of \pm 5%.

BET Measurement

The specific surface area of the powders was determined using the BET method (Brunauer-Emmett-Teller) from the 77 K nitrogen adsorption curves with a Quantachrome Nova 4200e equipment (Anton Paar).

Electrochemistry

Self-supported electrodes were fabricated by mixing, in a small amount of ethanol, 75% w/w Ag_{1-3x}La_x \Box_{2x} NbO₃, 15% w/w of conductive carbon (Carbon Black by Superior Graphite, Chicago, IL, United States) to increase electronic conductivity and 10% w/w poly (1,1,2,2-tetrafluoroethylene) dissolved in water (PTFE,



Sigma Aldrich) to form a homogeneous paste. This mixture was homogenized in a mortar and then cold-rolled until electrodes with a mass loading of about 5–10 mg cm⁻² were obtained. This level of loading enables reliable gravimetric values to be reported (Gogotsi and Simon 2011). Electrochemical measurements were performed using Swagelok cells. The positive electrode and metallic lithium (99.9%, Aldrich) were separated using a glass fiber membrane (70 mm, 10 mm diameter, GF/D Whatman) soaked with 1M LiPF₆ dissolved in 1:1 %wt. EC/DMC (Solvionic, France, battery grade purity). The Swageloks were assembled in a glove box containing less than 0.1 ppm of O_2 and H₂O. A VMP3 potentiostat (from Biologic run under ECLab software version V11.36, Seyssinet-Pariset, France) was used for electrochemical measurements.

Ex situ MAS NMR

For MAS NMR analysis, free-standing electrodes with about 5-10 mg cm⁻² were polarized for 10 h at different states of charge after performing a cyclic voltammogram (CV) at 0.1 mV s⁻¹. After disassembling the Swageloks in a glove box, electrodes were cleaned with a few drops of DMC and then dried overnight under vacuum in a Büchi oven at 60°C. Then, the electrolyte-free electrode was placed in a 2.5 mm-diameter zirconia rotor for MAS NMR experiments. ⁷Li MAS NMR spectra were acquired on a Bruker Avance 200 spectrometer (B0 = 4.7 T, Larmor frequencies v_0 (⁷Li = 77.78 MHz) at RT. A Bruker MAS probe with a cylindrical 2.5 mm (o.d) zirconia rotor spun at a frequency of 30 kHz was used. Spectra were obtained by applying a single pulse sequence, and a recycle delay (D1) of 3s ensured the acquisition of quantitative spectra. ⁷Li integrated intensities were determined by using spectral simulation (DMFit Software) (Massiot et al., 2002). The resulting integrated intensities were normalized with respect to the mass of the sample contained in the NMR rotor, the number of scans, and the receiver gain. Due to low amount of lithiated active material used for the analyses, it was not possible to rely on ⁶Li MAS NMR to characterize local structural features.

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RESULTS AND DISCUSSIONS

At room temperature, $AgNbO_3$ crystallizes in an orthorhombic perovskite structure (space group Pbcm) with distorted [BO₆] octahedra, similar to most perovskites (Sciau et al., 2004). Historically, AgNbO₃ has been studied in material science as antiferroelectric material for energy storage applications. Substitutions in this lead-free material have been widely examined to stabilize the antiferroelectric phase and increase the power density. Various studies have explored the substitution of Ag⁺ in AgNbO₃ by Li⁺ (Farid et al., 2019), Na⁺ (Takeda et al., 2003), and multivalent cations (Li et al., 2009; Juang et al., 2016; Gao et al., 2020) (Sr²⁺, La³⁺, Sm³⁺, etc.) to create A-site vacancies. All the substitutions by multivalent cations show an increase in

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the symmetry of the material until the presence of impurities at a high degree of substitution (Juang et al., 2016; Gao et al., 2019; Gao et al., 2020). In order to investigate the possible Li-ion insertion into A site vacancies of this perovskite, we synthesized La-doped AgNbO₃ with different substitution ratios from x = 0 to x = 0.20. In a perovskite lattice, the coordination number of the A-site is 12, and 6 for the B-site. The ionic radius of silver is 1.54 Å, whereas that of niobium is 0.64 Å (Shannon and Prewitt 1969; Shannon 1976). Since the ionic radius of La for a coordination number of 12 is 1.36 Å, the silver-to-lanthanum substitution should be effective in the A site of the perovskite Ag_{1-3x}La_x \Box_{2x} NbO₃, where \Box depicts a cation, vacancy in the A site of the perovskite, following reaction Eq. 1:

$$La_2O_3 \rightarrow 2La^{\cdot}_{Ag} + 3O^x_o + 4V'_{Ag} \tag{1}$$

Here, we will name the samples $Ag_{0.85}La_{0.05}\Box_{0.10}NbO_3$, $Ag_{0.70}La_{0.10}\Box_{0.20}NbO_3$, $Ag_{0.55}La_{0.15}\Box_{0.30}NbO_3$ and $Ag_{0.40}La_{0.20}\Box_{0.40}NbO_3$, respectively for x = 0.05, x = 0.10, x = 0.15 and x = 0.20. Figure 1 represents the crystallographic arrangement of $Ag_{0.70}La_{0.10}\Box_{0.20}NbO_3$ which shows both distortion of $[NbO_6]$ octahedra and the partial substitution of Ag by La in A-site with the corresponding vacancies.

The synthesis of Ag_{1-3x}La_x $\square_{2x}NbO_3$ by a ceramic route was difficult to achieve. One reason is the reduction of Ag₂O to metallic Ag for a temperature higher than 150°C (Chun et al.,

2009; Shin et al., 2013). A second reason is the thermodynamic competition between AgNbO3 and Ag2Nb4O11 does not allow one to easily obtain a phase pure material, even by adding an excess of Ag₂O (Valant et al., 2007). For this reason, the different stoichiometries of AgNbO3 were synthesized by a sol-gel (SG) process which has been demonstrated to be effective for the synthesis of perovskite materials (Huang et al., 1996; Y.; Li et al., 2010; Huízar-Félix et al., 2012). Moreover, the heat treatment at lower temperature (650°C) of the amorphous AgNbO3 particles will avoid the reduction of silver. Figure 2A,B shows both AgNbO₃ and Ag_{0.70}La_{0.10}D_{0.20}NbO₃ agglomerated nanoparticles which are typical morphologies of sol-gel synthesis. AgNbO3 particles are larger than those of Ag_{0.70}La_{0.10}D_{0.20}NbO₃, a feature confirmed by nitrogen adsorption measurements (BET method; Supplementary Table S1). These measurements revealed a specific surface area of $3 \text{ m}^2 \text{g}^{-1}$ for AgNbO₃ and $13 \text{ m}^2 \text{g}^{-1}$ for Ag_{0.70}La_{0.10}□_{0.20}NbO₃. In addition, as shown in Supplementary Table S2, EDX cationic ratio between Ag, La and Nb for every Ag1-3xLax^D2xNbO3 confirms the presence of vacancies in all the powders of La-substituted AgNbO3.

XRD was used to better understand the structural differences among all $Ag_{1-3x}La_x\Box_{2x}NbO_3$ powders. As shown in **Figure 3A**., AgNbO₃ has a perovskite structure with no secondary phase, although splitting of several peaks is observed. $Ag_{0.85}La_{0.05}\Box_{0.10}NbO_3$ (x = 0.05) and $Ag_{0.70}La_{0.10}\Box_{0.20}NbO_3$ (x

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TABLE 1 | *b* value of $Ag_{1-3x}La_x^{\Box}_{2x}NbO_3$ for different value of x for reduction and oxidation peaks.

	Reduction	Oxydation
Ag _{0.85} La _{0.05} D _{0.10} NbO ₃	0.94	0.95
Ag _{0.70} La _{0.10} D _{0.20} NbO ₃	0.92	0.95
Ag _{0.55} La _{0.15} D _{0.30} NbO ₃	0.87	0.87
Ag _{0.40} La _{0.20} D _{0.40} NbO ₃	0.9	0.91

= 0.10) also show the perovskite structure with no secondary phase visible in the diffractograms. However, starting from x = 0.15, impurity peaks appear, perhaps due to the lack of cations on the A-site, resulting in collapse of the structure. This is in agreement with previous reports on the A-site substitution in AgNbO₃ (Li et al., 2009; Juang et al., 2016). Depending on the size of the dopant cation, the perovskite structure can accept up to a certain amount of substitution, sometimes accompanied by the appearance of extra peaks which correspond to secondary phases. The decrease in peak intensity for Ag_{0.55}La_{0.15}□_{0.30}NbO₃ and

Ag_{0.40}La_{0.20} $\square_{0.40}$ NbO₃, compared to other samples, is an indicator of the stress caused by the high proportion of La in the perovskite. For the substituted oxides, a decrease in peak splitting was observed with increasing lanthanum substitution (**Figures 3B–C**). Further, the disappearance of peak splitting by x = 0.15 suggests a higher degree of symmetry in the substituted materials due to lower [NbO₆] octahedra distortion.

To get greater insight into the structure of the synthesized materials, Le Bail structural refinements were performed for each composition. First, as indicated in **Supplementary Figure S1**, the refinement of AgNbO₃ confirms that the Pbcm space group well represents the structure of AgNbO₃. Cell parameters of AgNbO₃ were extracted from the refinement as shown in **Supplementary Figure S2** and **Supplementary Table S3**. We found that the cell parameters and the cell volume increase with increasing substitution of La for Ag_{1-3x}La_x $\square_{2x}NbO_3$, which is in agreement with a previous report (Li et al., 2009). Moreover, this is consistent with a decrease of NbO₆ octahedra distortions previously described above. Refinements using a higher symmetry space group (Pm3m) have been performed to



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check that no phase transition appears with the substitution of silver by lanthanum. However, they did not lead to conclusive results. For this reason, we assume that the same space group (Pbcm) can be used to describe the crystallographic structure of all the $Ag_{1-3x}La_x^{-1}a_xNbO_3$ powders.

To characterize the ability of this family of materials to reversibly store lithium ions, cyclic voltammetry at 0.1 mV s⁻¹ was first performed. Note that this sweep rate should be considered as a low rate for power applications (around 5.5 h of charge). As depicted in **Figure 4A**, AgNbO₃ does not show any electrochemical activity between 1.2 and 3.0 V vs. Li^+/Li at the selected scan rate. A negligible specific capacity of 6 mAh.g⁻¹ is reported. However, for each substituted material, broad and reversible peaks appear between 2.2 and 1.2 V vs. Li^+/Li , characteristic of lithium insertion into the host structure. Considering no insertion is visible for the unsubstituted oxide, we propose the following reaction **Eq. 2** to describe the present electrochemical reaction.

$$Ag_{1-3x}La_x \square_{2x} \text{NbO}_3 + yLi_x + ye^- \rightarrow Li_y Ag_{1-3x}La_x \square_{2x} \text{NbO}_3$$
(2)

At 0.1 mV s^{-1} , the specific capacity increases with the number of vacancies. During the first cycle at 0.1 mV s⁻¹, specific capacities are close to the theoretical capacity considering the insertion of one Ag_{0.55}La_{0.15}D_{0.30}NbO₃, Ag_{0.40}La_{0.20}D_{0.40}NbO₃, respectively. Considering only the mass of active materials the gravimetric capacity is found to be equal to 38 mAh cm⁻³, 109 mAh cm⁻³, 206 mAh cm⁻³, 219 mAh cm⁻³ and 264 mAh cm⁻³ for AgNbO₃, $Ag_{0.85}La_{0.05}\square_{0.10}NbO_3$, $Ag_{0.70}La_{0.10}\square_{0.20}NbO_3$, $Ag_{0.55}La_{0.15}\square_{0.30}NbO_3$, $Ag_{0.40}La_{0.20}\square_{0.40}NbO_3\text{,}$ respectively. If the entire volume of the practical electrode is now considered (porosity volume ~70%), the gravimetric capacity is found to be equal to 12 mAh cm⁻³, 32 mAh cm^{-3} , 62 mAh cm^{-3} , 66 mAh cm^{-3} and 79 mAh cm^{-3} for AgNbO₃, Ag_{0.85}La_{0.05}D_{0.10}NbO₃, Ag_{0.70}La_{0.10}D_{0.20}NbO₃, Ag_{0.40}La_{0.20} []0.40NbO3, respectively. Ag_{0.55}La_{0.15}D_{0.30}NbO₃, Interestingly, no reduction of silver is observed in these materials indicating the strong interaction of silver cations within the perovskite structure, contrary to most silver-based materials reported in the literature, i.e., silver vanadates (West and Crespi 1995; Marschilok et al., 2010; Sauvage et al., 2010).

Cyclic voltammetry was used to characterize the performance of the lanthanum-substituted oxides at a higher sweep rate of 2 mV s^{-1} (**Figure 4B**). This sweep rate corresponds to 15 min of charge/discharge, which is consistent with the current goal for the development of electric vehicles (Colclasure et al., 2019). As was observed at 0.1 mV s⁻¹, the CVs shown at 2 mV s⁻¹ present very broad and reversible redox peaks.

As expected, the capacity of AgNbO3 remains very low compared to the substituted oxides. Its capacity is 5 mA h.g^{-1} . $Ag_{0.85}La_{0.05}\square_{0.10}NbO_3$ is the least substituted material and the one with the lower capacity at both 0.1 mV s⁻¹ and 2 mV s⁻¹ (32 mAh g^{-1}). Interestingly, at 2 mV s⁻¹, Ag_{0.40}La_{0.20} $\square_{0.40}$ NbO₃ has a lower capacity than $Ag_{0.70}La_{0.10}\Box_{0.20}NbO_3$ and $Ag_{0.55}La_{0.15}\Box_{0.30}NbO_3$, even though Ag_{0.40}La_{0.20} $\square_{0.40}$ NbO₃ shows the higher theoretical capacity most likely attributed to the higher amount of vacancies per unit cell. Such a decrease in capacity is explained by the lower degree of crystallinity which does not allow adequate diffusion of lithium ions in this substituted oxide. Moreover, the defects detected by the presence of peaks that did not belong to the orthorhombic lattice provides another possible explanation to the lower capacity of Ag_{0.40}La_{0.20} $\square_{0.40}$ NbO₃ at 2 mV s⁻¹. In addition, these CVs show the polarization between the oxidation and reduction peaks to be very small for each compound, even for CV at 2 mV s⁻¹. This result suggests that the intercalation process is not limited severely by low ionic diffusion, a consideration which will be discussed later.

CVs at different scan rates were performed to assess the capacity retention as a function of increasing scan rate. Scan rates from 0.1 mV s⁻¹ to 50 mV s⁻¹ were chosen, corresponding to 5.5h and 40s of charge, respectively. **Figures 4C,D** shows the specific capacity and relative capacity of every material at the mentioned scan rates. Ag_{0.40}La_{0.20} $\square_{0.40}$ NbO₃, the material with the highest number of vacancies, provides the highest capacity at a low sweep rate (**Figure 4C**). However, when the scan rate is increased, a rapid decrease in capacity is observed starting at 0.2 mV s⁻¹. As shown in **Figure 4D**, at 50 mV s⁻¹, Ag_{0.40}La_{0.20} $\square_{0.40}$ NbO₃ retains only 34% of the initial capacity

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Specific capacity / mAh/g 0 0 0 0 0 0 0 0 AgNbO Ago as Lao os Do to NbO • Ag_{0,70}La_{0,10}D_{0,20}NbO₃ Ag_{0,55}La_{0,15}D_{0,30}NbO Ag_{0,40}La_{0,20}□_{0,40}NbO 0 100 200 300 400 500 600 700 800 Number of cycle FIGURE 8 | Cycling stability of Ag1-3xLax 2xNbO3 at 2 mV s⁻¹

measured at 0.1 mV s⁻¹. Similarly, Ag_{0.55}La_{0.15}□_{0.30}NbO₃ demonstrates a relatively high capacity at low scan rates but a rapid drop at higher rates. In contrast, while less substituted materials such as Ag_{0.85}La_{0.05}□_{0.10}NbO₃ and Ag_{0.70}La_{0.10}□_{0.20}NbO₃ exhibit lower capacities at 0.1 mV s⁻¹, they demonstrate better capacity retention. At 50 mV s⁻¹, Ag_{0.85}La_{0.05}□_{0.10}NbO₃ exhibit capacity retentions of 53 and 64%, respectively, for a 500 times faster rate of charge/discharge compared to their capacities measured at 0.1 mV s⁻¹. All the specific capacities are summarized in **Supplementary Table S4**.

In order to get a better understanding of the charge storage mechanism, *b*-values from the power law relationship in **Eq. 3** have been calculated,

$$\mathbf{i} = \mathbf{a} \cdot \mathbf{v}^b \tag{3}$$

where i is the intensity of reduction/oxidation peak, v the corresponding scan rate, a and b are constant values. If b is close to 0.5, charge storage can be described as limited by ionic diffusion in the host material, as described in the Randles-Ševčík equation (Ševčík 1948; Randles 1948). When the value of b is equal or close to 1, charge storage occurs in agreement with nondiffusion limited mechanism, as in the case of pseudocapacitive materials (Choi et al., 2020). Regarding Ag_{1-3x}La_{x^D2x}NbO₃ compounds, as shown in Figure 5A,B, a linear relationship between specific current and scan rate (0.1 mV s⁻¹ and 50 mV s^{-1}) is observed, the *b*-values of which are listed in Table 1. The values of b vary between 0.87 and 0.95, which seems to indicate weak diffusion limitation during charge/ discharge processes. Additionally, the smaller b values calculated for $Ag_{0.55}La_{0.15}\square_{0.30}NbO_3$ and $Ag_{0.40}La_{0.20}\square_{0.40}NbO_3$ support the difference in capacity retention observed previously, as compared to $Ag_{0.85}La_{0.05}\square_{0.10}NbO_3$, and $Ag_{0.70}La_{0.10}\square_{0.20}NbO_3$.

As displayed in **Figure 6**, the behavior of the different oxides during lithium insertion was investigated by *in situ* XRD, to better understand the filling of the vacant A-sites of the Ag_{1-3x}La_x \Box_{2x} NbO₃ perovskite. Ag_{0.70}La_{0.10} $\Box_{0.20}$ NbO₃ was used because no structural defects were observed in this phase compared to Ag_{0.55}La_{0.15} $\Box_{0.30}$ NbO₃ and Ag_{0.40}La_{0.20} $\Box_{0.40}$ NbO₃. First, no new peak appears (and/or disappears) on the XRD patterns during charge and discharge. This behavior indicates that a solid solution type mechanism predominates upon charge storage, as previously reported for intercalation materials dedicated to power application with a *b* value close to 1 (Come et al., 2014). Moreover, it is observed that the peaks initially present do not move during lithiation. The three diffraction peaks observed in the studied 2θ range present the three crystallographic directions, implying that the perovskite structure does not modify its lattice parameters during lithium cation insertion in the vacant A sites. Thus, this material can be considered as a zero strain oxide during lithium insertion, similar to the well-known Li₄Ti₅O₁₂ (Thackeray and Amine 2021).

In another series of measurements, self-discharge and NMR experiments carried out on cycled Ag_{0.70}La_{0.10}□_{0.20}NbO₃ electrodes provide further evidence of Li⁺ insertion in the material. For these experiments, electrodes were cycled to 1.8 and 1.2 V vs. Li^+/Li at 0.1 mV s⁻¹ and subsequently polarized for 10 h to reach a thermodynamic equilibrium. As shown in Figure 7A,B, both electrodes (cycled at 1.2 and 1.8 V vs. $Li^+/$ Li) present relatively low self-discharge. The electrode polarized at 1.8V shows a potential of 1.82 V vs. Li⁺/Li after almost 80 h of OCV. The electrode polarized at 1.2 V shows a potential of 1.59 V vs. Li⁺/Li in the same condition. These low self-discharge levels at 1.2 and 1.8 V are a strong indication that lithium cations are inserted in a stable way into the vacancies of the material. Ex situ ⁷Li MAS NMR measurements have been performed after these self-discharge experiments. ⁷Li MAS NMR spectra were also recorded for the pristine and the fully discharged electrode (3.0V) in addition to the charged samples at 1.2 V vs. Li^+/Li , at a similar scan rate of 0.1 mV s⁻¹ As expected, the pristine electrode has a negligible quantity of Li detected. For the partially and fully charged samples, a peak is observed at around -1 ppm. The integrated intensity of the NMR peak, which is intrinsically proportional to the detected amount of lithium in the materials, is also found to be proportional to the specific capacity of the materials at 1.8 and 1.2 V (Figure 7B,C). The spectrum of the fully discharged electrode at 3.0V displays a small amount of lithium assigned to the partial irreversibility of the reaction during the first cycle and is also found to be in agreement with the first cycle of the CV. Due to the amount of lithium inserted in the materials, the signal to noise ratio remains relatively low even for a large

number of scans. For this reason, spectra with a narrower linewidth and thus better resolution, were not possible. Thus, it is difficult to conclude as to the number of lithium sites, even at the fully charged state, as only one apparent resonance is observed in ⁷Li MAS NMR. Taken together, the combination of *ex situ* NMR and self-discharge provide convincing evidence that lithium ions are inserted in this perovskite material, most probably in the vacant A site.

The cycling characteristics for $Ag_{1-3x}La_x\Box_{2x}NbO_3$ were determined as cycle life is a key property for the development of batteries based on high rate electrode materials. As observed in **Figure 8**, all the materials exhibit exceptional stability upon cycling. After 800 cycles at 2 mV s^{-1} , $Ag_{0.85}La_{0.05}\Box_{0.10}$ NbO₃, $Ag_{0.70}La_{0.10}\Box_{0.20}$ NbO₃, $Ag_{0.55}La_{0.15}\Box_{0.30}$ NbO₃ and $Ag_{0.40}La_{0.20}\Box_{0.40}$ NbO₃ show a capacity retention of 95, 95, 97 and 88%, respectively. The *in situ* XRD experiments and *b*-value calculation, which show zero-strain materials and non-diffusion limited charge storage mechanisms, respectively, are consistent with the outstanding cyclability observed for these materials.

In contrast to the classical design of insertion materials, our approach was to synthesize an oxide with vacancies in order to create potential sites for cation insertion in a perovskite. As proven by ex situ MAS NMR, lithium ions can be reversibly stored in the A site of Ag_{0.70}La_{0.10}D_{0.20}NbO₃ and by extension to every $Ag_{1-3x}La_x\square_{2x}NbO_3$ composition. To further demonstrate this point, Supplementary Figure S3A-D presents the difference between lithium and sodium insertion by cyclic voltammetry at different scan rates. While Li⁺ insertion leads to characteristic redox peaks, in the case of Na⁺, no redox reaction can be observed. It is likely that sodium ions cannot be inserted into the structure of Ag_{0.70}La_{0.10}D_{0.20}NbO3 and therefore cannot generate redox reactions due to the larger ionic radius This is also the case for the pseudocapacitive T-Nb2O5, which shows highly reversible Li-ion intercalation but negligible Na-ion insertion (Kim et al., 2012). Moreover, kinetic analysis provides compelling evidence that a not diffusion-limited insertion occurs during the charge and discharge processes.

CONCLUSION

This work presents the partial substitution of AgNbO₃ perovskite by lanthanum in the A-site, resulting in the creation of cationic vacancies. We report on a gradual increase of the capacity at low scan rates as a function of the increase of the substitution. In addition, the different oxides present excellent behavior at high scan rates. At 50 mV.s⁻¹Ag_{0.70}La_{0.10} $\Box_{0.20}$ NbO₃ retains 64% of its capacity measured at 0.1 mV s⁻¹. Moreover, the combination of *ex situ* MAS NMR and *in situ* XRD experiments confirm that the insertion of lithium ions in the A site of the perovskite is responsible for the observed capacity and does not cause any structural change of the material. Together, these observations help to explain the good cycling behavior observed. In addition to structural insight, kinetic analysis indicates a non-diffusion limited ion insertion process for these oxides.

Nevertheless, some questions still remain. A better understanding of the solvation/desolvation occurring at the Ag_{1-3x}La_xNbO₃ High-Rate Electrode

surface of particles during alkali ion insertion is critical towards understanding the small limitation of diffusion in charge storage process (Wang et al., 2019). Further experiments such as EQCM or *operando* atomic force microscopy can provide more insight in the charge storage mechanism. From another point of view, the promising observations reported here should be explored with other vacancy-designed materials and with different alkali cations. Moreover, these oxides present a charge storage mechanism which are between double layer capacitor and battery type electrodes (as observed for MnO_2 (Toupin et al., 2004; Brousse et al., 2006), T-Nb₂O₅ (Augustyn et al., 2013; Griffith et al., 2016) or MXenes (Naguib et al., 2012; Anasori et al., 2017) and represent an interesting model material for fundamental understanding in general.

In conclusion, the new approach reported in this work presents a different type of material design which widens the opportunities for creating the next generation of negative electrodes for high power Li- ion batteries. Although the oxide presented here contains silver, we believe this study can open the way toward the search of more practical materials for high-power battery electrodes.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

ELC: Investigation, Methodology, Writing—review and editing. JCEA and ND: Investigation, Writing—review. BD and GW: Writing—review. OC and TB: Conceptualization, Methodology, Supervision, Writing—review and editing.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2022.873783/full#supplementary-material

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Supplementary Material

2		
		Specific surface area / m ² .g ⁻¹
x= 0	AgNbO₃	3 m².g ⁻¹
x= 0.05	Ag _{0.85} La _{0.05} □ _{0.10} NbO ₃	6 m².g ⁻¹
x= 0.10	Ag _{0.70} La _{0.10} □ _{0.20} NbO ₃	13 m ² .g ⁻¹
x= 0.15	Ag _{0.55} La _{0.15} □ _{0.30} NbO ₃	15 m ² .g ⁻¹
x= 0.20	Ag _{0.40} La _{0.20} □ _{0.40} NbO ₃	16 m².g ⁻¹

 $Supplementary \ Table \ 1. \ Specific \ surface \ area \ of \ Ag_{1\cdot 3x}La_{x} \square_{2x}Nb \ O_{3} \ for \ different \ values \ of \ x.$

Supplementary Table 2. Experimental obtain by EDX (in bold) and theoretical percentage of Ag, La and Nb of $Ag_{1-3x}La_x\Box_{2x}NbO_3$ for different values of x.

	%Ag	%La	%Nb
AgNbO₃	49/ 50	0/ 0	51/ 50
Ag _{0.85} La _{0.05} □ _{0.10} NbO₃	40 /44	5/ 3	55/ 33
Ag₀.7₀La₀.1₀□₀.2₀NbO₃	33/ 39	8/ 6	59 /55
Ag₀.₅₅La₀.₁₅□₀.₃₀NbO₃	30 /32	11 /9	59 /59
Ag₀.4₀La₀.2₀□₀.4₀NbO₃	26 /25	13/1 2.5	61 /62.5

Supplementary Material



Supplementary Figure 2. Le Bail refinement using the space group Pbcm of (a) AgNbO₃ (b) Ag_{0.85}La_{0.05}D_{0.10}NbO₃ (c) Ag_{0.70}La_{0.10}D_{0.20}NbO₃ (d) Ag_{0.55}La_{0.15}D_{0.30}NbO₃ (e) Ag_{0.40}La_{0.20}D_{0.40}NbO₃



Supplementary Figure 2. (a) Cell parameters of Ag_{1-3x}La_{x□2x}NbO₃ for different value of x.

	a / A°	b/A°	c / A°	Volume / A°³
AgNbO₃	5.547	5.612	15.723	489.453
Ag₀.85La₀.05⊡₀.10NbO₃	5.563	5.655	15.813	497.4557
Ag _{0.70} La _{0.10} □ _{0.20} NbO₃	5.575	5.657	15.817	498.833
Ag₀.55La₀.15⊡₀.30NbO3	5.579	5.659	15.822	499.525
Ag _{0.40} La _{0.20} □ _{0.40} NbO₃	5.578	5.659	15.822	499.436

 $Supplementary \ Table \ 3. \ Cell \ parameters \ of \ Ag_{1\cdot 3x}La_x \square_{2x}Nb \ O_3 \ for \ different \ values \ of \ x.$

Supplementary Material

Supplementary Table 4. Specific capacity for every material at different scan rate during CV experiments.

	AgNbO₃	Ag₀.85La₀.05□₀.10NbO₃	Ag₀.7₀La₀.1₀□₀.2₀NbO₃	Ag₀.55La₀.15□₀.30NbO3	Ag₀.₄₀La₀.₂₀□₀.₄₀NbO₃
0.1 mV.s ⁻¹	6.0	17.0	32.2	34.2	41.1
0.2 mV.s ⁻¹	5.9	12.1	26.6	34.0	27.7
0.5 mV.s ⁻¹	5.9	11.6	25.8	32.3	25.3
1.0 mV.s ⁻¹	5.7	11.5	25.6	31.0	24.1
2.0 mV.s⁻¹	4.8	11.0	25.1	31.0	21.9
5.0 mV.s⁻¹	4.6	10.9	24.6	25.9	19.7
10.0 mV.s ⁻¹	3.8	10.6	24.0	23.3	19.7
20.0 mV.s ⁻¹	3.1	10.1	23.2	20.2	17.5
50.0 mV.s ⁻¹	2.3	9.1	20.7	15.2	13.9



Supplementary Figure 3. (a-b-c) CV at 0.1 mV.s⁻¹, 2 mV.s⁻¹, 50 mV.s⁻¹ respectively between 1.2V and 3V of Ag_{0.70}La_{0.10}D_{0.20}NbO₃. (d) Specific capacity of Ag_{0.70}La_{0.10}D_{0.10}NbO₃ for different type of electrolytes. (1M LiPF₆ in EC/DMC (1:1) and 1M NaClO₄ in PC (1:1).

IV. Conclusion

Grâce à cette publication, il a été démontré que la formation de lacunes dans une pérovskite par substitution cationique permet de rendre possible l'insertion d'ions lithium. A faible courant, plus la pérovskite est substituée, plus elle va insérer d'ions lithium. Cependant, dues aux impuretés et à la baisse de cristallinité pour les hauts degrés de substitution $(Ag_{0.55}La_{0.15}\square_{0.30}NbO_{3}et Ag_{0.40}La_{0.20}\square_{0.40}NbO_{3})$, les capacités à haute vitesse de balayage (> 1 mV.s⁻¹) diminuent plus rapidement que dans le cas de Ag_{0.70}La_{0.10}D_{0.20}NbO₃. Une capacité de 25 mAh.g⁻¹ à 0.1 mV.s⁻¹ est observée dans le cas de la pérovskite avant été le plus largement étudiée Ag_{0.70}La_{0.10}, and book a solution de capacité à 50 mV.s⁻¹ de 64% de la capacité mesurée à 0.1 mV.s⁻¹. Cette faible perte de capacité est expliquée par une diffusion des ions facilitées dans la structure. Ceci a été démontré grâce au calcul de la b-value (paramètre b) qui se trouve être très proche de 1 comme pour les matériaux capacitifs ou pseudocapacitfs. De plus, des analyses par RMN ex situ démontrent un mécanisme d'insertion des ions lithiums dans les cages A de la pérovskite, tandis que l'acquisition de diffractogrammes in situ nous permet de comprendre que l'insertion des ions lithium. Elle se fait sans changement des paramètres de maille durant la lithiation et la délithiation indiquant le faible stress qu'engendre les ions lithium sur la structure de la pérovskite et plus particulièrement sur les octaèdres (NbO₆) lors du cyclage électrochimique. On parle alors de « zero strain materials ».

D'autres expériences sont envisagées dans le but de mieux comprendre les intéressantes propriétés que présence cette famille de pérovskite. Parmi celles-ci, une meilleure résolution de la structure par des affinements Rietveld et/ou des images « haute résolution » par microscopie électronique à transmission pour connaitre l'organisation des lacunes, de l'argent ainsi que du lanthane dans les cages A de la pérovskite pourraient permettre de mieux expliquer les propriétés électrochimiques du matériau. Des calculs DFT permettraient également de mieux visualiser les différents sites d'insertion ainsi que la diffusion du lithium durant la réduction.² De manière générale, une meilleure compréhension des mécanismes de stockage de charge et des paramètres permettant une diffusion favorisée des ions lithiums dans les structures cristallographiques étudiées permettront de synthétiser des matériaux plus performants car ayant les propriétés physico-chimiques ciblées.

L'objectif autour de cette thèse est d'augmenter la densité de puissance ainsi que la densité d'énergie de ce type de matériaux pour permettre diverses applications (voitures

électriques, véhicules à guidage automatique, ...). A cet égard, $Ag_{1-3x}La_x\Box_{2x}NbO_3$ peut être considéré comme un matériau modèle pour la compréhension des mécanismes de stockage de charge. Cependant, les capacités relativement faibles de cette nouvelle famille de matériaux ainsi que l'utilisation d'argent et de lanthane, qui sont des éléments présentant un coût élevé, ne permettront pas d'imaginer une possible application future. La création de lacunes par substitution dans des matériaux présentant déjà des propriétés d'insertion comme SrVO₃ pourrait être étudié dans le but d'augmenter les capacités initiales des oxydes ainsi qu'améliorer la diffusion des ions lithium dans ces pérovskites.^{2,3} Dernièrement, un stagiaire de M2 MESC+ au laboratoire, a étudié la création de lacunes dans AgNbO₃ par substitution du Nb par du W donnant la formule chimique, $Ag_{1-x}\Box_xNbO_3$ démontrant une augmentation progressive de la capacité avec l'augmentation de la substitution. Un doctorant de l'équipe, a utilisé une synthèse polyacrylamide de Ag_{1-3x}La_x□_{2x}NbO₃ confirmant les propriétés électrochimiques découvertes lors de la présente étude.

Suivant la même philosophie vis-à-vis de la création de site de lithiation dans les matériaux, nous nous sommes ensuite tournés vers des matériaux présentant des propriétés d'échanges ioniques. En échangeant un ion volumineux par un ion ayant un rayon ionique moindre, il semble également possible de créer des sites d'insertion pour les ions alcalins comme le Li⁺. Aussi, nous avons décidé de limiter la présence de l'argent dans le but d'amoindrir le coût de ces oxydes ainsi que d'augmenter la capacité théorique des matériaux étudiés.

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Chapitre IV. Etude de l'influence de la taille des particules dans le stockage de charge de KTiNbO₅, HTiNbO₅ et Ti₂Nb₂O₉

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I. Introduction

1. L'échange ionique comme voie pour l'insertion d'ions lithium

Dans les années 70-80, sous l'impulsion du groupe dirigé par le Pr. Bernard Raveau, de nombreux oxydes de métaux de transition contenant des ions alcalins et montrant des propriétés d'échanges ioniques sont découverts. Ces oxydes peuvent être des pyrochlores de type $A^IB_2O_6$ (A = K, Cs, Rb) ^{1,2}, des structures lamellaires telles que $A^I_nM_{2n}O_{4n+2}$ (A=K, Rb, Cs)³⁻⁶, ou encore des pérovskites lamellaires $A^IM_{n-1}Nb_nO_{3n+1}(A=K, Rb, Cs)^{7-9}$. D'autres structures plus complexes pouvant être décrites comme l'intercroissance d'une structure de type bronze hexagonal et d'une structure pyrochlore (A₁₂Nb₃₀W₃O₉₀ ou A₂Nb₆TiO₁₈ (A=Rb, Cs))¹⁰⁻¹² démontrent également des propriétés d'échanges ioniques.

Le Tableau.III. 1 décrit les rayons ioniques des ions impliqués dans les échanges pour un nombre de coordination égal à $6^{13,14}$ Malgré le fait que les paramètres de maille se trouvent modifiés après un échange ionique^{4,7}, la forte différence entre les rayons ioniques de tous ces ions démontre l'intérêt d'échanger des ions volumineux dans le but de créer des sites vacants pour une insertion facilitée des ions lithium. Ainsi, il est possible dans ces matériaux de remplacer les ions Rb⁺, Cs⁺ ou encore K⁺ par des ions plus petits comme Na⁺, Li⁺, H⁺ ou H₃O⁺.

	<i>Ionic radius</i> (CN = 6)
\mathbf{H}^+	Négligeable
Li^+	0.76
Na ⁺	1.02
K+	1.38
Rb ⁺	1.52
Cs ⁺	1.67

Tableau.III. 1. Comparaison des rayons ioniques pour les différents ions alcalins ainsi que H⁺.^{13,14}

Expérimentalement, l'échange ionique est réalisé dans le cas des métaux alcalins (Li⁺, Na⁺) par un mélange du précurseur à base de Rb, Cs, K et d'un sel de Li/Na jusqu'à atteindre la température de fusion de ce sel (400-500°C). Cette méthode est appelée synthèse par sels fondus.^{15,16} Dans le cas du proton, l'oxyde précurseur est inséré dans une solution d'acide concentré (classiquement 3-5M HNO₃), le plus souvent à température ambiante, pendant quelques jours puis récupéré et lavé pour obtenir une phase protonée.^{4,6–9}

2. HTiNbO₅, un cas modèle dans l'étude de cette famille

Dans notre première étude vis-à-vis de cette famille de matériaux, notre attention s'est portée sur un oxyde présentant une structure relativement simple, KTiNbO₅. Une étude détaillée des propriétés cristallographiques et électrochimiques a été réalisée dans le chapitre bibliographique. Le peu de publications scientifiques disponibles à ce sujet démontre la simplicité de l'échange ionique permettant le passage de KTiNbO₅ à HTiNbO₅ ainsi que la possibilité d'insérer un nombre important d'ions lithium dans HTiNbO₅ alors que très peu de lithium peut être inséré dans le cas de KTiNbO₅.¹⁷ De plus, une réaction topotactique par déshydratation permet d'obtenir un oxyde vierge de tout ions alcalins et/ou de protons, il s'agit de la phase Ti₂Nb₂O₉.¹⁸ Ainsi, trois matériaux, très similaires d'un point de vue cristallographique, peuvent être comparés dans le but d'étudier l'influence du potassium, du proton ou de l'absence de ces derniers dans la capacité qu'auront ces oxydes à insérer des ions lithium.

3. Utilisation de l'exfoliation et d'une synthèse par voie sol-gel pour modifier la morphologie de particules

Comme illustré dans la partie bibliographique, il est parfois possible pour des matériaux lamellaires ayant des protons dans leur espace interfeuillet d'exfolier ses couches dans le but d'obtenir une solution colloïdale de feuillets en suspension.^{19–21} Dans le cas de HTiNbO₅ ainsi que d'autres oxydes lamellaires de cette famille, le mélange avec une solution aqueuse contenant de l'hydroxyde de tétrabutylammonium (TBA⁺OH⁻) permet l'exfoliation des particules après 15 jours en suspension. HTiNbO₅ étant un acide faible et le TBAOH étant une base forte, une réaction acide/base se déroule à température ambiance permettant l'échange du proton avec l'ion tétrabutylammonium. Ce dernier va exfolier les feuillets (TiNbO₅⁻)_n car sa taille moléculaire est trop élevée pour maintenir la structure lamellaire de ce titanoniobate. En ajoutant dans cette solution, quelques gouttes d'acide concentré (HNO₃) dans le but de rendre la solution légèrement acide, les nanofeuillets se ré-empilent formant des particules micrométriques de HTiNbO₅ ayant une surface spécifique très élevée (~ 100 m²/g) grâce au réempilement aléatoire et spontané des nanofeuillets.^{22–26} Il a souvent été reporté l'intérêt de ce genre de morphologie pour des applications dans les électrodes de puissance.^{22,27}

Deuxièmement, une synthèse par voie sol-gel utilisant la méthode dite de Pechini permet d'obtenir des particules nanométriques de KTiNbO₅.^{28–32} La méthode de synthèse est explicitée

dans les publications associées à ce chapitre. De plus, le même processus que celui utilisé pour les particules synthétisées par voie céramique permet l'obtention de HTiNbO₅ puis Ti₂Nb₂O₉.

Ainsi, une étude de l'influence de la morphologie entre des particules micrométriques (SS pour *solid state synthesis*), des particules nanométriques (SG pour *sol-gel synthesis*) ainsi que des nanofeuillets ré-empilés (NS pour *nanosheet*) a été réalisée pour mettre en lumière l'importance de la caractérisation des matériaux pour la compréhension des propriétés électrochimiques observées.

4. Prélude aux publications

L'intérêt et l'originalité du travail réalisé dans ce présent chapitre s'exprime en plusieurs points. Premièrement, la diversité des méthodes de synthèse a permis de comprendre l'influence de la taille des particules et de la cristallinité vis-à-vis des propriétés électrochimiques de KTiNbO₅, HTiNbO₅ et Ti₂Nb₂O₉. Ensuite, une étude des propriétés d'insertion des ions lithium à différentes vitesses de charge/décharge a été réalisée permettant de mettre en application ce type de matériau comme électrode négative pour batterie Li-ion. Dernièrement, les mécanismes de stockage de charge ont été revisités grâce à l'utilisation de méthodes de caractérisation telles que la DRX *in situ*, la RMN *ex situ*, les mesures de potentiel entropique à différent état de charge/décharge ou bien la mesure de la chaleur émise par les électrodes par calorimétrie *operando*.

Deux articles scientifiques ont été publiés grâce à l'étude de ses phases. La première relate l'étude des liens entre la morphologie des particules et les propriétés électrochimiques de HTiNbO₅. L'influence du proton dans l'espace interfeuillets ainsi que la variation des paramètres de maille de la structure pendant l'insertion a été étudiée avec l'aide respectivement de la RMN et de la DRX. Ensuite, une collaboration avec le groupe du Pr. Laurent Pilon (*University of California at Los Angeles*) a permis la publication d'un article scientifique qui visait à mieux comprendre les différences entre Ti₂Nb₂O₉ synthétisé par voie céramique et par voie sol-gel vis-à-vis de leurs propriétés thermodynamiques et cinétiques durant le processus de charge-décharge par mesure de potentiel entropique et par calorimétrie.

- II. Les publications
- 1. HTiNbO₅

Effect of particle morphology and the role of proton on the lithium insertion properties of HTiNbO₅ electrode material.

Etienne Le Calvez, Nicolas Dupré, Éric Gautron, Camille Douard, Olivier Crosnier, and Thierry Brousse, Electrochimica acta, under review.

Effect of particle morphology and the role of proton on the lithium insertion properties of HTiNbO₅ electrode material

Etienne Le Calvez^{1,2}, Nicolas Dupré¹, Éric Gautron¹, Camille Douard^{1,2}, Olivier Crosnier^{1,2}, and Thierry Brousse^{1,2}*

¹ Nantes Université, CNRS, Institut des Matériaux Jean Rouxel, IMN, F-44000 Nantes, France

² Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR 3459,
33 rue Saint Leu, 80039 Amiens Cedex, France

Keywords: *Li-ion batteries, high-rate negative electrode, ion exchange, fast intercalation, in situ XRD, ex situ MAS NMR*

Highlights:

- Synthesis of three different morphologies of HTiNbO₅ has been carried out (solid state, sol-gel, exfoliation-restacking methods)
- High-resolution electron microscopy demonstrates niobium and titanium ordering in (MO₆) octahedra sites.
- The impact of morphology on lithium ion intercalation in HTiNbO₅ has been studied.
- Solid solution mechanism governs lithium intercalation after an initial and irreversible phase change.
- Protons play a key role on lithium intercalation abilities at high-rate.

Abstract

Layered oxides showing edge-sharing octahedra are promising negative electrode for high-power Li-ion batteries. In this sense, we propose the synthesis of the lamellar HTiNbO₅ by solid-state (SS), sol-gel (SG) and exfoliation-restacking (NS) syntheses investigating in the same way the charge storage mechanism of this oxide and the influence of the morphology on material and electrochemical properties. An arsenal of characterization has been performed for these three types of particles using XRD, electron microscopy but also by associating mass spectroscopy to TGA. Their ability to intercalate lithium has been compared showing interesting and very similar specific capacity for solid-state and sol-gel synthesis (> 100 mAh.g⁻¹ at 0.5 A.g⁻¹). In addition, it was shown the inferiority of the synthesis giving rise to nanosheet (NS) due to the presence of organic molecule in its interlayer. Lastly, when *in situ* XRD propose a solid-solution reaction for HTiNbO₅ with initial and irreversible phase change forming Li_{0.4}HTiNbO₅, *ex situ* ¹H MAS NMR measurements highlight the essential role of the proton in the charge storage of HTiNbO₅. Thus, this paper demonstrates the interest of HTiNbO₅ as negative electrode for Li-ion batteries as well as the predominant role that the proton can play in the diffusion of lithium ions inside a confined space.

Introduction

The climate change forces people to use cleaner energies, i.e. less consuming greenhouse gases. Thus, renewable energies must be deployed as well as vehicles running on electric energy thanks to electrochemical storage (batteries and/or fuel cell). In this regard, the batteries need to be charged more quickly to allow a larger deployment of this technology. Thus, it seems necessary to replace the negative graphite electrode in order to charge these electrochemical systems in a few minutes.^{1–4} The capacity of graphite is lower during a fast charge because the insertion of lithium is largely limited by the diffusion of ions in the interlayer of graphite. In addition to this, graphite inserts lithium ions at a potential that can go below 0.1 V vs Li⁺/Li. This interesting property in order to obtain a high energy density can also lead to the formation of lithium metal in the form of dendrites by lithium plating, resulting in possible short circuits and thermal runaway.^{5,6}

With regard to this quest for more power, different types of materials have been proposed. Among this wide range of choices, niobium and titanium oxides seem to be interesting.⁷⁻¹⁰ The hexagonal form of niobium oxide (T-Nb₂O₅) exhibits a capacity of 130 mAh.g⁻¹ for a 6 minutes charge while titanium dioxide presents a high theoretic capacity of 335 mAh.g⁻¹ for one electron exchanged per transition metal.¹⁰ Even if it is still challenging to achieve this capacity, different strategies to reach the theoretical capacity of TiO₂, like the creation of cationic vacancies, fluorine doping or the reduction of the particle size to improve the ionic and electrical conductivity, have been tried.^{7,8,11,12} Another strategy was to synthesize a metastable form of TiO₂, called TiO₂-B. After an ionic exchange reaction from K₂Ti₄O₉ to H₂Ti₄O₉, TiO₂-B is synthesized by a topotactic dehydration reaction of H₂Ti₄O₉.^{13,14} This material presents edge-sharing octahedra which have been showed to be interesting for fast charge application.¹⁵ It proposes relatively high capacities for fast charging without the need to obtain nanometric particles.⁷ Moreover in a recent study, Fleichmann et al. investigate the electrochemical characteristics of the different intermediate oxides during the dehydration of H₂Ti₄O₉ leading to TiO₂-B.¹⁶ They demonstrate that the oxide with partial deprotonation offers the highest capacities for all the currents tested. Their works shed light on the impact of protons and water molecules located between the sheets in the charging mechanisms of titanium oxides.

In the 60s and 70s, Raveau et al. studied the ion exchange properties of various niobium, titanium and/or tungsten based multicationic oxides.^{17–24} In most cases, the materials studied seem to be able to present interesting intercalation properties. Our previous study proposed the ion exchange of Rb₂TiNb₆O₁₈ and the investigation of the intercalation properties of the protonated material.²⁵ H₂TiNb₆O₁₈.2H₂O exhibited significantly higher capacities than Rb₂TiNb₆O₁₈ as well as a volume change during lithium ion insertion of only 1%. Among the materials presented by the group of Raveau, KTiNbO₅ offers interesting features. It is a lamellar oxide with 2x2 units of octahedra sharing their edges. These blocks form (TiNbO₅)_n layers by corner sharing. Between these layers are potassium ions. First described by Wadsley²⁶, KTiNbO₅ crystallizes in an orthorhombic lattice and Pnma space group. The material is then described as lamellar along c direction with a = 6.459 Å, b = 3.792 Å, and c = 18.742 Å cell parameters. The titanium ions are mainly on the internal octahedra of the layers because these are less distorted. Moreover, KTiNbO₅ proposes interesting ion exchange properties. By its lamellar crystallographic form, protons are not found with water molecules because they are necessary for the stability of the interlayer.^{22,26}

Thanks to the use of HTiNbO₅, we propose to combine the double strategy of using a material based on titanium and niobium having 2x2 units of octahedra sharing their edges but also an oxide offering ionic exchange properties (and so proton which can help the lithium insertion). Several groups have studied this material as negative electrode for Li-ion batteries. First, in 2008, J-F Colin et al. studied lithium intercalation properties of HTiNbO₅. They show the possible insertion of 2 Li⁺ per formula unit giving rise to Li₂HTiNbO₅ between 1.0V and 3.0V vs Li⁺/Li. A modification of the orientation of the layers is observed in a very similar way to LiTiNbO₅.²⁷ Moreover, the authors propose a phase change at the beginning of the first lithiation giving rise to Li_{0.4}HTiNbO₅, which is irreversibly formed. Lastly, it is shown that Li₃HTiNbO₅ can be formed if this oxide is reduced to 0V vs Li⁺/Li showing a rocksalt-like structure with very low cyclability. It was not until the work of Y. Yuan et al. that this material was studied at higher currents as negative electrode in high-power Li-ion battery.²⁸ In this study, HTiNbO₅ is presented as nanowires and proposes a capacity of about 100 mAh.g⁻¹ at 5C. As well, an initial phase change is observed and then the insertion is governed by a solid solution type mechanism. As this material can be exfoliated, a recent study by J. Zhang et al. proposes a study of restacked HTiNbO₅ nanosheets in combination with MXenes nanosheets.²⁹ Specific capacity higher than 100 mAh.g⁻¹ at 5 A.g⁻¹ has been demonstrated. Nevertheless, no publication reports on the influence of morphologies on charge storage mechanism and capacities of this oxide. As well, no study on the influence of proton in the interlayer on the storage ability of HTiNbO₅ has been achieved to date.

In this paper, we study the lithium intercalation behavior of three different morphologies of HTiNbO₅ (microparticles, nanoparticles and restacked nanosheets). A systematic study of the relationship between the physicochemical properties of the material and their electrochemical characteristics is proposed. Thanks to the use of thermogravimetric analysis (TGA) combined with mass spectroscopy (MS) as well as *in situ* XRD and *ex situ* ⁶Li MAS NMR, we propose a clear understanding of the insertion properties of the different HTiNbO₅. Moreover, *ex situ* ¹H MAS NMR gives some keys on the comprehension of protons influence in the charge storage mechanism in this oxide.

1. Experimental section

a. Synthesis method of KTiNbO5, HTiNbO5 i. KTiNbO5 solid state (SS)

In this study, KTiNbO₅ powder was synthesized by solid-state or sol-gel method. In the solid-state synthesis method, Nb₂O₅ (Alfa Aesar, 99.9%), TiO₂ (Alfa Aesar, \geq 99%), and K₂CO₃ (ACS Reagent, \geq 99.0%) powders was mixed with a molar ratio of 1:2:1.2. Here, a 20% excess of K₂CO₃ was added because of its volatility at high temperatures. This mixture was ground in an agate mortar for 10 minutes to obtain a homogeneous powder. This powder was calcined at 1100 °C in a platinum crucible under air for 12 hours to produce KTiNbO₅ powder.

ii. KTiNbO5 sol-gel (SG)

In the sol-gel synthesis method, 1.351 mg of NbCl₅ (Sigma Aldrich, 99%) was dissolved in 30 mL of ethanol. At the same time, 1.703 mg of titanium isopropoxide (Alfa Aesar, 97%) and 0.370 mg of KCl (ACS Reagent, 99.0-100.5%) were dissolved in 200 mL of ethylene glycol. Then citric acid (Alfa Aesar, \geq 99%) was added to this second solution to achieve a 10:1 molar ratio of citric acid to the total number of cations in the two solutions (Nb, Ti, and K). After waiting 1 hour to ensure complete dissolution of all species, the two solutions were mixed, then stirred and heated to 120 °C until a blackish gel was formed. This gel was dehydrated at 300 °C in air overnight to ensure complete evaporation of the organic species. It was then calcined at 700 °C in air for 2 hours to produce KTiNbO₅ powder. It should be noted that it was necessary to cautionary evacuate the chlorinated gases out of the handling room.

iii. HTiNbO5 SS and SG

The final step, common to both SS and SG synthesis, was to mix and stir the KTiNbO₅ powder in a 3M HNO₃ aqueous solution for 3 days. The acidic solution was changed daily to ensure complete exchange of potassium cations with protons. The resulting suspension containing HTiNbO₅ powder was then centrifuged and rinsed with DI water until neutral pH of the wastewater was obtained.

iv. HTiNbO5 nanosheets (NS)

The acid-base reaction of HTiNbO₅ SS acid with tetrabutylammonium (TBA⁺OH⁻) in aqueous solution allows the exfoliation of TiNbO₅⁻ sheets which are then in suspension in this aqueous solution. More precisely, 250mL of aqueous solution at pH=10 containing DI water and TBAOH is prepared. Then, 1g of HTiNbO₅ SS powder is introduced for 14 days and stirred. Then, the solution containing suspended TiNbO₅ nanosheets is recovered by centrifugation. Finally, the nanosheets are restacked by a progressive addition of acid in the solution (typically HCl or HNO₃) until complete restacking. The resulting HTiNbO₅ NS powder was then centrifuged and rinsed with DI water until neutral pH wastewater was obtained.

b. Characterization i. Powder X-ray diffraction

X-ray diffraction (XRD) pattern was collected using a PANalytical X'Pert Pro diffractometer (Malvern Panalytical, Almelo, Netherlands). X'Celerator detector with Cu-K_{α 1}-K_{α 2} (λ = 1.54060, 1.54439 Å) radiation was used acceleration voltage and current were 40 kV and 40 mA, respectively. With a step scan of 0.0167°, diffraction patterns have been collected between 20° and 80° (2 θ). Moreover, i*n situ* XRD patterns have been collected using homemade Leriche-like cell.³⁰ During charge-discharge experiment, a current of 0.02 A.g⁻¹ was applied during 60 min and stopped during 30 min for XRD pattern acquisition.³⁰

ii. Scanning electron microscopy

Scanning electron microscopy (SEM) images were obtained using a Zeiss Merlin instrument and chemical analysis with EDX using X-max, detector 50 mm² at a working distance of 8 mm on the same device.

iii. Transmission electron microscopy

Scanning/Transmission electron microscopy (S/TEM) was performed in order to characterize the HTiNbO₅ powders synthesized by solid-state or sol-gel methods. Powders were dispersed in ethanol and then deposited on a holey carbon film coated copper grid before insertion in a probe-corrected S/TEM Themis Z G3 (Thermo Fisher Scientific). TEM micrographs were collected at 300 kV using a OneView CMOS camera (Gatan).High-angle annular dark-field (HAADF-STEM) images were acquired at 300 kV, with 20 mrad convergence angle and 39-200 mrad collection angles.

iv. NMR

For MAS NMR analysis, free-standing electrodes with about 5-10 mg.cm⁻² were polarized for 10h at different states of charge after performing a cyclic voltammogram (CV) at 0.1 mV.s⁻¹. After disassembling the Swagelok in a glove box, electrodes were cleaned with a few drops of DMC and then dried overnight under *vacuum* in a Büchi oven at 60°C. Then, the electrolyte-free electrode was placed in a 2.5 mm-diameter zirconia rotor for MAS NMR experiments. ⁷Li, ⁶Li and ¹H MAS NMR spectra were acquired on a Bruker Avance 200 spectrometer (B₀ = 4.7 T, Larmor frequencies v₀ (⁷Li = 77.78 MHz, ⁶Li = 29.45 MHz and ¹H = 200.15 MHz) at RT. A Bruker MAS probe with a cylindrical 2.5 mm (o.d) zirconia rotor spun at a frequency of 30 kHz was used. ⁷Li Spectra were obtained by applying a single pulse sequence with a recycle delay of 3s. ¹H Spectra were obtained by applying a single pulse sequence with a recycle delay of 30s. D1 values were chosen to ensure the acquisition of quantitative spectra. Integrated intensities were determined by using spectral simulation (DMFit Software).³¹ The resulting integrated intensities were normalized with respect to the mass of the sample contained in the NMR rotor, the number of scans, and the receiver gain.

v. Electrochemistry

To shape the material, self-supported electrodes were fabricated by mixing, in small amount of ethanol, 75% w/w HTiNbO₅, 15% w/w of conductive carbon (Carbon Black by Superior Graphite, Chicago, IL, USA) to increase electronic conductivity and 10% w/w poly (1,1,2,2-tetrafluoroethylene dissolved in water (PTFE, Sigma Aldrich) to form a homogeneous paste. Then, this mixture is introduced and mix into a mortar to homogenize the solution and then cold-rolled until the obtention of electrodes with a weight of about 5-10 mg.cm⁻² according to recommendations.³² Using Swagelok, electrochemical measurements were performed by separating positive electrode and metallic lithium (99.9%, Aldrich) with glass fiber membrane (70 mm, 10 mm diameter, GF/D Whatman) soaked with 1M LiPF₆ dissolved in 1:1 % wt. EC/DMC (Solvionic, France, battery grade purity). The Swagelok were assembled in a glove box containing less than 0.1 ppm of O₂ and H₂O. VMP3 potentiostat (from Biologic run under ECLab software version V11.36) were used for electrochemical measurements.

2. Results

In this work, three different HTiNbO₅ samples are presented: HTiNbO₅ synthesized by solid-state route called HTiNbO₅ SS, restacked HTiNbO₅ nanosheet particles obtained by the exfoliation of HTiNbO₅ SS particles designated as HTiNbO₅ NS, and a material called HTiNbO₅ SG synthesized by sol-gel process using the Pechini method. This nomenclature will be used throughout this publication.

As described in the introduction for its analog KTiNbO₅ and in the Figure 1, HTiNbO₅ is a lamellar oxide with 2x2 units of octahedra sharing their edges. The presence of proton as well as the strong bond O-H allow considering this oxide as an acid.²⁴ It is the reason why insertion of basic organic molecules by acid-base reaction is possible, as for example butylamine as explained in Supplementary Information.^{33–35} Moreover, due to the reduction of the interlayer distance after the ion exchange (from c = 18.742 Å for KTiNbO₅ to c = 16.656 Å for HTiNbO₅), an O-H-O bond is formed between two (TiNbO₅)_n layers.²⁴ This reinforces the lamellar structure of this material.



Figure 1. Crystal structure of HTiNbO₅ projected along b axis.²⁴ (TiNbO₅)_n layers are built up by the formation of 2x2 block of edge-sharing octahedra that combine together the edges to form the layer. In between, protons can be found forming hydrogen bond with oxygen from the layer. It shown with the use of VESTA.⁵¹

To confirm these assessments taken from the literature, XRD patterns were collected. As shown in Figure 2.A, the oxides HTiNbO₅ SS and HTiNbO₅ SG have the same diffraction peaks that are consistent with the literature data. Thus, we can consider these materials as pure phases with complete ion exchange due to the absence of peaks corresponding to KTiNbO₅. Since HTiNbO₅ NS was obtained *via* HTiNbO₅ SS, this material can also be considered pure. Nevertheless, HTiNbO₅ NS do not have the same peaks than SS and SG, which is due to the exfoliation-stacking process that damage the crystallites. Despite the presence of the peak (002), the absence of (004) and (008) peaks shows the low order in the restacking of the layers (TiNbO₅). By the way, the presence of (002) peak allows us to know the average interlayer distance for this morphology. In this respect, we observe a value of the parameter c equal to 16.62 Å, ~18.20 Å, and ~22.21 Å for SS, SG, and NS respectively. These c parameters have been calculated from the (002) peak using the Bragg law and are more visible thanks to Figure 2.B. The value for SS is very close to the literature confirming the decrease of the interlayer distance during the ion exchange process. However, the higher value found for HTiNbO₅ SG can be explained by the difference in crystallinity compared to SS. Indeed, the recrystallization at 700° allows the formation of smaller crystallites as observed by XRD (broader peaks for SG than for SS). This lower crystallinity may lead to structural differences as well as further changes during ion exchange (difference in amount of water in the interlayer space). These will be more largely discussed during the explanation of thermogravimetric and mass spectroscopy analyses later in the text. For HTiNbO₅ NS, the c parameter is very close to the literature data



and can be explained by the disorder created during restacking which, forms larger interlayer distance.^{36–38}

Figure 2. XRD pattern of HTiNbO5 for the three different morphologies (SS/SG/NS) between (A) 5-50° and (B) 5-14° 2-theta angles. XRD patterns highlight the difference in the interlayer distance thanks to the (002) peak shift.

To corroborate the observation made from XRD patterns, SEM and TEM images of HTiNbO₅ SS, SG and NS are shown Figure 3. Clear lamellar morphology is observed for the micro size particles of HTiNbO₅ SS with preferential growth along c parameters (Figure3.A-B-C). In the case of HTiNbO₅ SG, smaller spherical particles of about 50 nm are observed as shown in Figure 3.(D-E-F). The particles are agglomerated as often observed in the case of sol-gel synthesis using the Pechini method.^{39–41} Interestingly, for HTiNbO₅ NS, the random stacking of HTiNbO₅ sheets is observed by SEM. The SEM/TEM image presented in Figure 3.(G-H-I) demonstrates this assumption but also shows a certain organization of the sheets along the c direction which explains the visualization of the (002) peak in the corresponding XRD pattern. These observations also corroborate the XRD pattern in the sense that smaller particles are observed in the case of HTiNbO₅ SG and HTiNbO₅ NS compared to HTiNbO₅ SS. Moreover, the high intensity of the (002) diffraction peak compared to the other peaks in the case of HTiNbO₅ SG.



Figure 3. SEM and TEM images of (A-B-C) HTiNbO₅ solid-state (SS) (D-E-F) HTiNbO₅ sol-gel (SG) (G-H-I) HTiNbO₅ nanosheets (NS).

Lastly, Figure 4 displays a HAADF-STEM image of HTiNbO₅ SS acquired along [110] showing its lamellar structure along c. The intensities in this image are comparable to those of the simulated one (inset) calculated with the structure given by Rebbah et al.²⁴ This provides further evidences that titanium cations occupy preferential site in the inner position of the layer as mentioned previously in literature thanks to Rietveld refinement and HRTEM images on Ti₂Nb₂O₉.^{24,42} The lower distortion of the inner octahedra that favors the presence of Ti⁴⁺ explains the observed cation ordering in HTiNbO₅.⁴² Moreover, a good crystallinity of the sample is observed with no staking faults.



Figure 4. Experimental HAADF-STEM image (Radial Wiener Filtered) of HTiNbO₅ SS viewed along [110] (scale bar: 2 nm). Inset : simulated HAADF image (Dr Probe⁵², using ICSD file #31797²⁴ as input structure.

For a better understanding of the difference in the (002) peak position between HTiNbO₅ SS, SG and NS, TGA combined with MS has been done. The TGA analysis shows a large difference between SS, SG and NS with respect to mass loss as shown Figure 5.A. For HTiNbO₅ SS, a mass loss of about 99% is observed before 300°C assigned to surface and possibly small amount of structural water. Then, a transition from HTiNbO₅ to Ti₂Nb₂O₉ causes an additional 4% mass loss.⁴³ This mass loss corresponds to one water molecule (H₂O). *A contrario*, HTiNbO₅ SG loses 4% of its mass before the transition to Ti₂Nb₂O₉, which also leads to a 4% mass loss. This higher mass loss is attributed to the presence of a greater number of water molecules in the interlayer accompanying the protons. This observation, together with the observed difference in crystallinity, explains the difference between the c-parameters of SS and

SG. The case of HTiNbO₅ NS is more complex to analyze because of the almost linear decrease of the mass loss during the analysis. At the end, about 11% of the total mass is lost. Then, mass spectroscopy has been combined to TGA at both m/z = 18 to know about water molecule evaporation (Figure 5.B) and m/z=40 to know about CO₂ evolution (Figure 5.C). Thanks to these experiments, in the case of HTiNbO₅ NS, we notice that the mass loss is both related to the evaporation of water molecule (chemisorption, physisorption, and transition to Ti₂Nb₂O₉) but also to the loss of CO₂, which shows the presence of organic molecule and more precisely of TBAOH in the interlayer, used for the exfoliation. This observation helps to highlight one reason why the interlayer distance is higher in HTiNbO₅. Lastly, as previously mentioned, we notice that the transition to Ti₂Nb₂O₉ is done around 250-300°C which demonstrates the strength of the O-H bond and the importance of protons in the stability of the structure.



Figure 5. (A) Thermogravimetric analysis of the three different morphologies (SS/SG/NS) coupled with corresponding mass spectroscopy considering to (B) H_2O (m/z=18) and (C) CO_2 (m/z=40)

To characterize the potential lithium ion insertion in these materials and compare them, charge-discharge experiments at different current densities have been done and are displayed Figure 6. All electrodes were tested between 1.0V and 3.0V vs Li⁺/Li to ensure the stability of the materials along cycling. Various current densities from 0.02 A.g⁻¹ to 2.0 A.g⁻¹ were used to evaluate the potential of different materials for power applications. At low current as 0.02 A.g⁻¹, the first cycle shows a specific capacity of 204, 318 and 250 mAh.g⁻¹ for respectively HTiNbO₅ SS, SG and NS (Figure 6(A-B-C)). However, low coulombic efficiency in the first cycle specifically for HTiNbO₅ SG and NS leads to a decrease in capacity. Thus, during the 3rd cycle at 0.02 A.g⁻¹, a specific capacity of 225, 204 and 113 mAh.g⁻¹ is observed for respectively HTiNbO₅ SS, SG and NS. At low current, HTiNbO₅ SS and SG show comparable specific capacity but NS exhibits smaller one. From our understanding that can be explained by the steric effect due to the presence of TBAOH molecules in the interlayer space of HTiNbO5 NS which considerably reduced the number of available lithium site even if interlayer is larger than for SS and SG. Moreover, the very low coulombic efficiency of the first cycle indicates that a large amount of lithium is not deinserted, impeding the further intercalation of lithium during the subsequent cycle. Concerning the shape of the charge-discharge curve, we observe in the case of HTiNbO₅ SS a very pronounced plateau at 1.6 V vs Li⁺/Li. For HTiNbO₅ SG, the insertion of lithium ions takes place in a wider potential range (mostly between 1.7V and 1.3V vs Li⁺/Li) with a lower average potential than HTiNbO₅ SS. In contrast to the other two morphologies, HTiNbO₅ NS proposes a charge-discharge curve almost linear as a function of potential between 1.7 V and 1.0 V vs Li⁺/Li.



Figure 6. Charge-discharge experiments at different current densities for (A) HTiNbO5 solid-state (SS) (B) HTiNbO₅ sol-gel (SG) (C) HTiNbO₅ nanosheet (NS). (D) Capacity in function of number of cycle at different current densities for the three different morphologies (SS/SG/NS) of HTiNbO5

The charge storage mechanism that governs lithium insertion in HTiNbO₅ will be more discussed below thanks to in situ XRD and ex situ solid-state MAS NMR. When increasing the current density, a similar decrease of the specific capacity is observed for HTiNbO₅ SS and SG offering very similar specific capacity at each current. Despite the supposedly good diffusion of lithium ions in between the exfoliated HTiNbO5 sheets, a lower capacity is observed as shown Figure 6.C. To better visualize the differences between each of the materials, Figure 6.D exposes the specific capacity as a function of the number of cycles at different current densities and for the three morphologies presented here. Except for the first few cycles, comparable specific capacities are carried forward for SS and SG. For example, a specific capacity of 149 mAh.g⁻¹ to 0.10 A.g⁻¹ and 82 mAh.g⁻¹ to 1.0 A.g⁻¹ are reported for HTiNbO₅ SS that represented respectively 65% and 35% of his specific capacity at 0.02 A.g⁻¹. For the same current, HTiNbO₅ NS shows specific capacity of only 63 and 25 mAh.g⁻¹. From these observations, we can

conclude that the architecture of the particles in the form of nanosheets (HTiNbO₅ NS) is not adequate for high power Li-ion batteries as the low capacity is due to the presence of organic molecule in the nanosheets. To prove this hypothesis, the intercalation of organic molecule was performed on HTiNbO₅ SS as described in Supplementary Materials. Figure S1.A shows the effective presence of butylamine in the interlayer space of HTiNbO₅ by comparing the XRD of the material before and after mixing with butylamine. Moreover, Figure S1.B shows that even if the capacities at very low current show a higher capacity in the case of butylamine-HTiNbO₅, a rapid decrease of the capacities is observed due to the steric effect caused by the presence of these very large organic molecules.⁴⁴ These results are in line with the observations made on HTiNbO₅ NS. As well, Figure S2 show the poor electrochemical behavior of KTiNbO₅ SS showing the non-insertion of lithium due to the presence of the large K⁺ ion in the interlayer.

To better understand the charge storage mechanism that governs HTiNbO₅ according to the different morphologies, we perform in situ XRD for HTiNbO5 SS, SG, and NS. All these results are presented Figure 7. Unfortunately, due to differences in crystallinity and orientation of the particles during the shaping of the electrodes, each material when it is in the form of an electrode does not show the same diffraction peaks.⁴³ Thus, it is impossible for us to trace the change in volume in these materials. However, it is possible to understand the mechanisms that govern HTiNbO₅ as well as the differences according to the various morphologies. If we first look at HTiNbO₅ SS, we observe an initial phase change during the first lithiation. Li_{0.4}HTiNbO₅ phase are formed irreversibly and then the material shows a solid solution type lithiation mechanism during the subsequent charging and discharging steps.²⁸ This is highlighted by the reversibility of the (002) peak as shown in Figure 7.A. It is also extracted that the parameter c decreases during the insertion of lithium ions because the positive charge of these ions allows the approach of the negatively charged layers (TiNbO₅)_n. On the other hand, when lithium ion is extracted during discharge, the c-parameter increases back. Interestingly, HTiNbO₅ SG shows a very similar behavior, a phase change seems to appear at the beginning of the first lithiation as shown in Figure 7.B. Indeed, the (011) peak initially at 24° disappears leaving place when another peak appears at 25.5°. The latter shows the formation of Li_{0.4}HTiNbO₅ phase. As for HTiNbO₅ SS, after this initial and irreversible formation, solid-solution reaction take place during the following cycle. The (002) peak variation in HTiNbO₅ SG electrode is more easily visible thanks to the top view presented in Figure S3.D. Thus, by comparing the variation of the (002) peak between HTiNbO₅ SS and

HTiNbO₅ SG, we notice that the variation of the parameter c is very similar with an initial change follows by a progressive variation in the same order of magnitude. In the case of HTiNbO₅ NS, due to the low crystallinity of the material, it is more complex to trace the ion insertion mechanism by *in situ* XRD (Figure 7.C). Nevertheless, we notice that lower peak variations are observed. The (002) peak shows an irreversible variation during the insertion of lithium ion as seen in Figure 7.C and Figure S3.(E-F). This explains the low coulombic efficiency of this material. Also, a lower and lower intensity of the peaks seems to demonstrate a decrease of the crystallinity of the structure which in this case could result in a disorganization of the (TiNbO₅)_n layers between them leading to a poor diffusion of the lithium ions in the intraparticulate and/or interlayer space. To summarize, these *in situ* XRD experiments demonstrate, in the case of HTiNbO₅ SS and SG, the formation of a phase described as $Li_{0.4}$ HTiNbO₅ during the first lithiation that then reversibly inserts lithium ions through a solid solution mechanism. In the case of NS, a disorganization of the layers leads to amorphization and a reduction of the interlayer distance that result in low coulombic efficiency and low specific capacities.



Figure 7. *In situ* XRD pattern at a current of 0.02 A.g⁻¹ between 1.0V and 3.0V vs Li⁺/Li of (A) HTiNbO₅ solid-state (SS) (B) HTiNbO₅ sol-gel (SG) (C) HTiNbO₅ nanosheets (NS) with corresponding voltage-time curve.

Lastly, *ex situ* solid-state MAS NMR was performed on HTiNbO₅ SS at several charge and discharge potentials in order to follow the evolution of lithium and protons local environments upon cycling (Pristine state, 1.5V, 1.0V and 3.0V *vs* Li⁺/Li). Associated CV are shown Figure 8.A. Indeed, several groups have demonstrated the value of solid-state MAS NMR to better understand the redox mechanisms, monitor different lithiation sites population and distribution as well as the changes in the physico-chemical properties of electrodes for batteries and supercapacitors during charging and discharging process.^{45–49} Here, ⁷Li and ⁶Li *ex* *situ* MAS NMR give some insight on lithium local environments as well as the reversibility of the process while ¹H *ex situ* MAS NMR allows us to better understand the role of the proton as well as how the particular proton local environment is altered during the insertion of lithium ions by solid solution.

As shown in Figure 8.B, the ⁷Li MAS NMR spectrum show a relatively broad peak for each potential at 0 ppm corresponding to lithium inserted into the material. Compared to 1.5V, the peak at 1.0V is broader implying a higher number of lithium ion in the material. The peak at 1.5V correspond to 70% of the one at 1.0V. Interestingly, the lithiation-delithiation process is not fully reversible with the presence of a peak for the sample recovered after 1 cycle (3.0V) corresponding to 14% of the lithium present at 1.0V as calculated in Figure S4. This observation is in agreement with the results obtained by electrochemistry and by *in situ* XRD where we notice that part of the lithium inserted at the beginning of the first reduction process is consumed to irreversibly formed Li_{0.4}HTiNbO₅.

In an attempt to obtain more information on the lithiation sites in this material, ⁶Li solidstate NMR was performed on HTiNbO₅ with the same cycled electrodes. Thanks to Figure 8.C, we notice that at 3.0V (after one cycle) the material shows two distinct resonances. A first one at 1 ppm, very sparsely populated and another one at -0.5 ppm more populated. A contrario, at 1.5V and 1.0V, only an intense non-symmetrical resonance can be observed with a maximum close to 1 ppm. This resonance increases clearly during the lithiation process from 1.5 to 1.0 V. This result indicates that the related lithium local environment corresponds to the main lithiation site. In addition, the signals observed at 1.0 and 1.5 V seem to include a shoulder at approx. -0.5ppm. This result suggests that the major resonance remaining after delithiation at 3.0V is already present during the lithiation process. We then tentatively assign the resonance at -0.5 ppm to the Li site populated upon the irreversible formation of the Li_{0.4}HTiNbO₅ phase during the initial lithiation. The peak at 0.5 ppm could also correspond to lithium in the SEI layer. However, we thought this hypothesis less likely as the electrode never goes below a potential of 1V. The potential at which the SEI starts to form is about 0.8V vs Li⁺/Li. Furthermore, ¹⁹F MAS NMR spectrum appear to indicate that the amount of LiF (a typical SEI component) is only very weakly observed at 1.0V and even less at 3.0V (Figure S5). In addition, at 3.0V, the less populated site (at 1 ppm) could correspond to lithium that did not deintercalate during the oxidation but different from the 0.4 lithium of Li_{0.4}HTiNbO₅. Thus, we can conclude

that when the first site (-0.5 ppm) is completed, giving rise to the phase change, the lithium ions that are further intercalated fill a different site (1ppm).



Figure 8. (A) CV of HTiNbO₅ solid-state (SS) at different potential (1.5V/1.0V/3.0V vs Li⁺/Li). (B) *ex situ* ⁷Li MAS NMR normalized spectrum of HTiNbO₅ solid-state (SS) at different potential. (C) *ex situ* ⁶Li MAS NMR normalized spectrum of HTiNbO₅ solid-state (SS) at different potential. (D) *ex situ* ¹H MAS NMR normalized spectrum of HTiNbO₅ solid-state (SS) at different potential.

Based on these observations, ¹H MAS NMR was also done on the same electrodes to understand the parallel changes in proton local environment in the interlayer space as a function of the amount of associated lithium. In 2004, Takagaki et al. reported ¹H MAS NMR on HTiNbO₅ nanosheet.⁵⁰ They assigned a resonance at 12 ppm to the proton in the interlayer space. As shown Figure 8.D, the pristine HTiNbO₅ SS also shows a peak at 12 ppm corresponding to an -OH group of the interlayer space, in agreement with previously reported results. An additional small proton resonance, barely visible, is also superimposed on the empty rotor signal at 7 ppm and is attributed to -OH outside the layers (at the surface of the particles). Interestingly, on electrodes reduced to 1.5V and 1.0V, the 12 ppm resonance disappears completely while a new signal at 3.4 ppm appears. This indicates that the local environment of all protons present in the interlayer space has changed. The displacement to lower chemical shifts and the narrowing of the resonance indicates more acidic and more mobile protons, respectively. Thus, the lithiation process implies a movement and reorganization of the interlayer protons, due to the insertion of lithium ions. The higher mobility of the protons suggests that the insertion of lithium in the interlayer space leads to a greater instability of the protons in the structure. After one full cycle of the material to 3V, two signals corresponding to protons are observed (Figure 8.D). The resonance at 12 ppm reappears and indicates the presence of protons with a local environment very similar to the pristine material. This resonance is nevertheless much less intense compared to the case of the pristine material, consistent with a partial reversibility of the redox reaction. Another resonance at 5.6 ppm, wider and more intense than the one at 12 ppm, implies the presence of protons that are more acidic than those in the pristine material but less mobile than the protons in the samples lithiated to 1.5 and 1.0V, suggesting an intermediate state of local environment. Overall, these observations also seem to confirm the irreversible phase change observed by *in situ* XRD. Lastly, ¹H MAS NMR on the pristine HTiNbO₅ SG has been performed (Figure S6). It shows very similar properties of protons that the HTiNbO₅ SS. This provides an additional argument to explain the observed electrochemical similarities between HTiNbO5 SS and HTiNbO5 SG.

Conclusion

This work presents the synthesis and the characterization, from both materials and electrochemical point of view, of different morphologies of HTiNbO₅. Microparticles (SS), nanoparticles (SG) as well as restacked nanosheets (NS) present different amount of water in its interlayer based on XRD and TGA coupled with MS. The similar electrochemical signature of nano- and microparticles are explained by the very close charge storage mechanism with an initial and irreversible phase change followed by continuous solid-solution reaction during further cycles. As well, ¹H solid state MAS NMR on HTiNbO₅ SS highlight the importance of proton in the interlayer for the fast charging abilities of this oxide. In fact, change in the proton properties help the intercalation by being more mobile and more acidic. In contrast, nanosheet morphologies show very poor electrochemical activity because of the organic molecule in its interlayer space. An exfoliation process of HTiNbO₅ without the use of organic molecule as exfoliation agent can be of interest to increase the electrochemical performance of HTiNbO₅ nanosheet (NS). Nevertheless, several insightful conclusions can be extracted from this work.

First, in contrast to Ti₂Nb₂O₉, nanosizing the structure does not seems to be useful and effective to achieve higher specific capacity at high rate.⁴³ This is explained by the main role that protons are playing in the charge storage mechanism. By the way, it can be interesting to complete this type of study on other materials made up of protons to generalize the assumptions proposed here. More globally, layered materials presenting protons in its interlayer can be materials of choice as negative electrode for next generation of high rate Li-ion batteries.

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Supplementary Information

Butyl-Amine HTiNbO5 synthesis:

For the synthesis of Butylamine-HTiNbO₅, 200 mL of an ethanol-based solution containing 1M of butylamine (95.5%, Sigma Aldrich) was mixed with 0.5 g of HTiNbO₅. This solution was stirred during 1 day and then centrifuged to recover the Butylamine-HTiNbO₅ powder. Washing process was carried out until the obtainment of neutral pH washing water. The powder is finally dried at 60°C for 12h to avoid the presence of any chemically adsorbed water.



Figure S1. (A) XRD pattern of HTiNbO₅ SS and Butyl-Amine HTiNbO₅ (B) Capacity in function of number of cycle at different current densities for HTiNbO₅ SS and Butyl-Amine HTiNbO₅.



Figure S2. Charge-discharge experiments at different current densities for KTiNbO₅ solid-state (SS).



Figure S3. Heat map for *in situ* XRD pattern (A-B) HTiNbO₅ solid-state (SS) (C-D) HTiNbO₅ sol-gel (SG) (E-F) HTiNbO₅ nanosheet (NS) with corresponding voltage-time curve. (A-C-E) show the full pattern range (5-40°) when (B-D-F) show (002) peak of respectively SS, SG and NS.



Figure S4. Comparison between quantity of Li⁺ extract from ⁷Li MAS NMR and the quantity of Li⁺ in HTiNbO₅ calculated based on electron exchanged during cyclic voltammetry (with normalization in function of the quantity observed at 1.0 V vs Li⁺/Li).



Figure S5. *Ex situ* ¹⁹F MAS NMR normalized spectrum of HTiNbO₅ solid-state (SS) at different potential (Pristine state, 1.0V and 3.0V vs Li⁺/Li)



Figure S6. ¹H MAS NMR normalized spectrum of HTiNbO5 solid-state (SS) and HTiNbO5 sol-gel (SG) electrodes at pristine state.

2. $Ti_2Nb_2O_9$

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Effect of Particle Size on Thermodynamics and Lithium Ion Transport in Electrodes Made of Ti₂Nb₂O₉ Microparticles or Nanoparticles.

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Effect of particle size on thermodynamics and lithium ion transport in electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles

Yucheng Zhou^a, Etienne Le Calvez^{b,c}, Sun Woong Baek^a, Matevž Frajnkovič^a, Camille Douard^{b,c}, Eric Gautron^b, Olivier Crosnier^{b,c}, Thierry Brousse^{b,c}, Laurent Pilon^{*,a,d,e}

^a Mechanical and Aerospace Engineering Department, Henry Samueli School of Engineering and Applied Science, University of California, Los Angeles, CA 90095, USA

^b Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, 44000 Nantes, Franc

^c Réseau sur le Stockage Électrochimique de l'Énergie (RS2E), CNRS FR 3459, 33 rue Saint Leu, 80039 Amiens, France

^d California NanoSystems Institute, University of California, Los Angeles, CA 90095, USA

^e Institute of the Environment and Sustainability, University of California, Los Angeles, CA 90095, USA

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ABSTRACT

Keywords: Lithium-ion battery Entropic potential Intercalation Galvanostatic intermittent titration technique Calorimetry Thermal management

This study compares the charging mechanisms, thermodynamics, lithium ion transport, and operando isothermal calorimetry in lithium-ion battery electrodes made of Ti2Nb2O9 microparticles or nanoparticles synthesized by solid-state or sol-gel methods, respectively. First, electrochemical testing showed that electrodes made of Ti₂Nb₂O₉ nanoparticles exhibited larger specific capacity, smaller polarization, and better capacity retention at large currents than those made of Ti2Nb2O9 microparticles. Furthermore, potentiometric entropy measurements revealed that electrodes made of either Ti₂Nb₂O₉ microparticles or nanoparticles showed similar thermodynamics behavior governed by lithium intercalation in solid solution, as confirmed by in situ XRD measurements. However, electrodes made of $Ti_2Nb_2O_9$ nanoparticles featured smaller overpotential and faster lithium ion transport than those made of Ti2Nb2O9 microparticles. In fact, operando isothermal calorimetry revealed smaller instantaneous and time-averaged irreversible heat generation rates at electrodes made of Ti2Nb2O9 nanoparticles, highlighting their smaller resistive losses and larger electrical conductivity. Finally, the measured total heat generation over a charging/discharging cycle matched the measured net electrical energy loss. Overall, Ti₂Nb₂O₉ nanoparticles synthesized by the novel sol-gel method displayed excellent cycling performance and reduced heat generation as a fast-charging lithium-ion battery anode material. These features present major advantages for actual battery systems including larger energy and power densities, simpler thermal management, and enhanced safety.

1. Introduction

Fast-charging lithium-ion batteries (LIBs) constitute a promising technology amid the global transition towards renewable energy and widespread electrification. The anode material of fast-charging commercial LIBs is generally graphite. However, graphite inserts lithium ions at potential close to 0.1 V vs. Li/Li⁺. This can result in the formation of solid electrolyte interphase (SEI) and dendrites and eventually overheating and short circuiting of the battery [1,2]. Moreover, the limited lithium ion mobility in graphite reduces the specific capacity during fast charging. To address these issues, alternative anode materials have been proposed to enable fast charging at potentials above 1.0 V vs. Li/Li^+. Among those, transition metal oxides such as Li₄Ti₅O₁₂ [3,4], Nb₂O₅ [5,

6], and TiNb₂O₇ [7] have emerged as anode materials of choice. In addition, Wadsley-Roth shear phase materials such as Nb₁₈W₁₆O₉₃ [8] and PNb₉O₂₅ [9] have shown impressive rate capabilities. This has prompted great interest in understanding the mechanisms behind such performance. For example, a recent series of studies on PNb_9O_{25} [9–11] used multiple characterization techniques to gain insight into the electrochemical processes, structural and property changes occurring in the material during cycling. These studies found that the corner-sharing and edge-sharing NbO_6 octahedra not only facilitated the fast diffusion of lithium ions in the structure, but also permitted relatively small change of the cell volume during cycling.

Ti₂Nb₂O₉ is another promising transition metal oxide offering large specific capacity and small cycling degradation [12]. The topotactic

* Corresponding author.

E-mail address: pilon@seas.ucla.edu (L. Pilon).

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dehydration of the lamellar-structured HTiNbO5 gives rise to the tunnel-structured Ti_2Nb_2O_9. The tunnels are formed by 2 \times 2 units of edge-sharing octahedra connecting their corners along the a- and c-axes. Moreover, the crystallographic structure of Ti2Nb2O9 is close to a Wadsley-Roth structure due to its units of edge-sharing octahedra. Therefore, Ti₂Nb₂O₉ should also exhibit excellent cycling performance, especially during fast charging. However, Colin et al. [13] first reported a reversible specific capacity for Ti₂Nb₂O₉ electrodes in 1 M LiPF₆ in EC: DMC 1:1 w/w electrolyte of only 144 mAh/g at C/10 compared with the theoretical specific capacity of 252 mAh/g. A more recent study [14] performed ion exchange from KTiNbO5 to HTiNbO5 to NH4TiNbO5 followed by thermal decomposition of NH4TiNbO5 to synthesize Ti2Nb2O9 microparticles. The corresponding electrodes achieved a reversible specific capacity of 201 mAh/g at C/10 in 1 M LiPF6 in EC:DMC 1:1 v/v electrolyte. Nevertheless, the Ti2Nb2O9 in both studies did not present sufficient capacity retention at large currents for potential applications as a fast-charging LIB anode material.

Here, we hypothesize that one way to approach the theoretical specific capacity of Ti₂Nb₂O₉ is to decrease the particle size to nanoscale and increase the nanoporosity to facilitate access and transport of lithium ions. First, electrodes with smaller particles generally have larger electrical conductivity which is crucial in reducing resistive losses during cycling [15,16]. Moreover, decreasing the particle size of an electrode material generally leads to better capacity retention at high C-rates [17]. This can be explained by considering the diffusion length L given by Fick's first law of diffusion as $L \propto \sqrt{Dt}$ where *D* is the lithium ion diffusion coefficient and t is the diffusion time. Decreasing the particle size shortens the time required for lithium ion insertion into the host material, thereby enabling faster charging and discharging [17]. Finally, in some cases, even the same material composition can feature very different charging mechanisms and/or thermodynamics behavior depending on the particle size [18]. For example, during delithiation of Li_xFePO₄, a lithium-rich and a lithium-poor phase could coexist in the 170-nm nanoparticles but not in the 40-nm nanoparticles [19]. In addition, during lithiation of anatase TiO2, the 130-nm nanoparticles featured different two-phase coexistence regions in the open-circuit voltage compared to the 15-nm nanoparticles [20]. Several studies [21-23] investigated nanosheets of Ti2Nb2O9 as a sodium-ion battery electrode material. The nanosheets were produced after an exfoliation process of the bulk material. However, they showed poor stability as the restacking of exfoliated nanosheets led to an abrupt and irreversible formation of agglomerate microparticles. Therefore, more stable nanostructures are desirable in particular for use in lithium-ion batteries considering their superior gravimetric and volumetric energy densities compared to sodium-ion batteries. In fact, to the best of our knowledge, the synthesis and characterization of more stable Ti2Nb2O9 nanoparticles as a lithium-ion battery electrode material has not been reported to date. Note that several studies [24-26] have provided in depth reviews of the general benefits and drawbacks of nanomaterials for electrical energy storage.

This study presents a novel sol-gel method to synthesize mesoporous Ti₂Nb₂O₉ nanoparticles [27]. The structures and performance of electrodes made of Ti₂Nb₂O₉ nanoparticles were systematically compared with those made of Ti₂Nb₂O₉ microparticles synthesized by the traditional solid-state method [13]. Characterization techniques including *in situ* X-ray diffraction (XRD), cyclic voltammetry, and galvanostatic cycling were combined with state-of-the-art potentiometric entropy measurements and *operando* isothermal calorimetry. Together they should reveal the effect of the particle size on the electrochemical cycling performance, thermodynamics behavior, and lithium ion transport in Ti₂Nb₂O₉ electrodes. Overall, this study aims to extend our general understanding of transition metal oxides as fast-charging LIB electrode materials by optimizing their particle size to achieve better performance and cycling stability and to reduce electrical losses and heat generation.

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2. Background

2.1. Potentiometric entropy measurements

Potentiometric entropy measurements consist of determining the open-circuit voltage $U_{OCV}(x, T)$ and entropic potential $\partial U_{OCV}(x, T)/\partial T$ of a battery cell at constant temperature T and pressure as functions of lithium composition x, specific capacity C_m , or state of charge. Our previous study [11] has not only described the fundamental relationships between $U_{OCV}(x, T)$, $\partial U_{OCV}(x, T)/\partial T$, and the material thermodynamics properties, but also proposed an interpretation guide of their measurements. In brief, the open-circuit voltage $U_{OCV}(x, T)$ of a battery cell with a Ti₂Nb₂O₉ working electrode and a lithium metal counter electrode can be expressed as [11,28],

$$U_{OCV}(x,T) = -\frac{1}{e} \left[\frac{\partial g_{TNO}(x,T)}{\partial x} - g_{Li}^*(T) \right]$$
(1)

where *e* is the elementary charge, $g_{TNO}(x, T)$ is the Gibbs free energy of Li_xTi₂Nb₂O₉ per unit of Ti₂Nb₂O₉, and $g_{Li}^*(T)$ is the standard Gibbs free energy per unit of lithium metal independent of *x*. Similarly, the entropic potential $\partial U_{OCV}(x, T)/\partial T$ can be expressed as [11,29],

$$\frac{\partial U_{OCV}(x,T)}{\partial T} = \frac{1}{e} \left[\frac{\partial s_{TNO}(x,T)}{\partial x} - s_{Li}^*(T) \right]$$
⁽²⁾

where $s_{TNO}(x, T)$ is the entropy of Li_xTi₂Nb₂O₉ per unit of Ti₂Nb₂O₉ and $s_{Li}^*(T)$ is the standard entropy per unit of lithium metal also independent of x. The evolution of $U_{OCV}(x, T)$ and $\partial U_{OCV}(x, T)/\partial T$ during lithiation and delithiation can give insight into the charging mechanisms of the battery cell including lithium ion insertion in a homogeneous solid solution, two-phase coexistence, phase transition, and intralayer lithium ion ordering [11,30].

Moreover, the apparent diffusion coefficient $D_{Li^+}(x, T)$ of lithium ions in the Ti₂Nb₂O₉ working electrode can be estimated from galvanostatic intermittent titration technique (GITT) measurements based on Fick's second law of diffusion according to [31].

$$D_{LI^+}(x,T) = \frac{4}{\pi \tau} \left(\frac{V_{TNO}}{A_{TNO}} \right)^2 \left[\frac{\Delta U_{OCV}(x,T)}{\Delta V(x,T)} \right]^2.$$
(3)

Here, τ is the duration of the current pulse, A_{TNO} and V_{TNO} are respectively the surface area and volume of the Ti₂Nb₂O₉ working electrode, $\Delta V(x, T)$ is the cell potential change caused by the current pulse but excluding the initial IR drop, and $\Delta U_{OCV}(x, T)$ is the open-circuit voltage change caused by the current pulse.

2.2. Heat generation in batteries

The instantaneous total heat generation rate $\dot{Q}_T(x, T)$ (in W) in a battery cell can be divided into several contributions including (i) Joule heating $\dot{Q}_J(x, T)$, (ii) reversible entropic heat generation $\dot{Q}_{rev}(x, T)$, (iii) enthalpy or heat of mixing $\dot{Q}_{mix}(x, T)$, and (iv) heat generation due to side reactions $\dot{Q}_{sr}(x, T)$, i.e. [11,30,32–34],

$$\dot{Q}_T(x,T) = \dot{Q}_J(x,T) + \dot{Q}_{rev}(x,T) + \dot{Q}_{mix}(x,T) + \dot{Q}_{sr}(x,T).$$
 (4)

The heat generation rate $\dot{Q}_i(x,T)$ is positive (or negative) when the associated phenomena are exothermic (or endothermic) and release (or absorb) heat.

The heat generation rate from Joule heating $\dot{Q}_J(x, T)$ due to irreversible resistive losses can be expressed as [11,30,32–34],

$$\dot{Q}_{J}(x,T) = I[V(x,T) - U^{avg}(x,T)].$$
 (5)

Here, *I* is the imposed current, V(x, T) is the cell potential, and $U^{avg}(x, T)$ is the open-circuit voltage evaluated at the volume-average concentra-

tion in the cell considering a single electrochemical reaction [35]. In other words, $U^{\text{avg}}(x, T)$ is the potential to which the cell would relax if the current was interrupted [32]. It is equivalent to the open-circuit voltage $U_{OCV}(x, T)$ obtained from potentiometric entropy measurements but for current pulses corresponding to the same C-rate as that imposed during galvanostatic cycling in the *operando* isothermal calorimetry measurements of $\dot{Q}_T(x, T)$ [11]. The overpotential $[V(x, T) - U^{\text{avg}}(x, T)]$ is the potential drop across the cell due to internal resistance. Therefore, it increases with (i) increasing charge transfer resistance [36], (ii) decreasing ionic conductivity [36], and (iii) increasing cell degradation due to electrode deformation and/or electrolyte decomposition during cycling [37,38].

The reversible heat generation rate $\dot{Q}_{rev}(x, T)$ due to entropic changes can be expressed as [32–34],

$$\dot{Q}_{rev}(x,T) = IT \frac{\partial U^{avg}(x,T)}{\partial T}.$$
(6)

In addition, based on Eq. (2), $\dot{Q}_{rev}(x, T)$ can be defined as the sum of the reversible heat generation rates at the Ti₂Nb₂O₉ working electrode $\dot{Q}_{rev,TNO}(x, T)$ and at the lithium metal counter electrode $\dot{Q}_{rev,Ll}(T)$ such that $\dot{Q}_{rev}(x, T) = \dot{Q}_{rev,TNO}(x, T) + \dot{Q}_{rev,Ll}(T)$ with [11],

$$\dot{Q}_{rev,TNO}(x,T) = \frac{IT}{e} \frac{\partial s_{TNO}(x,T)}{\partial x} = \frac{IT}{e} s_{Li}^*(T) + IT \frac{\partial U^{avg}(x,T)}{\partial T}$$
and $\dot{Q}_{rev,Li}(T) = -\frac{IT}{e} s_{Li}^*(T).$
(7)

However, the reversible heat generation rate is associated not only with entropic changes due to electrochemical reactions [32–34,39] but also with other physicochemical phenomena including ion adsorption/desorption [40–45] and ion solvation/desolvation accompanied by ion-pairing [46–50]. Finally, at extremely small currents, the overpotential and ion concentration gradients in the cell are negligible, and the total heat generation rate is dominated by $\dot{Q}_{rev}(x, T)$ [51].

The heat generation rate from enthalpy of mixing $\dot{Q}_{mix}(x, T)$ due to ion concentration gradients can be expressed as [32–34],

$$\dot{Q}_{mix}(x,T) = \int_{V_{\infty}} \sum_{i} [\bar{h}_{i}(x,T) - \bar{h}_{i}^{avg}(x,T)] \frac{\partial c_{i}}{\partial t} dV$$
(8)

where V_{∞} is the volume of the cell, $\overline{h}_i(x, T)$ and $\overline{h}_i^{avg}(x, T)$ are respectively the local and the volume-averaged partial molar enthalpy of ion species *i*, and c_i is the local concentration of ion species *i* in the electrolyte or the electrode. The heat generation rate from enthalpy of mixing is caused by ion concentration gradients (i) across the electrolyte due to diffusion limitations, (ii) across the electrode due to non-uniform current distribution, (iii) within the pores of the electrode filled with electrolyte, and (iv) among intercalated lithium ions in the electrode due to electrochemical reactions. The latter is typically the dominant contribution [32,35,52]. Therefore, fast lithium ion transport in the electrode reduces the heat generation rate $\dot{Q}_{mix}(x, T)$.

Finally, the heat generation rate due to side reactions $\dot{Q}_{sr}(x, T)$ can be expressed as [32–34],

$$\dot{Q}_{sr}(x,T) = -\sum_{i} \Delta H_i \dot{r}_i(t)$$
(9)

where ΔH_i is the enthalpy of reaction for side reaction *i* occurring at reaction rate $\dot{r}_i(t)$. However, past studies on heat generation in a battery cell have generally neglected $\dot{Q}_{sr}(x, T)$ [32–34]. Indeed, side reactions usually arise from the ageing process of a battery cell, which is relatively slow unless the cell is operating under extreme conditions [33,34,53]. Therefore, in this study $\dot{Q}_{sr}(x, T)$ was also neglected.

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2.3. Energy balance

The net thermal energy Q_i (in J) attributed to the different contributions previously mentioned and released over a charging/discharging cycle can be expressed as [34],

$$Q_i = \oint_{cycle} \dot{Q}_i(x, T, t) dt \quad \text{with } i = T, J, \text{ or } mix.$$
(10)

Note that the reversible heat generation rate $\dot{Q}_{rev}(x, T, t)$ averaged over a cycle yields zero, i.e., $Q_{rev} = 0$.

Moreover, the net electrical energy loss ΔE_e (in J) over a charging/ discharging cycle corresponds to the area enclosed by the hysteresis of $V(\mathbf{x}, T)$ vs. the charge transferred q such that [54],

$$\Delta E_e = \oint_{cycle} V(x, T) \mathrm{d}q = \oint_{cycle} V(x, T, t) I(t) \mathrm{d}t.$$
(11)

According to the first law of thermodynamics, the total thermal energy released during a cycle is equal to the net electrical energy loss such that [11,30],

$$\Delta E_e = Q_T = Q_J + Q_{mix}. \tag{12}$$

3. Materials and methods

3.1. Synthesis of Ti2Nb2O9 powder

In this study, Ti₂Nb₂O₉ powder was synthesized by either a solidstate or a sol-gel process. In the solid-state synthesis method, powder of Nb₂O₅ (Alfa Aesar, 99.9%), TiO₂ (Alfa Aesar, \geq 99%), and K₂CO₃ (ACS Reagent, \geq 99.0%) was mixed with a molar ratio of 1:2:1.2. Here, 20% excess of K₂CO₃ was added owing to its volatility at high temperatures. This mixture was ground in an agate mortar for 10 min to obtain a homogeneous powder. This powder was calcined at 1100 °C in a platinum crucible in air for 12 h to produce KTiNbO₅ powder [55,56].

In the sol-gel synthesis method, 1.351 mg of NbCl₅ (Sigma Aldrich, 99%) was dissolved in 30 mL of ethanol. Meanwhile, 1.703 mg of titanium isopropoxide (Alfa Aesar, 97%) and 0.370 mg of KCl (ACS Reagent, 99.0–100.5%) were dissolved in 200 mL of ethylene glycol. Then, citric acid (Alfa Aesar, \geq 99%) was added to this second solution to achieve a molar ratio of 10:1 between citric acid and the total number of cations in both solutions (Nb, Ti, and K). After waiting for 1 h to ensure complete dissolution of all species, the two solutions were mixed, then stirred and heated at 120 °C until a blackish gel was formed. This gel was dehydrated at 300 °C in air overnight so that the organic species completely evaporated. It was then calcined at 700 °C in air for 2 h to produce KTiNbO₅ powder. Note that it was necessary to evacuate the chlorinated gases out of the handling room.

The final step, common to both synthesis methods, consisted of mixing and stirring 1 g of the $KTiNbO_5$ powder in 200 mL of 3 M aqueous HNO_3 for 3 days. The acid solution was changed daily to ensure the complete exchange of potassium cations with protons [55]. The resulting suspension containing $HTiNbO_5$ powder was then centrifuged and rinsed with DI water until waste water at neutral pH was obtained. Finally, the dried $HTiNbO_5$ powder was calcined at 400 °C in air for 2 h to obtain $Ti_2Nb_2O_9$ powder synthesized by solid-state or sol-gel methods [13].

3.2. Electrode and device fabrication

A first set of self-supported electrodes were fabricated from a slurry prepared by mixing one of the Ti₂Nb₂O₉ powders previously synthesized by solid-state or sol-gel methods with conductive carbon (carbon black, Superior Graphite) and aqueous polytetrafluoroethylene (PTFE, Sigma Aldrich) in a small amount of ethanol with a mass ratio of 7.5:1.5:1. This slurry was homogenized with a pestle in a mortar and then cold-rolled

until self-supported electrodes were obtained with mass loading between 4 and 5 mg/cm² and thickness between 60 and 75 μ m [57]. These self-supported electrodes were used for in situ X-ray diffraction (XRD), cyclic voltammetry, galvanostatic cycling, and potentiometric entropy measurements. In situ XRD was performed on cells made according to the procedure first reported by Leriche et al. [58] and consisting of (i) a self-supported solid-state or sol-gel Ti2Nb2O9 working electrode, (ii) a polished lithium metal (Sigma Aldrich, 99.9%) counter electrode, (iii) a 675 μ m thick glass microfiber filter (Whatman, Grade GF/D) as the separator, impregnated with (iv) 1 M LiPF₆ in EC:DMC 1:1 w/w (Solvionic, battery grade) electrolyte. Similarly, cyclic voltammetry and galvanostatic cycling measurements were performed on Swagelok cells consisting of (i) a self-supported solid-state or sol-gel Ti₂Nb₂O₉ working electrode, (ii) a polished lithium metal (Sigma Aldrich, 99.9%) counter electrode, (iii) a 675 μm thick glass microfiber filter (Whatman, Grade GF/D) as the separator, impregnated with (iv) 1 M LiPF $_6$ in EC:DMC 1:1 w/w (Solvionic, battery grade) electrolyte. Finally, potentiometric entropy measurements at C-rate of C/10 were performed on coin cells consisting of (i) a self-supported solid-state or sol-gel Ti2Nb2O9 working electrode, (ii) a polished lithium metal (Sigma Aldrich, 99.9%) counter electrode, (iii) a 260 μ m thick glass microfiber filter (Whatman, Grade GF/C) as the separator, impregnated with (iv) 1 M LiPF_6 in EC:DMC 1:1 v/v (Sigma Aldrich, battery grade) electrolyte. Here, the in situ XRD cells, Swagelok cells, and coin cells were assembled in a glove box containing Ar gas with less than 0.1 ppm of O2 and H2O.

Another set of electrodes were fabricated on copper current collectors from a slurry prepared by dispersing one of the Ti2Nb2O9 powders previously synthesized by solid-state or sol-gel methods and conductive carbon (carbon black, Superior Graphite) in N-methyl-2-pyrrolidone (NMP) solvent with a Ti₂Nb₂O₉:conductive carbon mass ratio of 5:1. After dispersion in the solvent, polyvinylidene fluoride (PVDF) dissolved in NMP (7 wt%) was added to achieve a $\mathrm{Ti}_2\mathrm{Nb}_2\mathrm{O}_9\mathrm{:}\mathrm{PVDF}$ mass ratio of 7.5:1. Next, the slurry was spread on a large copper substrate using a doctor blade and then dried in ambient air overnight. The obtained slurry-cast electrodes had a Ti2Nb2O9:conductive carbon:PVDF mass ratio of 7.5:1.5:1, mass loading around 5.5 mg/cm², and thickness around 150 μ m. These electrodes were used to make two-electrode cells for operando isothermal calorimetry. The cells consisted of (i) a slurrycast solid-state or sol-gel Ti2Nb2O9 working electrode and cut into 1 $\mbox{cm}\times 1$ cm square shape, (ii) a polished lithium metal (Sigma Aldrich, 99.9%) counter electrode also cut into 1 cm imes 1 cm square shape, (iii) two 50 µm thick polypropylene/polyethylene (Celgard, C380) sheets acting as separators and thermal insulators, impregnated with (iv) 1 M LiPF₆ in EC:DMC 1:1 v/v (Sigma Aldrich, battery grade) electrolyte. Similarly, potentiometric entropy measurements at C-rates of 1.5C and 6C were performed on coin cells consisting of (i) a slurry-cast solid-state or sol-gel $\mathrm{Ti}_2\mathrm{Nb}_2\mathrm{O}_9$ working electrode, (ii) a polished lithium metal (Sigma Aldrich, 99.9%) counter electrode, (iii) a 260 μ m thick glass microfiber filter (Whatman, Grade GF/C) as the separator, impregnated with (iv) 1 M LiPF₆ in EC:DMC 1:1 v/v (Sigma Aldrich, battery grade) electrolyte. Here also, the calorimetric cells and coin cells were assembled in a glove box containing Ar gas with less than 0.1 ppm of O_2 and $H_2O.$

3.3. Structural characterization

Transmission electron microscopy (TEM) and *in situ* XRD were performed in order to characterize the structure and phases of Ti₂Nb₂O₉ powder synthesized by solid-state or sol-gel methods. TEM images were collected using a probe-corrected Themis Z G3 microscope (Thermo Fisher Scientific) equipped with a high-angle annular dark-field detector (Fischione). Here, the Ti₂Nb₂O₉ powder was dispersed in ethanol and then deposited on a copper grid. Both the XRD patterns of pristine Ti₂Nb₂O₉ powders and the *in situ* XRD patterns of Ti₂Nb₂O₉ electrodes were collected using a PANalytical X'Pert Pro diffractometer (Malvern Panalytical). An X'Celerator detector with Cu-K_{a1}-K_{a2} ($\lambda = 1.54060$ Å, Energy Storage Materials 52 (2022) 371-385

1.54439 Å) radiation was used at acceleration voltage of 40 kV and current of 40 mA. During charging and discharging of the cell, a series of constant current pulses at 0.02 A/g of Ti₂Nb₂O₉ were imposed. Each current pulse lasted 20 min followed by a relaxation period of 30 min for pattern acquisition between $2\theta = 5^{\circ}$ and 40° .

3.4. Electrochemical characterization

Cyclic voltammetry measurements consisted of imposing a triangular waveform as the cell potential *V* and recording the cell current *I* with a high accuracy potentiostat (BioLogic, VMP3). The specific capacity $C_m(\nu)$ (in mAh/g) at scan rate ν was calculated according to [59],

$$C_m(\nu) = \frac{1}{m} \oint_{cycle} \frac{I}{2\nu} dV \tag{13}$$

where *m* is the mass loading of $Ti_2Nb_2O_9$ at the working electrode.

Similarly, the cell potential *V* under galvanostatic cycling at constant current $\pm I$ was also recorded by a high accuracy potentiostat (BioLogic, VMP3). The IR drop ΔV can be identified as the sharp potential change observed when switching between charging and discharging or vice versa. Then, the internal resistance R_{GC} of the cell was calculated according to [40,60-63],

$$R_{GC} = \frac{\Delta V}{2I}.$$
 (14)

3.5. Potentiometric entropy measurements

A 17

The open-circuit voltage $U_{OCV}(C_m, T)$ and entropic potential $\partial U_{OCV}(C_m, T)/\partial T$ of the coin cells with working electrodes made of Ti2Nb2O9 microparticles or nanoparticles synthesized by solid-state or sol-gel methods were measured as functions of specific capacity Cm using the potentiometric entropy measurement technique and the apparatus described in Refs. [11,30]. The measurements consisted of imposing a series of constant current pulses at a C-rate of C/10 at 20 °C. Each current pulse lasted 30 min followed by a relaxation period of 270 min during which a step-like temperature profile was applied to the coin cell from 15 °C to 25 °C in 5 °C increments with a thermoelectric cold plate (TE technology, CP-121). The corresponding coin cell potential evolution was recorded by a high accuracy potentiostat (BioLogic, VSP-300). Before recording the open-circuit voltage $U_{OCV}(C_m, T)$ at a given specific capacity C_m and temperature T, we verified that the coin cell had reached thermodynamic equilibrium by ensuring that (i) the temperature difference between the cold plate and the surface of the coin cell was less than 0.1 °C and (ii) the time rate of change of the open-circuit voltage $\partial U_{OCV}(C_m, T)/\partial t$ was less than 1 mV/h.

3.6. Operando isothermal calorimetry

Operando isothermal calorimetry was performed in the aforementioned two-electrode cells using the apparatus described in Ref. [64]. Here, galvanostatic cycling was imposed using a high accuracy potentiostat (BioLogic, SP-150). Simultaneously, the instantaneous heat generation rates $\hat{Q}_i(t)$ (in mW) at the working electrode made of Ti₂Nb₂O₉ microparticles or nanoparticles and at the lithium metal counter electrode were calculated from the instantaneous heat fluxs $q_i^{"}(t)$ (in mW/cm²) measured by a 1 cm × 1 cm thermoelectric heat flux sensor (greenTEG, gSKIN-XP) in thermal contact with the back of each electrode "i" according to [64],

$$\dot{Q}_i(t) = q_i''(t)A_i = \frac{\Delta V_i(t)}{S_i}A_i \quad \text{with } i = TNO \text{ or } Li.$$
(15)

Here, A_i (in cm²) is the footprint area of the electrode and $\Delta V_i(t)$ (in μV) is the instantaneous voltage difference measured by the heat flux sensor with sensitivity S_i [in $\mu V/(W/cm^2)$]. Then, the instantaneous total heat

generation rate in the entire calorimetric cell $\dot{Q}_T(t)$ can be expressed as the sum of those at each electrode such that,

$$\dot{Q}_T(t) = \dot{Q}_{TNO}(t) + \dot{Q}_{Li}(t).$$
 (16)

In addition, the instantaneous heat generation rates $\dot{Q}_i(t)$ at each electrode can be divided into an irreversible $\dot{Q}_{irr,i}(t)$ and a reversible $\dot{Q}_{rev,i}(t)$ contribution such that,

$$\dot{Q}_{i}(t) = \dot{Q}_{irr,i}(t) + \dot{Q}_{rev,i}(t).$$
 (17)

To minimize the white noise in the signal from the heat flux sensors, the instantaneous heat generation rates $\dot{Q}_i(t)$ measured at each electrode were averaged over the last three consecutive cycles at any given current I, i.e.,

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$$\dot{Q}_i(t) = \frac{1}{3} \sum_{j=1}^3 \dot{Q}_i[t + (j-1)t_{cd}].$$
(18)

Finally, the time-averaged irreversible heat generation rates $\overline{Q}_{trr,l}$ during a charging/discharging cycle can be calculated according to [11, 30],

$$\overline{\dot{Q}}_{irr,i} = \overline{\dot{Q}}_i = \frac{1}{t_{ccl}} \oint_{cycle} \dot{Q}_i(t) dt \quad \text{with } i = TNO \text{ or } Li.$$
(19)

Note that $\dot{Q}_{rev,i}(t)$ averaged over a cycle yields zero.



(b) Ti₂Nb₂O₉ microparticles synthesized by solid-state method



(c) Ti₂Nb₂O₉ nanoparticles synthesized by sol-gel method



Fig. 1. (a) Crystallographic structure of $Ti_2Nb_2O_9$. Transmission electron microscopy (TEM) images of $Ti_2Nb_2O_9$ (b) microparticles and (c) nanoparticles. Mesopores formed during the dehydration synthesis step are marked by green circles.

4. Results and discussion

4.1. Structural characterization

Fig. 1(a) shows the crystallographic structure of Ti₂Nb₂O₉, demonstrating its tunnel structure which facilitates lithium ion intercalation. Figs. 1(b) and 1(c) show the transmission electron microscopy (TEM) images of Ti₂Nb₂O₉ microparticles or nanoparticles synthesized by solid-state or sol-gel methods, respectively. Here, the solid-state synthesis method produced microparticles with size around 1 μ m while the sol-gel synthesis method produced nanoparticles with size around 50 nm. Furthermore, mesopores formed during the dehydration synthesis step were marked by green circles, showing that the sol-gel method created more nanoporosity in the synthesized Ti₂Nb₂O₉ than the solid-state method. In fact, the specific surface area measured by low-temperature nitrogen adsorption porosimetry of Ti₂Nb₂O₉ microparticles or nanoparticles reached 1.4 and 24.6 m²/g, respectively. The respective volumes of micropores and mesopores were 3.16×10^{-5} and 0.0092 cm³/g in Ti₂Nb₂O₉ microparticles, or 0.008 and 0.095 cm³/g in Ti₂Nb₂O₉ microparticles. In other words, both types of particles were



Fig. 2. (a) XRD patterns of pristine Ti₂Nb₂O₉ powder. In situ XRD patterns of electrodes made of Ti₂Nb₂O₉ (b) microparticles or (c) nanoparticles.

dense and slightly porous. The pore size distributions were bimodal with an average pore width of Ti₂Nb₂O₉ microparticles and nanoparticles recorded as 17.5 and 4.7 nm, respectively (see Fig. S1 in Supplementary Materials). According to the IUPAC classification [65], the Ti₂Nb₂O₉ microparticles contained primarily mesopores with pore width between 2 and 50 nm while the Ti₂Nb₂O₉ nanoparticles had nanopores with pore width < 2 nm. Initially for both types of particles, the mesopores were mainly created during the synthesis of the precursor HTiNbO₅ while the nanopores were generated mostly due to the final calcination step of HTiNbO₅ to obtain Ti₂Nb₂O₉.

First, Fig. 2(a) shows the XRD patterns of pristine $Ti_2Nb_2O_9$ powders. Here, $Ti_2Nb_2O_9$ microparticles exhibited preferential orientation along the c-axis based on the high intensity of the (002) and (004) peaks. By contrast, $Ti_2Nb_2O_9$ nanoparticles did not develop preferential growth while the larger peak widths indicate their smaller crystallite size. Furthermore, Fig. 2 shows the *in situ* XRD patterns of self-supported electrodes made of $Ti_2Nb_2O_9$ (b) microparticles or (c) nanoparticles. It indicates that not every expected diffraction peak was observed in the patterns for electrodes made of $Ti_2Nb_2O_9$ microparticles. This was due to (i) the aforementioned preferential orientation of the synthesized $Ti_2Nb_2O_9$ microparticles and (ii) the treatment during synthesis of the powder to form a self-supported paste. Nevertheless, the (002) peak Energy Storage Materials 52 (2022) 371-385

around $2\theta = 12^{\circ}$ and the (004) peak around $2\theta = 24^{\circ}$ were clearly visible and could be attributed to Ti2Nb2O9 [13,55,66]. Similarly, not every expected diffraction peak was observed for electrodes made of Ti2Nb2Oa nanoparticles. This was due to the low crystallinity of the synthesized $Ti_2Nb_2O_9$ nanoparticles. Nonetheless, the (011) peak around $2\theta=24^\circ$ and the (110) peak around $2\theta = 27^{\circ}$ were clearly visible and could be attributed to Ti₂Nb₂O₉ [13,55,66]. In addition, in both cases the peak around $2\theta = 18^{\circ}$ did not shift and could be attributed to PTFE in the binder [67]. It is interesting to note that every diffraction peak was maintained at constant intensity and featured small and continuous shifts during lithiation and delithiation which returned to their original position after each cycle. This suggests that the prevailing charging mechanism corresponded to reversible lithium ion insertion in a homogeneous solid solution of Ti2Nb2O9 for electrode material synthesized by either method. In other words, the lithiation and delithiation processes caused only minor and reversible distortions to the crystallographic structure of Ti₂Nb₂O₉. Finally, the recent study by Drozhzhin et al. [14] reported, during the first lithiation half-cycle, an irreversible phase transformation between two orthorhombic phases within the same space group (Pnmm) along with changes in the unit cell parameters. We hypothesize that this discrepancy possibly appears due to (i) the different specifications of the diffractometers used in the two studies and



Fig. 3. Cyclic voltammogram of Swagelok cells with working electrodes made of Ti₂Nb₂O₉ (a) microparticles or (b) nanoparticles cycled between 1.0 and 3.0 V vs. Li/Li⁺ at scan rates ν ranging between 0.1 and 50 mV/s, along with (c) peak specific current $I_{m,peak}(\nu)$, and (d) specific capacity $C_m(\nu)$ as functions of scan rate ν .

(ii) differences in the synthesis methods. Indeed, Drozhzhin et al. [14] produced the intermediate compound NH_4TiNbO_5 and the residue NH_3 which potentially created a slight difference in the initial structure. Intercalation in a solid solution was reported for subsequent half-cycles, as observed in the present study.

4.2. Electrochemical characterization

Fig. 3 plots the cyclic voltammogram of the Swagelok cells with selfsupported working electrodes made of Ti₂Nb₂O₉ (a) microparticles or (b) nanoparticles cycled between 1.0 and 3.0 V vs. Li/Li⁺ at scan rates ν ranging between 0.1 and 50 mV/s. It also shows (c) the peak specific current $I_{m,peak}(\nu)$, and (d) the specific capacity $C_m(\nu)$ as functions of scan rate ν . The pair of cathodic and anodic peaks around 1.4/1.6 V vs. Li/ Li⁺, observed at $\nu = 0.1$ mV/s, could be attributed to both Ti⁴⁺/Ti³⁺ and Nb⁵⁺/Nb⁴⁺ redox reactions [13,68,69]. At any given scan rate ν , the polarization of the cell with Ti₂Nb₂O₉ nanoparticles was smaller than that with Ti₂Nb₂O₉ microparticles. This resulted in greater cycling reversibility for the cell with Ti₂Nb₂O₉ nanoparticles than that with Energy Storage Materials 52 (2022) 371-385

Ti₂Nb₂O₉ microparticles. Moreover, the b-value associated with this pair of redox peaks was obtained by least squares fitting of the peak specific current $I_{m,peak}$ according to the power law $I_{m,peak} = a\nu^b$ [70]. Note that the b-value analysis is a qualitative technique widely used to assess the charging mechanisms in both battery and pseudocapacitive electrode materials ranging between the limiting cases of slow redox reactions limited by ion diffusion in a semi-infinite medium (b = 0.5) and fast redox reactions without ion transport limitation (b = 1). In fact, a series of studies [71,72] validated the b-value analysis in hybrid pseudocapacitors using state-of-the-art numerical simulations and physicochemical models based on first principles. Between $\nu = 0.1$ and 2 mV/s, the b-value of the cell with Ti2Nb2O9 microparticles or nanoparticles was 0.51 and 0.88, respectively. This suggests that redox reactions and lithium ion intercalation were faster and less diffusion-limited in the working electrode made of Ti2Nb2O9 nanoparticles than that made of Ti2Nb2O9 microparticles thanks to their larger surface area and smaller size. Finally, at any given scan rate $\nu,$ the specific capacity $C_m(\nu)$ of the cell with Ti2Nb2O9 nanoparticles was larger than that with Ti2Nb2O9 microparticles. In addition, the decrease in the specific capacity $C_m(\nu)$



Fig. 4. Potential profiles during galvanostatic cycling of Swagelok cells with working electrodes made of $Ti_2Nb_2O_9$ (a) microparticles or (b) nanoparticles cycled between 1.0 and 3.0 V vs. Li/Li^+ at specific current I_m ranging between 0.02 and 2 A/g of $Ti_2Nb_2O_9$, along with (c) the specific capacity $C_m(I_m)$ as a function of cycle number at different specific current I_m , and (d) the capacity retention ratio over 100 cycles with respect to $C_m(I_m)$ of the second cycle at $I_m = 0.2$ A/g of $Ti_2Nb_2O_9$ (~1C).

with increasing scan rate ν was less significant for the cell with $Ti_2Nb_2O_9$ nanoparticles than that with $Ti_2Nb_2O_9$ microparticles.

Fig. 4 plots the potential profiles during galvanostatic cycling of the Swagelok cells with self-supported working electrodes made of $Ti_2Nb_2O_9$ (a) microparticles or (b) nanoparticles cycled between 1.0 and 3.0 V vs. Li/Li⁺ at specific current I_m ranging between 0.02 and 2 A/g of ${\rm Ti}_2{\rm Nb}_2{\rm O}_9.$ It also shows (c) the specific capacity $C_m(I_m)$ as a function of cycle number at different specific current I_m , and (d) the capacity retention ratio over 100 cycles with respect to $C_m(I_m)$ of the second cycle at $I_m = 0.2 \text{ A/g of Ti}_2\text{Nb}_2\text{O}_9$ (~1C). At any given specific current I_m , the specific capacity $C_m(I_m)$ of the cell with Ti₂Nb₂O₉ nanoparticles was larger than that with $Ti_2Nb_2O_9$ microparticles. For example, at 0.02 A/g of Ti₂Nb₂O₉ (~C/10), the cell with Ti₂Nb₂O₉ nanoparticles showed a reversible specific capacity of 230 mAh/g compared with 157 mAh/g for the cell with Ti2Nb2O9 microparticles. The former achieved an improvement of 14% over the specific capacity previously reported in the literature [13,14]. Moreover, at large specific currents I_m , the capacity retention of the cell with Ti2Nb2O9 nanoparticles was superior to that with Ti2Nb2O9 microparticles. In fact, at 2 A/g of Ti2Nb2O9 (~10C), the cell with Ti2Nb2O9 nanoparticles still retained a specific capacity of 97 mAh/g compared with 19 mAh/g for the cell with Ti2Nb2O9

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microparticles. Finally, the long-term cycling degradation of both types of $Ti_2Nb_2O_9$ working electrodes was minimal. After 100 cycles at 0.2 A/g of $Ti_2Nb_2O_9$, the ratio of the specific capacity of the cell with $Ti_2Nb_2O_9$ microparticles or nanoparticles relative to the second cycle was 1.01 and 0.96, respectively. Note that in many battery electrode materials such as graphite and NMC, the first cycle features low coulombic efficiency and/or substantial irreversible loss in the specific capacity [73]. Accordingly, it is more appropriate to use the specific capacity of the second cycle as the reference when calculating the capacity retention [74–76].

4.3. Potentiometric entropy measurements

Fig. 5 plots the open-circuit voltage $U_{OCV}(C_m, T)$ and entropic potential $\partial U_{OCV}(C_m, T)/\partial T$ of the coin cells with self-supported working electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles as functions of specific capacity C_m during lithiation and delithiation of the first two cycles at C-rate of C/10. Here, the Ti₂Nb₂O₉ active material mass loading of the cell with Ti₂Nb₂O₉ microparticles or nanoparticles was 4.7 and 4.3 mg/cm², respectively. First, within the same potential window of 1.0 to 3.0 V vs. Li/Li⁺, the maximum specific capacity of the



Fig. 5. Open-circuit voltage $U_{OCV}(C_m, T)$ and entropic potential $\partial U_{OCV}(C_m, T)/\partial T$ of coin cells with working electrodes made of Ti₂Nb₂O₉ microparticles or nano-particles as functions of specific capacity C_m during lithiation and delithiation of the first two cycles at C-rate of C/10.

cell with Ti₂Nb₂O₉ nanoparticles was larger than that with Ti₂Nb₂O₉ microparticles during both lithiation or delithiation half-cycles. These results are consistent with those previously observed in galvanostatic cycling measurements (Fig. 4). Second, $U_{OCV}(C_m, T)$ and $\partial U_{OCV}(C_m, T) / \partial T$ of both cells monotonously decreased with increasing lithium composition during the lithiation half-cycle. This behavior is characteristic of lithium ion insertion in a homogeneous solid solution [11,30]. These observations are also consistent with those previously made from *in situ* XRD measurements (Fig. 2).

Furthermore, $U_{OCV}(C_m, T)$ and $\partial U_{OCV}(C_m, T)/\partial T$ of both cells were the same during the first lithiation half-cycle. This suggests that for pristine Ti₂Nb₂O₉, the contrasting particle sizes resulting from distinct synthesis methods had no influence on the thermodynamics properties of the electrodes. However, $U_{OCV}(C_m, T)$ and $\partial U_{OCV}(C_m, T)/\partial T$ between the two cells showed minor discrepancies during the subsequent delithiation half-cycle which could be attributed to several factors. First, it could result from the hysteresis of $U_{OCV}(C_m, T)$ and $\partial U_{OCV}(C_m, T)/\partial T$ between lithiation and delithiation. Moreover, it could be caused by the specific capacity loss between the first lithiation and delithiation halfEnergy Storage Materials 52 (2022) 371-385

cycles. On the one hand, such initial specific capacity loss could arise when certain lithium ions lithiated into the pristine structure became trapped and therefore unable to be delithiated [77]. On the other hand, it could also emerge due to increasing kinetic barriers including (i) growing passivation layers on both working and counter electrodes which inhibit lithium ion transport and (ii) broken or cracked Ti₂Nb₂O₉ particles which reduce the number of available intercalation sites [78]. For example, cracking can affect the grain boundaries along which electronic and ionic transports occur [79,80]. In fact, a more recent study [81] applied *operando* optical scattering microscopy to monitor the actual process of particle cracking in anode materials leading to nonfunctional particle fragments and degradation of performance caused by the loss of electrical connection to the rest of the electrode.

As previously proposed by Hudak et al. [78], Fig. 6(a) plots the entropic potential $\partial U_{OCV}(C_m, T)/\partial T$ of the coin cells with working electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles as a function of open-circuit voltage $U_{OCV}(C_m, T)$ during lithiation and delithiation of the first two cycles at C-rate of C/10. Here, the entropic potential profiles of both types of electrodes overlapped. This suggests that the



Fig. 6. (a) Entropic potential $\partial U_{OCV}(C_m, T)/\partial T$ of coin cells with working electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles as a function of open-circuit voltage $U_{OCV}(C_m, T)$ during lithiation and delithiation of the first two cycles at C-rate of C/10. Cell potential $V(C_m, T)$ and open-circuit voltage $U_{OCV}(C_m, T)$ as functions of specific capacity C_m during the first lithiation half-cycle at C-rate of C/10 for coin cells with working electrodes made of Ti₂Nb₂O₉ (b) microparticles or (c) nanoparticles. (d) Apparent diffusion coefficient $D_{Li^+}(C_m, T)$ [Eq. (3)] of lithium ions in the working electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles.

thermodynamics behavior of Ti₂Nb₂O₉ powder synthesized by either method remained similar and stable, at least during the first two cycles. Therefore, the aforementioned minor discrepancies in $U_{OCV}(C_m, T)$ and $\partial U_{OCV}(C_m, T)/\partial T$ vs. C_m between the two cells could be attributed to the lithiation/delithiation hysteresis of $U_{OCV}(C_m, T)$ and $\partial U_{OCV}(C_m, T)/\partial T$ as well as the initial specific capacity loss from trapped lithium ions and/or increasing kinetic barriers.

Moreover, Figs. 6(b) and 6(c) plot the cell potential $V(C_m, T)$ and open-circuit voltage $U_{OCV}(C_m, T)$ as functions of specific capacity C_m during the first lithiation half-cycle at C-rate of C/10 for the coin cells with working electrodes made of Ti₂Nb₂O₉ microparticles or nano-particles, respectively. It is evident that, for a given state of charge, the overpotential $[V(C_m, T) - U_{OCV}(C_m, T)]$ of the cell with Ti₂Nb₂O₉ nano-particles was smaller than that with Ti₂Nb₂O₉ microparticles. This indicates that the working electrode made of Ti₂Nb₂O₉ manoparticles had larger electrical conductivity and/or faster lithium ion transport than that made of Ti₂Nb₂O₉ microparticles [36].

Finally, Fig. 6(d) plots the apparent diffusion coefficient $D_{Li^+}(C_m, T)$ of lithium ions in the working electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles calculated according to Eq. (3). It indicates that,

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for a given state of charge, $D_{Li^+}(C_m, T)$ of the working electrode made of Ti₂Nb₂O₉ nanoparticles was larger than that made of Ti₂Nb₂O₉ microparticles, particularly in the second part of the lithiation process. This result confirms the faster lithium ion transport in Ti₂Nb₂O₉ nanoparticles compared with microparticles, which manifested itself in the less polarized cyclic voltammograms, the larger b-value, and the larger specific capacity C_m at high C-rates (Figs. 3 and 4).

4.4. Operando isothermal calorimetry

4.4.1. Cell potential

Fig. S2 in Supplementary Materials plots the temporal evolution of the potential V(t) of the calorimetric cells with slurry-cast working electrodes made of Ti₂Nb₂O₉ (a) microparticles or (b) nanoparticles and lithium metal counter electrodes for six consecutive galvanostatic cycles with potential window between 1.0 and 3.0 V vs. Li/Li⁺ for each current *I* ranging from 2 to 8 mA. It indicates that the cycle period t_{cd} of both cells decreased with increasing current *I*. In fact, larger currents *I* led not only to faster charging and discharging rates but also to smaller specific capacity C_m , as observed in Fig. 4. Furthermore, the cycle period t_{cd} of



Fig. 7. Instantaneous heat generation rates (a, b) $\dot{Q}_{TNO}(t)$ measured at the working electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles and (c, d) $\dot{Q}_{Li}(t)$ measured at the corresponding lithium metal counter electrodes as functions of dimensionless time t/t_{cd} averaged over the last three consecutive cycles for current *I* ranging from 2 to 8 mA.

the cell with Ti₂Nb₂O₉ nanoparticles was longer than that with Ti₂Nb₂O₉ microparticles and did not decrease as much with increasing current *I*. This reflects the larger specific capacity C_m and the better capacity retention of the cell with Ti₂Nb₂O₉ nanoparticles compared with the cell with Ti₂Nb₂O₉ microparticles.

4.4.2. Instantaneous heat generation rates

Fig. 7 plots the instantaneous heat generation rates (a, b) $\dot{Q}_{TNO}(t)$ measured at the working electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles and (c, d) $\dot{Q}_{Ll}(t)$ measured at the respective lithium metal counter electrodes as functions of dimensionless time t / t_{ed} averaged over the last three consecutive cycles for current *I* ranging from 2 to 8 mA. Note that the measurements of $\dot{Q}_{TNO}(t)$ and $\dot{Q}_{Ll}(t)$ were repeatable cycle after cycle (see Figs. S3 and S4 in Supplementary Materials). First, the magnitudes of $\dot{Q}_{TNO}(t)$ and $\dot{Q}_{Ll}(t)$ in both cells increased with increasing current *I*. Moreover, Figs. 7(a) and 7(b) show that, for any given current *I*, $\dot{Q}_{TNO}(t)$ was significantly larger at the working electrode made of Ti₂Nb₂O₉ microparticles than at that made of Ti₂Nb₂O₉

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nanoparticles. Furthermore, $\dot{Q}_{TNO}(t)$ in both cells increased with time during both lithiation or delithiation half-cycles. This could be attributed to the increase in the reversible heat generation rate $\dot{Q}_{rev,TNO}(x,T)$ [Eq. (7)] caused by the monotonously decreasing entropic potential $\partial U_{OCV}(C_m, T) / \partial T$ with increasing lithium composition x, as observed in Fig. 5. On the other hand, Figs. 7(c) and 7(d) establish that, for any given current I, $\dot{Q}_{ij}(t)$ was similar in both cells and was positive and relatively constant during the lithiation half-cycle of the Ti2Nb2O9 working electrode. This was associated with lithium ion stripping and exothermic solvation with ion pairing at the lithium metal counter electrode [11]. By contrast, $\dot{Q}_{Li}(t)$ increased towards the end of the delithiation half-cycle of the Ti2Nb2O9 working electrode accompanied simultaneously by plating of the lithium metal counter electrode. As such, the rise in $\dot{Q}_{Li}(t)$ could be attributed to the exothermic dendrite formation on the surface of the lithium metal counter electrode [82,83]. These phenomena were also observed in cells with PNb₉O₂₅ working electrodes and lithium metal counter electrodes in 1 M LiPF₆ in EC:DMC 1:1 v/v electrolyte [11].



Fig. 8. (a) Time-averaged irreversible heat generation rates $\dot{Q}_{irr,INO}$ and $\dot{Q}_{irr,II}$ as functions of current *I* for calorimetric cells with working electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles. (b) Resistances $R_{GC,I}$ [Eq. (14)] of calorimetric cells with working electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles in delithiated or lithiated states during cycling at a given current *I*. Net electrical energy loss ΔE_e [Eq. (11)] and total thermal energy dissipated Q_T [Eq. (10)] over a charging/discharging cycle for calorimetric cells with working electrodes made of Ti₂Nb₂O₉ (c) microparticles or (d) nanoparticles.

In our previous studies with TiNb₂O₇ [30] and PNb₉O₂₅ [11], the heat generation rate $\dot{Q}_I(x, T) + \dot{Q}_{rev}(x, T)$ calculated according to Eqs. (5) and (6) agreed well with the measurements of $\dot{Q}_T(x, T)$. However, in the present study, such a comparison was not possible. Indeed, during *operando* isothermal calorimetry, the cells were tested under galvano-static cycling at high C-rates resulting in poor capacity retention. However, the values of $U_{OCV}(C_m, T)$ and $\partial U_{OCV}(C_m, T)/\partial T$ determined by potentiometric entropy measurements with current pulses at the same high C-rates spanned a wider range of specific capacity C_m thanks to the long relaxation periods imposed during the measurements $U_{OCV}(C_m, T)$ and $\partial U_{OCV}(C_m, T)$ and $\partial U_{OCV}(C_m, T)$ did not represent the actual values of $U^{avg}(x, T)$ and $\partial U^{avg}(x, T)/\partial T$ did not represent the actor all values of $U^{avg}(x, T)$ and $\partial U^{avg}(x, T)/\partial T$ of the cells during *operando* isothermal calorimetry.

4.4.3. Time-averaged heat generation rates

Fig. 8(a) plots the time-averaged irreversible heat generation rates $\overline{\dot{Q}}_{irr,TNO}$ and $\overline{\dot{Q}}_{irr,Li}$ as functions of current *I* for calorimetric cells with working electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles. First, $\overline{\dot{Q}}_{irr,INO}$ and $\overline{\dot{Q}}_{irr,Li}$ in both cells increased with increasing current *I*. In fact, least squares fitting revealed that $\overline{\dot{Q}}_{irr,Li}$ increased quadratically with respect to current *I*, i.e., $\overline{\dot{Q}}_{irr,Li} \propto I^2$. This suggests that Joule heating dominated the irreversible heat generation at the lithium metal counter electrode whose electrical resistivity was independent of current *I*. Furthermore, for any given current *I*, $\overline{\dot{Q}}_{irr,Li}$ was identical in both cells. Indeed, each lithium metal counter electrode was cut from the same piece into the same size and therefore should have approximately the same resistance.

By contrast, in both calorimetric cells $\dot{Q}_{irr,TNO}$ increased linearly with respect to current I, i.e., $\overline{\dot{Q}}_{irr,TNO} \propto I$. However, $\overline{\dot{Q}}_{irr,TNO}$ was larger at the working electrode made of $\mathrm{Ti}_2\mathrm{Nb}_2\mathrm{O}_9$ microparticles than at that made of Ti₂Nb₂O₉ nanoparticles. This could be due, in part, to the fact that the electrical resistivity of the working electrode made of Ti2Nb2O9 microparticles was larger than that made of Ti₂Nb₂O₉ nanoparticles. In fact, Fig. 8(b) plots the resistances $R_{GC,d}$ and $R_{GC,l}$ calculated from the IR drop [Eq. (14)] in the calorimetric cells with working electrodes made of Ti2Nb2O9 microparticles or nanoparticles at the end of the delithiation or lithiation steps during cycling at a given current I. First, the resistances R_{GC,d} and R_{GC,l} of the cell with Ti₂Nb₂O₉ microparticles were systematically larger than that with Ti₂Nb₂O₉ nanoparticles for any given current I. Moreover, the resistances $R_{GC,d}$ and $R_{GC,l}$ of both cells decreased with increasing current I. This could be attributed to the smaller range of lithium composition x reached at larger currents I. Finally, both cells had larger resistance in delithiated state than in lithiated state, i.e., $R_{GC,d} > R_{GC,l}$. To the best of our knowledge, the electrical resistivity of Ti2Nb2O9 as a function of state of charge has not been reported to date. However, the closely-related TiNb2O7 is known to be an insulator in its unlithiated state and its resistivity decreases sharply upon lithiation up to x = 0.5 [30]. Thus, a similar behavior could be the origin of the changes in the electrical resistivity of the Ti2Nb2O9-based electrodes.

4.4.4. Energy balance

Fig. 8 plots the net electrical energy loss ΔE_e [Eq. (11)] and the total thermal energy dissipated Q_T [Eq. (10)] over a charging/discharging cycle for calorimetric cells with working electrodes made of Ti₂Nb₂O₉ (c) microparticles or (d) nanoparticles. For the cell with Ti₂Nb₂O₉ microparticles, the total thermal energy Q_T (in J) released over a cycle decreased with increasing current *I*. This was due to the decrease in the cycle period t_{cd} with increasing current *I* [Fig. S2(a) in Supplementary Materials] which was more significant than the concurrent increase in the instantaneous total heat generation rate $\dot{Q}_T(t)$ (in W) [Figs. 7(a) and 7(c)]. By contrast, Q_T increased with increasing current *I* for the cell with Ti₂Nb₂O₉ nanoparticles as the increase in $\dot{Q}_T(t)$ [Figs. 7(b) and 7 Energy Storage Materials 52 (2022) 371-385

(d)] was more significant than the decrease in t_{cd} [Fig. S2(b)]. Finally, for both cells at any given current *I*, the total dissipated thermal energy Q_T measured by *operando* isothermal calorimetry fell within 10% of the net electrical energy loss ΔE_e measured by the potentiostat. In other words, the net electrical energy loss was entirely dissipated in the form of heat. These results confirm the accuracy of our measurements.

5. Conclusion

This study investigates the tunnel-structured Ti₂Nb₂O₀ with fast charging capabilities at potentials above 1.0 V vs. Li/Li⁺ which reduces SEI and dendrite formation. A novel sol-gel method was proposed to synthesize Ti2Nb2O9 nanoparticles for use in lithium-ion battery electrodes. These electrodes were compared with those made of Ti2Nb2O9 microparticles synthesized by the traditional solid-state method using unique characterization techniques including potentiometric entropy measurements and operando isothermal calorimetry. Cyclic voltammetry and galvanostatic cycling demonstrated the superior specific capacity, greater cycling reversibility, and smaller capacity drop with increasing current for electrodes made of Ti2Nb2O9 nanoparticles compared to those made of Ti2Nb2O9 microparticles. Furthermore, in situ XRD measurements revealed only minor and reversible distortions to the crystallographic structure of Ti₂Nb₂O₉. In addition, potentiometric entropy measurements indicated that both types of electrodes underwent lithium ion intercalation/deintercalation in a homogeneous solid solution of Ti₂Nb₂O₉ during cycling. In fact, overlapping entropic potential profiles suggested that the particle size had no influence on the thermodynamics behavior of Ti2Nb2O9. However, electrodes made of Ti₂Nb₂O₉ nanoparticles exhibited smaller overpotential than those made of Ti2Nb2O9 microparticles, thanks to their smaller particle size and larger specific surface area which facilitate lithium ion transport. This, along with their larger electrical conductivity and thus smaller resistive losses, contributed to the smaller instantaneous and timeaveraged irreversible heat generation rates at electrodes made of Ti2Nb2O9 nanoparticles than those made of Ti2Nb2O9 microparticles at any given C-rate, as determined by operando isothermal calorimetry.

CRediT authorship contribution statement

Yucheng Zhou: Conceptualization, Data curation, Formal analysis, Investigation, Visualization, Writing – original draft, Writing – review & editing. Etienne Le Calvez: Conceptualization, Formal analysis, Investigation, Visualization, Writing – original draft, Writing – review & editing. Sun Woong Baek: Conceptualization, Investigation, Writing – review & editing. Matevž Frajnkovič: Conceptualization, Investigation, Writing – review & editing. Camille Douard: Investigation. Eric Gautron: Investigation. Olivier Crosnier: Conceptualization, Supervision, Writing – review & editing. Thierry Brousse: Conceptualization, Funding acquisition, Supervision, Writing – review & editing. Laurent Pilon: Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary material

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Supplementary Materials for: Effect of particle size on thermodynamics and lithium ion transport in electrodes made of $Ti_2Nb_2O_9$ microparticles or nanoparticles

Yucheng Zhou^a, Etienne Le Calvez^{b,c}, Sun Woong Baek^a, Matev Frajnkovi^a, Camille Douard^{b,c}, Eric Gautron^b, Olivier Crosnier^{b,c}, Thierry Brousse^{b,c}, and Laurent Pilon^{a,d,e,+}

^aMechanical and Aerospace Engineering Department, Henry Samueli School of Engineering and Applied Science, University of California, Los Angeles, CA 90095, USA ^bNantes Universit, CNRS, Institut des Matriaux de Nantes Jean Rouxel, IMN, F-44000

Nantes, France

^cRseau sur le Stockage lectrochimique de Inergie (RS2E), CNRS FR 3459, 33 rue Saint Leu, 80039 Amiens Cedex, France

^dCalifornia NanoSystems Institute, University of California, Los Angeles, CA 90095, USA
^eInstitute of the Environment and Sustainability, University of California, Los Angeles, CA 90095, USA

 +Corresponding Author: Phone: +1 (310)-206-5598, Fax: +1 (310)-206-2302 E-mail: pilon@seas.ucla.edu

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S.1 Structural characterization

Figure S1: Quantity adsorbed as a function of relative pressure p/p_0 in low-temperature nitrogen adsorption porosimetry of Ti₂Nb₂O₉ (a) microparticles or (b) nanoparticles. Pore size distribution as a function of pore width in low-temperature nitrogen adsorption porosimetry of Ti₂Nb₂O₉ (c) microparticles or (d) nanoparticles.

S.2 *Operando* isothermal calorimetry

S.2.1 Cell potential

Figure S2 plots the temporal evolution of the potential V(t) of the calorimetric cells with slurry-cast working electrodes made of Ti₂Nb₂O₉ (a) microparticles or (b) nanoparticles and lithium metal counter electrodes for six consecutive galvanostatic cycles with potential window between 1.0 and 3.0 V vs. Li/Li⁺ for each current *I* ranging from 2 to 8 mA. Here, the five colored regions corresponded to the different current *I* from 2 to 4 to 6 to 8 and back to 2 mA. The Ti₂Nb₂O₉ active material mass loading of both cells was identical at 5.5 mg, such that identical currents *I* would result in identical C-rates. The current I = 2, 4, 6, and 8mA amounted to C-rate of 1.5C, 3C, 4.5C, and 6C, respectively. Furthermore, the potential V(t) of both cells was nonlinear and asymmetric between charging and discharging. This followed the typical potential profiles under galvanostatic cycling. In addition, the potential V(t) was repeatable between every cycle for any given current *I*.



Figure S2: Temporal evolution of potential V(t) of calorimetric cells for six consecutive galvanostatic cycles with potential window between 1.0 and 3.0 V vs. Li/Li⁺ for each current *I* ranging from 2 to 8 mA with slurry-cast working electrodes made of Ti₂Nb₂O₉ (a) microparticles or (b) nanoparticles and lithium metal counter electrodes.

S.2.2 Instantaneous heat generation rates

Figures S3 and S4 plot the instantaneous heat generation rates $\dot{Q}_{TNO}(t)$ measured at the working electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles and $\dot{Q}_{Li}(t)$ measured at the lithium metal counter electrodes as functions of dimensionless time t/t_{cd} during the last three consecutive cycles at current (a) I = 2 mA, (b) I = 4 mA, (c) I = 6 mA, and (d) I = 8 mA. Here, $\dot{Q}_{TNO}(t)$ and $\dot{Q}_{Li}(t)$ in both cells showed negligible differences at any given current I. This indicates that heat generation had reached oscillatory steady-state after the first three consecutive cycles.



Figure S3: Instantaneous heat generation rates $\dot{Q}_{TNO}(t)$ measured at the working electrode made of Ti₂Nb₂O₉ microparticles and $\dot{Q}_{Li}(t)$ measured at the lithium metal counter electrode as functions of dimensionless time t/t_{cd} during the last three consecutive cycles at current (a) I = 2 mA, (b) I = 4 mA, (c) I = 6 mA, and (d) I = 8 mA.



Figure S4: Instantaneous heat generation rates $\dot{Q}_{TNO}(t)$ measured at the working electrode made of Ti₂Nb₂O₉ nanoparticles and $\dot{Q}_{Li}(t)$ measured at the lithium metal counter electrode as functions of dimensionless time t/t_{cd} during the last three consecutive cycles at current (a) I = 2 mA, (b) I = 4 mA, (c) I = 6 mA, and (d) I = 8 mA.

S.2.3 Total heat generation rate of the cell

Figure S5 plots the open-circuit voltage $U_{OCV}(C_m, T)$ and entropic potential $\partial U_{OCV}(C_m, T)/\partial T$ of the coin cells with slurry-cast working electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles as functions of specific capacity C_m during lithiation and delithiation of the first cycle at C-rates of 1.5C and 6C. Here, the values of $U_{OCV}(C_m, T)$ and $\partial U_{OCV}(C_m, T)/\partial T$ measured at 1.5C were used as the values of $U^{avg}(x,T)$ and $\partial U^{avg}(x,T)/\partial T$ in Equations (5) and (6) in Manuscript for both I = 2 and 4 mA, while those measured at 6C were used for both I = 6 and 8 mA. Note that the conversion between specific capacity C_m and lithium composition x was performed such that the theoretical specific capacity of 252 mAh/g corresponded to 4 units of lithium ion insertion per unit of Ti₂Nb₂O₉. Thus, Figures S6 to S9 plot the measured total heat generation rate $\dot{Q}_T(x,T)$ in the calorimetric cells with slurry-cast working electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles and lithium metal counter electrodes as a function of lithium composition x during lithiation or delithiation for current I ranging from 2 to 8 mA. The figures also show the heat generation rates $\dot{Q}_J(x,T)$ and $\dot{Q}_J(x,T) + \dot{Q}_{rev}(x,T)$ calculated according to Equations (5) and (6) in Manuscript. Previously in cells with TiNb₂O₇ [1] or PNb₉O₂₅ [2] working electrodes and lithium metal counter electrodes in 1 M LiPF₆ in EC:DMC 1:1 v/v electrolyte, the measured heat generation rate $\dot{Q}_T(x,T)$ agreed relatively well with that calculated as $\dot{Q}_J(x,T) + \dot{Q}_{rev}(x,T)$, with the difference attributed to heat of mixing $\dot{Q}_{mix}(x,T)$ [2]. Here however, major discrepancies were observed between the measurements of $\dot{Q}_T(x,T)$ and the calculations of $\dot{Q}_J(x,T) + \dot{Q}_{rev}(x,T)$ for nearly every current I in both cells. Moreover, for significant portions of the lithiation or delithiation steps, the calculated Joule heating $\dot{Q}_J(x,T)$ was negative.

Here, we hypothesize that the problem arose from limitations in the analysis. Specifically, the analysis is formulated upon the following assumption: the $U^{avg}(x,T)$ and $\partial U^{avg}(x,T)/\partial T$ in Equations (5) and (6) in Manuscript are equivalent to the $U_{OCV}(x,T)$ and $\partial U_{OCV}(x,T)/\partial T$ obtained from potentiometric entropy measurements but for current pulses corresponding to the same C-rate as that imposed during galvanostatic cycling in the *operando* isothermal

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calorimetry measurements of $\dot{Q}_T(x,T)$ [2]. However, this assumption could be invalid in some circumstances. For example, for the cell with $Ti_2Nb_2O_9$ microparticles, a specific capacity of $C_m = 203 \text{ mAh/g}$ was extracted during lithiation under potentiometric entropy measurements with current pulses at 6C [Figure S5(a)]. By contrast, during lithiation under galvanostatic cycling at I = 8 mA (~6C), the lithium composition varied from x = 1.8 to x =2.2 corresponding to a specific capacity of $C_m = 25 \text{ mAh/g only [Figure S7(c)]}$. Meanwhile, a specific capacity of $C_m = 254 \text{ mAh/g}$ with current pulses at 1.5C [Figure S5(a)] did not agree either with a specific capacity of $C_m = 82 \text{ mAh/g from } x = 1.6 \text{ to } x = 2.9 \text{ obtained at}$ $I = 2 \text{ mA} (\sim 1.5 \text{C})$ [Figure S6(a)]. Similar behavior was observed for the cell with Ti₂Nb₂O₉ nanoparticles: $C_m = 270 \text{ mAh/g}$ at 6C [Figure S5(c)] against $C_m = 139 \text{ mAh/g}$ from x =1.5 to x = 3.7 at $I = 8 \text{ mA} (\sim 6\text{C})$ [Figure S9(c)], or $C_m = 314 \text{ mAh/g at } 1.5\text{C}$ [Figure S5(c)] against $C_m = 189 \text{ mAh/g}$ from x = 1.2 to x = 4.2 at I = 2 mA (~1.5C) [Figure S8(a)]. These comparisons suggest that the actual $U^{avg}(x,T)$ and $\partial U^{avg}(x,T)/\partial T$ reached under galvanostatic cycling did not equate to the $U_{OCV}(x,T)$ and $\partial U_{OCV}(x,T)/\partial T$ determined by potentiometric entropy measurements, otherwise the specific capacity C_m from the two measurements at the same C-rate should be much closer. In fact, the discrepancy was more significant at higher C-rates when the capacity retention was the worst. Most likely, the long relaxation periods required in potentiometric entropy measurements mitigated some dynamic processes occurring in the cell. For instance, the ion concentration gradients had time to decay, the lattice displacements had time to recover, the intercalated lithium ions had time to migrate towards more energetically favorable sites. It is interesting to note that, while previous studies did achieve good agreement between the measured $\dot{Q}_T(x,T)$ and the calculated $\dot{Q}_J(x,T) + \dot{Q}_{rev}(x,T)$ heat generation rates in cells with TiNb₂O₇ [1] or PNb₉O₂₅ [2] working electrodes, the cells were only cycled at C-rates with good capacity retention. Therefore, the specific capacity C_m from potentiometric entropy measurements and galvanostatic cycling at the same C-rates were relatively close. As a result, in such cases the $U^{avg}(x,T)$ and $\partial U^{avg}(x,T)/\partial T$ in Equations (5) and (6) in Manuscript could be substituted with the measured $U_{OCV}(x,T)$ and $\partial U_{OCV}(x,T)/\partial T$.



Figure S5: Open-circuit voltage $U_{OCV}(C_m, T)$ and entropic potential $\partial U_{OCV}(C_m, T)/\partial T$ of coin cells with working electrodes made of Ti₂Nb₂O₉ microparticles or nanoparticles as functions of specific capacity C_m during lithiation and delithiation of the first cycle at C-rates of 1.5C and 6C.



Figure S6: Measured total heat generation rate $\dot{Q}_T(x,T)$, along with heat generation rates $\dot{Q}_J(x,T)$ and $\dot{Q}_J(x,T) + \dot{Q}_{rev}(x,T)$ calculated according to Equations (5) and (6) in Manuscript, as well as measured cell potential V(x,T) and open-circuit voltage $U_{OCV}(x,T)$ as functions of lithium composition x during (a) lithiation, (b) delithiation at current I =2 mA, (c) lithiation, (d) delithiation at current I = 4 mA in calorimetric cell with working electrode made of Ti₂Nb₂O₉ microparticles and lithium metal counter electrode.



Figure S7: Measured total heat generation rate $\dot{Q}_T(x,T)$, along with heat generation rates $\dot{Q}_J(x,T)$ and $\dot{Q}_J(x,T) + \dot{Q}_{rev}(x,T)$ calculated according to Equations (5) and (6) in Manuscript, as well as measured cell potential V(x,T) and open-circuit voltage $U_{OCV}(x,T)$ as functions of lithium composition x during (a) lithiation, (b) delithiation at current I =6 mA, (c) lithiation, (d) delithiation at current I = 8 mA in calorimetric cell with working electrode made of Ti₂Nb₂O₉ microparticles and lithium metal counter electrode.



Figure S8: Measured total heat generation rate $\dot{Q}_T(x,T)$, along with heat generation rates $\dot{Q}_J(x,T)$ and $\dot{Q}_J(x,T) + \dot{Q}_{rev}(x,T)$ calculated according to Equations (5) and (6) in Manuscript, as well as measured cell potential V(x,T) and open-circuit voltage $U_{OCV}(x,T)$ as functions of lithium composition x during (a) lithiation, (b) delithiation at current I =2 mA, (c) lithiation, (d) delithiation at current I = 4 mA in calorimetric cell with working electrode made of Ti₂Nb₂O₉ nanoparticles and lithium metal counter electrode.



Figure S9: Measured total heat generation rate $\dot{Q}_T(x,T)$, along with heat generation rates $\dot{Q}_J(x,T)$ and $\dot{Q}_J(x,T) + \dot{Q}_{rev}(x,T)$ calculated according to Equations (5) and (6) in Manuscript, as well as measured cell potential V(x,T) and open-circuit voltage $U_{OCV}(x,T)$ as functions of lithium composition x during (a) lithiation, (b) delithiation at current I =6 mA, (c) lithiation, (d) delithiation at current I = 8 mA in calorimetric cell with working electrode made of Ti₂Nb₂O₉ nanoparticles and lithium metal counter electrode.

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III. Résultats complémentaires, conclusions et perspectives

En ce qui concerne HTiNbO5, la première publication permet de mettre en avant l'observation de performances électrochimiques similaires pour les électrodes présentant des particules micrométriques synthétisées à haute température (SS) et celles nanométriques formées par voie sol-gel (SG). Ces similarités électrochimiques sont expliquées par le rôle prédominant du proton dans le stockage de charge. En effet, dans cet oxyde, le proton devient plus mobile et plus acide durant l'insertion des ions Li⁺ permettant ainsi une bonne diffusion de ces derniers dans la structure. La différence de la longueur de diffusion ne joue pas un rôle prépondérant dans la capacité à stocker rapidement les charges. De plus, la DRX in situ a permis de démontrer un changement initial de la structure dans le cas des synthèses SS et SG avec la formation irréversible de Li_{0.4}HTiNbO₅. Néanmoins, une large différence est observée dans le cas de nanofeuillets réempilés où l'ont obverse une capacité plus faible pour toutes les densités de courant imposées. Par exemple, à 0.02 A.g⁻¹, HTiNbO₅ SS propose une capacité spécifique de 225 mAh.g⁻¹ quand HTiNbO₅ NS possède une capacité spécifique de 113 mAh.g⁻¹. Ceci est expliqué par la présence des molécules organiques (TBAOH) utilisées durant l'exfoliation dans l'espace interfeuillets du matériau. Malgré une plus grande surface spécifique, ces molécules organiques limitent l'insertion des ions Li⁺.



*Figure.IV. 1 Capacité pour différentes densités de courant de KTiNbO*₅ SS, *HTiNbO*₅ SS, *HTiNbO*₅ SG, *HTiNbO*₅ SG, *Ti*₂*Nb*₂*O*₉ SS *et Ti*₂*Nb*₂*O*₉ SG.

Contrairement à HTiNbO₅, la morphologie des particules entre Ti₂Nb₂O₉ SS et SG modifie le processus de lithiation. Ti₂Nb₂O₉ SG présente des capacités spécifiques bien supérieures au matériau présentant des particules micrométriques (SS). Par exemple, à 0.02 A.g⁻¹, Ti₂Nb₂O₉ SG propose une capacité spécifique de 230 mAh.g⁻¹ quand Ti₂Nb₂O₉ SS possède une capacité spécifique de 157 mAh.g⁻¹. Des images HR(S)TEM ainsi que des mesures de porosité démontrent la formation de microporosité durant le processus de déshydratation de HTiNbO₅. Il a été démontré par ATG que HTiNbO₅ SG possède plus de molécule d'H₂O que HTiNbO₅ SS. Cette différence implique la formation d'un plus grand nombre de micropore dans le cas du matériau SG. Cette microporosité va entrainer une meilleure diffusion des ions lithium ainsi qu'une capacité de surface (*pseudocapacité*) exacerbée. De plus, une meilleure conductivité électronique ainsi qu'une longueur de diffusion bien inférieure permettent également d'expliquer les capacités largement plus élevées dans le cas du matériau synthétisé par voie sol-gel.

Ici, l'entièreté des matériaux étudiés dans ce chapitre ont été brièvement comparés pour comprendre l'influence du K⁺, du H⁺ ou de leurs absences sur les propriétés électrochimiques des matériaux de la famille de KTiNbO₅. La Figure.IV. 1 résume toutes les capacités spécifiques des matériaux étudiés à différents courants. Premièrement, on observe que KTiNbO₅ insère une quantité négligeable d'ions lithium du fait de la gêne stérique imposée par la présence d'ion potassium volumineux dans l'espace interfeuillets. Les propriétés similaires de HTiNbO₅ SS et SG sont à mettre en parallèle avec celle de HTiNbO₅ NS qui démontrent de plus faibles capacités. Dernièrement, Ti₂Nb₂O₉ SS propose des capacités spécifiques plus faibles que HTiNbO₅ SS et SG mais Ti₂Nb₂O₉ SG présente les meilleures performances électrochimiques avec une capacité d'environ 150 mAh.g⁻¹ pour un courant de 1 A.g⁻¹.

Comme décrit dans le Chapitre I, $Li_4Ti_5O_{12}$ est considéré comme une référence dans des applications de charge rapide et est commercialisé par exemple, par la compagnie japonaise Toshiba. La Figure.IV. 3 démontre que $Ti_2Nb_2O_9$ SG présente une capacité spécifique supérieure et une plage de potentiel similaire à $Li_4Ti_5O_{12}$. Ainsi, des cellules complètes ont été brièvement étudiées dans le cadre de cette thèse pour confirmer l'intérêt de cette famille de matériaux en tant qu'électrode négative dans les batteries Li-ion et pour les *Li-ion capacitors*. Grâce au Tableau.IV. 1, le ratio massique entre l'électrode positive et l'électrode négative (m_+/m_-) , ainsi que la densité de puissance et d'énergie des cellules complètes assemblées sont

présentés. Des masses d'environ 10 mg.cm⁻² ont été utilisées pour les différents oxydes utilisés dans le but d'être en adéquation avec les exigences industrielles. Dans le cas du carbone activé, des électrodes d'environ 30 mg.cm⁻² ont été utilisées.



Figure.IV. 2. Comparaison des courbes de charge décharge entre $Ti_2Nb_2O_9$ et $Li_4Ti_5O_{12}$ à un courant de à 0.20 A.g⁻¹ entre 1.0 et 3.0V vs Li^+/Li . Chaque électrode présente des masses ainsi qu'un ratio matériau actif, carbone conducteur et liant (75 :15 :10) similaires.

Comme illustré Figure.IV. 3 (A-B), LiMn₂O₄ (LMO) a été associé à Ti₂Nb₂O₉ SG avec un ratio m₊/m. de 1.9. LiMn₂O₄ est utilisé en tant qu'électrode positive car ce matériau possède des capacités spécifiques relativement élevées durant des charges rapides.^{33–36} Dans cette cellule complète, LiMn₂O₄ cycle entre 4.2V et 3.9V *vs* Li⁺/Li tandis que Ti₂Nb₂O₉ opère entre 1.0 V et 3.0V *vs* Li⁺/Li. A 0.02 A.g⁻¹, une énergie de 150 Wh.g⁻¹ est mesurée avec une puissance associée de 15 W.g⁻¹. Quand on applique un courant plus élevé de 0.1 A.g⁻¹, une énergie de 92 Wh.g⁻¹ et une puissance de 184 W.g⁻¹ sont obtenus. Ces résultats sont préliminaires mais démontrent que de tels systèmes fonctionnent relativement bien comme préalablement proposé par le groupe du Pr. Clare P. Grey avec l'utilisation d'un bronze Nb₁₆W₅O₅₅ et LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC 622).³⁷ Ainsi, dans le but d'augmenter la densité d'énergie, une électrode de LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC 811) a été utilisée à l'électrode positive. Avec un ratio m_+/m_- de 1.2, cette cellule complète propose une énergie de 209 Wh.g⁻¹ pour une puissance de 21 W.g⁻¹, LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ opérant à plus haut potentiel que LiMn₂O₄. Cependant, une rapide diminution de la capacité de LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ à courant élevé entraîne des densités d'énergie et de puissance à 0.2 A.g⁻¹ similaires à la cellule LiMn₂O₄/ Ti₂Nb₂O₉. Malgré les densités d'énergie et de puissance relativement faibles, l'exploration et l'amélioration de ce type de système pourrait permettre la mise sur le marché de batteries de puissance permettant des temps de charge de l'ordre de la minute. Plusieurs compagnies comme Niobolt ou Toshiba s'intéressent à l'industrialisation de batteries basées sur une électrode utilisant des oxydes multicationiques de niobium, de tungstène et/ou de titane.

Tableau.IV. 1. Ratio masse d'électrode positive sur la masse d'électrode négative ainsi énergie et puissance des différents cellules complètes assemblées (différent matériaux d'électrode positive ainsi que différents courants imposés)

Electrode positive	Electrode négative	Densité de courant / A.g ⁻¹	m_+/m	Energie / Wh.g ⁻¹	Puissance/ W.g ⁻¹
LiMn ₂ O ₄	Ti2Nb2O9 SG	0.02	1.9	150	15
LiMn ₂ O ₄	Ti ₂ Nb ₂ O ₉ SG	0.2	1.9	92	184
LiNi0.8Mn0.1C00.1	Ti2Nb2O9 SG	0.02	1.2	209	21
LiNi _{0.8} Mn _{0.1} Co _{0.1}	Ti ₂ Nb ₂ O ₉ SG	0.2	1.2	91	182
Carbone activé	Ti ₂ Nb ₂ O ₉ SG	0.1	4	70	70
Carbone activé	Ti ₂ Nb ₂ O ₉ SG	0.5	4	55	330



Figure.IV. 3. Courbe de charge-décharge à différents courants dans une cellule complète à trois électrodes avec une pseudo référence en lithium métal. (A) Cellule $LiMn_2O_4$ vs $Ti_2Nb_2O_9$ sol-gel avec un courant imposé de 0.02 A.g⁻¹ (B) Cellule $LiMn_2O_4$ vs $Ti_2Nb_2O_9$ sol-gel avec un courant imposé de 0.2 A.g⁻¹ (C) Cellule $LiNi_{0.8}Mn_{0.1}Co_{0.1}$ vs $Ti_2Nb_2O_9$ sol-gel avec un courant imposé de 0.2 A.g⁻¹ (D) Cellule $LiNi_{0.8}Mn_{0.1}Co_{0.1}$ vs $Ti_2Nb_2O_9$ sol-gel avec un courant imposé de 0.2 A.g⁻¹ (E) Cellule Carbone activé vs $Ti_2Nb_2O_9$ sol-gel avec un courant imposé de 0.1 A.g⁻¹ (F) Cellule Carbone activé vs $Ti_2Nb_2O_9$ sol-gel avec un courant imposé de 0.5 A.g⁻¹

Dernièrement, dans le but de réaliser un *Li-ion capacitor*, comme décrit dans le chapitre II, une cellule complète a été assemblée opposant une électrode de carbone activé et une électrode de Ti₂Nb₂O₉ SG. m_+/m_- est dans ce cas égal à 4 car la capacité du carbone activé est relativement faible (~ 40 mAh.g⁻¹). A un courant de 0.5 A.g⁻¹, une énergie de 55 Wh.g⁻¹ est

observée avec une puissance de 330 W.g⁻¹. Ces résultats sont comparables aux énergies et aux puissances reportées dans le cas d'un *Li-ion capacitor* formé par une électrode négative de graphite et une électrode positive de carbone activé avec un sel de lithium sacrificiel (Li₂DHBN).³⁸ Ainsi, il est également possible d'imaginer des applications dans les *Li-ion capacitors* qui sont des systèmes présentant des densités de puissance comparables aux supercondensateurs carbone/carbone mais avec des densités d'énergie bien supérieures.

Malgré la faible optimisation des systèmes présentés dans ce travail (équilibrage des masses entre électrode positive et électrode négative, taux de carbone conducteur et de liant dans l'électrode, potentiel de travail...), des énergies et des puissances non négligeables ont été mesurées pour des systèmes complets utilisant Ti₂Nb₂O₉ (Li-ion batteries et *Li-ion capacitors*) en association avec des matériaux tels que LiMn₂O₄, LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ ainsi que du carbone activé.

D'autres pistes d'améliorations vis-à-vis de la mise en forme des matériaux peuvent être proposées. Le groupe du Pr. Yuri Gogotsi travaille sur des matériaux 2D appelés MXene. Ces phases peuvent également être exfoliées. Par filtration, des feuillets MXenes forment en association avec d'autres matériaux électroactifs et/ou conducteurs électroniques (*graphene sheets, carbon nanotubes* (CNT), *polyaniline* (PANI)) des électrodes autosupportées avec une architecture qui favorisent la diffusion des ions dans l'électrode. Ainsi, ces électrodes dénouées de liants polymères présentent des caractéristiques électrochimiques très intéressantes et peuvent trouver des applications dans les systèmes « tout-solide » ou dans les micro-batteries (et micro-supercondensateurs).^{39–41} Ainsi, par ajout de graphène, de *reduced graphene oxide* (rGO) ou encore de CNT, il est possible d'imaginer la formation d'électrode nanocomposites avec les nanofeuillets de HTiNbO₅ permettant d'en améliorer les propriétés électrochimiques de ce dernier. Ce type d'électrode n'a été que très brièvement étudié durant cette thèse et les résultats ne sont pas présentés dans ce manuscrit.

Comme reporté dans différentes publications scientifiques, la diminution de la taille des grains du matériau actif jusqu'à des particules nanométriques peut entraîner une augmentation de la capacité ainsi qu'une meilleure rétention de capacité à courant élevé.^{42–44} Ces propriétés électrochimiques sont classiquement expliquées par une meilleure conductivité électronique, un chemin de diffusion plus court ou encore une plus faible génération de chaleur lors de

l'insertion d'ions alcalins. Cependant, les synthèses utilisées nécessitent souvent des solvants toxiques et polluants (méthanol, éthylène glycol dans le cas présent), des réactifs relativement chers (NbCl₅, Ti-n-butoxide) limitant l'applicabilité industrielle de ce genre de procédé. Limiter l'impact environnemental et le coût des batteries sont deux points clés que la nanostructuration ne semble pas respecter. De plus, les nanomatériaux présentent une densité d'énergie volumique plus faible que les matériaux micrométriques du fait de leurs densités réelles moins élevées. Pour toutes ces raisons, le développement de matériau se présentant sous forme micrométrique et ayant une masse volumique élevée semble être deux facteurs essentiels au développement des batteries de puissance si l'on prend en compte le respect de l'environnement ainsi que le coût de ces futures batteries. C'est pour cette raison, que le chapitre suivant se concentrera sur des matériaux synthétisés par voie « classique » à haute température présentant une densité relativement élevée comparativement aux matériaux présentés dans cette étude.
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Chapitre V. Revisiter des oxydes polycationiques pour le stockage de charge. L'exemple de Rb₂TiNb₆O₁₈ et CS_{0.5}Nb_{2.5}W_{2.5}O₁₄

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I. Introduction

Un large travail bibliographique a permis d'identifier différents oxydes prometteurs visà-vis du stockage électrochimique d'ions lithium. Les phases identifiées se devaient d'être dans la continuité du travail réalisé sur HTiNbO₅. Les oxydes de métaux de transition devaient contenir des ions alcalins volumineux et potentiellement échangeables. Aussi, fort du travail de thèse réalisé pas un étudiant dans le laboratoire visant à investiguer le comportement électrochimique de bronzes hexagonaux de tungstène A_xWO_3 , un regard a été porté sur les bronzes et les phases pouvant s'en rapprocher (bronze tétragonal et matériaux présentant des intercroissances et ayant des similarités avec les bronzes hexagonaux...).

Ainsi, un regard particulier a été porté sur des phases de bronze interconnectées $A_{12}Nb_{30}W_3O_{90}$ (A= Rb, Cs, Tl) et $A_2Nb_6TiO_{18}$ (A= Rb, Cs, Tl) mais également un bronze hexagonal $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$. Ils présentent tous des structures plus compactes que KTiNbO₅ avec des tunnels accueillant des ions alcalins potentiellement échangeables. Les paragraphes suivants proposent une brève revue de la littérature qui permettra de mieux comprendre le potentiel intérêt de ces phases pour des applications dans les électrodes négatives pour batteries Li-ion de puissance.

1. $A_{12}Nb_{30}W_{3}O_{90}$ (A= Rb, Cs, Tl) et $A_{2}Nb_{6}TiO_{18}$ (A= Rb, Cs, Tl)

Dans la continuité des travaux réalisés sur les matériaux multicationiques, l'équipe de B. Raveau a travaillé sur différents oxydes à base de niobium, montrant des structures de tunnels occupées par des espèces cationiques volumineuses (Rb⁺, Cs⁺, Tl⁺). Ces cations résident à l'origine dans les cages du matériau, stabilisant de grands tunnels hexagonaux interconnectés.

Par exemple, $A_{12}Nb_{30}W_3O_{90}$ (A= Rb, Cs, Tl) est un matériau présentant une structure tunnel de type bronze interconnectée. La structure cristallographique de $A_{12}Nb_{30}W_3O_{90}$ peut être observée sur la Figure.V. 1.A. Le matériau cristallise dans le système trigonal (groupe d'espace R3m).^{2,3} $A_{12}Nb_{30}W_3O_{90}$, peut être décrit comme l'intercroissance entre des couches (M_4O_{12})_n et (M_7O_{18})_n, formant des structures qui présentent des tunnels hexagonaux le long des directions [100], [010] et [110].^{2,3} Un empilement régulier de trois types différents d'octaèdres entraîne le déplacement périodique des tunnels. Ce matériau présente des propriétés d'échange A/H_3O^+ remarquables lorsqu'il est exposé à des milieux acides. Un très faible changement de paramètres de maille est entrainé par la substitution des ions alcalins par H_3O^+ . Il est à signaler qu'à l'opposé de KTiNbO₅, l'échange de cations se fait dans le cas présent avec l'arrivée d'une molécule d'eau.²



Figure.V. 1. Structure cristallographique de (A) Rb₁₂W₃Nb₃₀O₉₀ (B) Rb₂TiNb₆O₁₈.¹⁻³

De même, A₂Nb₆TiO₁₈ (A= Rb, Cs, Tl) est un autre matériau présentant également des tunnels interconnectés.¹ La structure cristallographique de A₂Nb₆TiO₁₈ est visualisée sur la Figure.V. 1B. Le matériau cristallise dans un système hexagonal, (groupe d'espace P3m1). La structure est composée de deux types d'octaèdres déformés (Nb/Ti)O₆ partageant des sommets et des arêtes.^{1,4,5} Plus précisément, A₂Nb₆TiO₁₈ est formée par l'intercroissance des couches (M₆O₁₅)_n et (MO₃)_n créant une structure tridimensionnelle. Les cations Ti⁴⁺ semblent être préférentiellement localisés dans les sites (MO₃) en raison d'une plus faible distorsion de ces octaèdres.⁵ Rb⁺ est situé dans de grandes cages O₂₁ (158,7 Å³) qui sont formées dans des tunnels hexagonaux de type bronze interconnectés le long des directions [100], [010] et [110]. Dans le cas de ce matériau aucune propriété d'échange protonique n'a été relevée dans la littérature.

Seuls quelques articles font état de la structure de ces phases et leurs propriétés d'échanges ioniques. Cependant, aucune de ces phases n'a été étudiée comme électrode pour

batterie Li-ion malgré l'attrait certain qu'elles pourraient présenter. En effet, la présence de cations Nb⁵⁺, W⁶⁺ et/ou Ti⁴⁺ en font des candidats pour des applications de puissance. De plus, la présence de tunnels et de cages ainsi que la rigidité probable de la structure du fait de la connexion par les arêtes de certains octaèdres renforcent l'idée d'une intercalation d'ions lithium favorisée.

Dans le cadre d'un stage MESC+ dans notre laboratoire, une étude approfondie des propriétés d'échanges ioniques dans les phases $Rb_{12}Nb_{30}W_3O_{90}$ et $Rb_2Nb_6TiO_{18}$ a été réalisée. Les résultats les plus prometteurs ont été découverts sur les phases à base de titane et de niobium, c'est pour cette raison que seule cette phase sera exposée ici. De fait, le trop faible nombre d'octaèdres (Nb(W)O₆) partageant leurs arêtes entraîne une rapide perte de capacité dans le cas de (H₃O⁺)₁₂Nb₃₀W₃O₉₀ comme explicité dans le cas de l'oxyde ReO₃.⁶

Les différences électrochimiques entre les phases originelles et protonées ont permis la publication d'un article sur Rb₂Nb₆TiO₁₈. D'autres échanges ioniques ont été réalisés avec des ions Ag⁺, Na⁺ et Li⁺ mais ne seront pas exposés ici car ils ne présentent pas de propriétés électrochimiques convaincantes.

2. $Cs_{0.5}Nb_{2.5}W_{1.5}O_{14}$, un bronze hexagonal

Un autre oxyde a attiré notre attention durant ce travail de thèse. $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ est un bronze hexagonal qui a été découvert par Monica Lundberg et Margareta Sundberg en 1993.⁷ Dans leur article, les auteures ont regardé $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ sous l'aspect structural à l'aide de microscopie électronique à transmission. Cet oxyde est formé d'octaèdres (MO₆) reliés entre eux par leurs sommets et de bipyramides pentagonales (MO₇) au centre de 5 octaèdres (MO₆). La connexion entre les octaèdres et les bipyramides pentagonales se fait par un partage des arêtes permettant d'envisager une certaine rigidité lors de l'insertion d'ions lithium. Ce squelette forme des tunnels à 6 et 7 côtés où des cations alcalins Cs⁺ peuvent être trouvés à l'intérieur de ces deux tunnels. Dans la publication initiale, les auteurs placent les ions Cs⁺ au centre des cages pentagonales comme illustré par la Figure.V. 2, cependant il est désormais admis que ces cations peuvent être trouvés dans les deux différents tunnels (hexagonal et heptagonal).^{8,9} Comme les phases de Wadsley-Roth, les bronzes hexagonaux ont été des matériaux très étudiés pour le développement de la microscopie électronique haute résolution.^{7–} ¹⁰ Cette phase a également été étudiée pour ces propriétés catalytiques.^{11,12}



Figure.V. 2. Structure cristallographique de Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄ selon Lundberg and Sundberg.⁷

Sans donner de détail sur le résultat de l'échange ionique effectué sur $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$, K. Omata *et al.* reporte les propriétés catalytiques du matériau après un passage dans une solution acide.¹¹ Ainsi, il est possible que le Cs^+ présent dans les cages du matériau puisse s'échanger avec un proton ou H₃O⁺.

Durant cette thèse les propriétés d'échanges ioniques de cet oxyde multicationique ont été étudiées grâce à l'utilisation de la microscopie électronique en transmission ainsi que par la diffraction des rayons X. Ensuite, les caractéristiques électrochimiques ont été largement analysées ainsi que la variation de la structure durant la lithiation (DRX *in situ*).

Les résultats de ces deux études sont exposés dans les publications ci-après. Le deuxième sur $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ n'étant pas encore soumis, il se trouve sous la forme d'un « *preprint* ».

- II. Les publications
- 1. Rb₂TiNb₆O₁₈

*Revisiting Rb*₂*TiNb*₆*O*₁₈ *as electrode materials for energy storage devices.*

Jeronimo Miranda, Etienne Le Calvez, Richard Retoux, Olivier Crosnier, and Thierry Brousse, Electrochemistry Communications, (2022).

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Revisiting $Rb_2TiNb_6O_{18}$ as electrode materials for energy storage devices

Jeronimo Miranda^{a,b}, Etienne Le Calvez^{a,b}, Richard Retoux^c, Olivier Crosnier^{a,b}, Thierry Brousse^{a,b,*}

^a Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, F-44000 Nantes, France

^b Réseau sur le Stockage Électrochimique de l'Énergie (RS2E), CNRS FR 3459, 33 rue Saint Leu, 80039 Amiens Cedex, France ^c CRISMAT-CNRS/UMR 6508, ENSICAEN Université de Caen Basse-Normandie Caen, 14050 Cedex 4, France

ARTICLE INFO	A B S T R A C T	
Keywords: Lithium-ion battery High rate electrode Negative electrode Tunnel structure Titanium niobiate	In the search of new materials for the future generation of Li-ion batteries, a look into the past has brought the multicationic oxide $Rb_2TiNb_6O_{18}$ to the foreground. Structural characterization of this material has been carried out thanks to the combination of XRD, SEM and HRTEM highlighting the complex structure of this material. Ion exchange was performed in order to replace the rubidium ions by hydrated protons. Then, a comparative study of $Rb_2TiNb_6O_{18}$ and the obtained proton exchanged analogues $H_2TiNb_6O_{18}$ when used as negative electrode materials is depicted in terms of both structure and electrochemical behavior. Interestingly, while only a negligible Li^+ insertion is evidenced in the rubidium phase, the $H_2TiNb_6O_{18}$ exhibits a much higher lithium intercalation between 1 V and 3 V vs Li/Li ⁺ . A specific capacity of 118 mAh.g ⁻¹ is reported when cycled at 0.02 A.g ⁻¹ . A solid solution type mechanism has been revealed by <i>in situ</i> XRD experiments. Moreover, during the lithiation, the volume of the material increases by only 1% showing the interest of this type of phase to develop "zero-strain" materials.	

1. Introduction

For a wider development of low-carbon mobility via electric cars, the synthesis of materials with the ability to charge quickly appears to be an essential point.[1-3] Graphite, the most commercially used negative electrode material, is not in line with this perspective. Despite a relatively large theoretical specific capacity of 372 mAh-g⁻¹ for graphite based electrodes, the reduction of Li⁺ to Li⁰ can occur at a potential down to 0 V vs. Li/Li⁺ during the charging step of graphite at high current densities, leading to a metallic dendritic growth of metallic lithium on the surface of graphite, that could cause possible overheating and short circuits.[4,5] Additionally, the formation of a solid electrolyte interface (SEI) passivates the graphite surface, which slows down the transfer of Li⁺ to and from the electrolyte, also lowering the power capabilities of graphite. Therefore, for LIBs to compete in the world of fast charging electrochemical devices, alternative negative electrode materials have been proposed and investigated. [6–9] In fact, the extension of LIBs into high-power applications can only be achieved if the undesired side reactions of Li⁺ on the surface of the negative electrode are prevented at high rates. A practical solution to this challenge has been to find redox-active materials where Li⁺ insertion occurs at a potential far

away from the thermodynamic reduction of Li⁺ (i.e., E greater than 1.0 V vs. Li/Li⁺) in order to avoid lithium plating but also SEI formation which decreases the power ability of electrodes and classically appears at a potential close to 0.8 V vs Li/Li⁺. [7,8,10,11] In this case, a classic example is T-Nb₂O₅ which show reversible Li⁺ intercalation between 1.0 V and 2.0 V vs Li/Li^+ with an extremely good capacity retention even at high rates over 20C[12,13].

In their extensive work on Nb-based polycationic materials, Raveau et al.[14-17] reported a different kind of tunneled Nb-based oxides showing pre-occupied cages. Large cationic species (i.e., K⁺, Rb⁺, Cs⁺, Tl⁺) are originally located within the cages of the material, stabilizing large interconnected hexagonal tunnels. Interestingly, remarkable cationic exchange behavior has been reported in some of these materials.[15,16] Consequently, the displacement of the original large alkali cations by smaller species (H⁺, Li⁺, ...) can liberate part of the accessible volume within the hexagonal channels, without triggering any phase change in the material.

Rb₂Nb₆TiO₁₈, exhibits an interconnected bronze-like tunnel structure, as well as the presence of possible Nb5+ and Ti4+ active redox centers. In this case, no ionic exchange properties were previously reported. In this work, for the first time, protonated substituted

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^{*} Corresponding author at: Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, F-44000 Nantes, France. E-mail address: thierry.brousse@univ-nantes.fr (T. Brousse).

 $Rb_2Nb_6TiO_{18}$ and consequent electrochemical characterization as LIB negative electrode material are reported. Both structural and electrochemical differences between $Rb_2TiNb_6O_{18}$ and $H_2TiNb_6O_{18}$ are discussed in the following parts of this communication.

2. Experimental section

2.1. Synthesis of Rb₂TiNb₆O_{18 / H₂TiNb₆O₁₈}

High-temperature solid state methods were used to synthesize $Rb_2TiNb_6O_{18}$. Stoichiometric amounts of Nb_2O_5 (Alfa Aesar, 99.9% metal basis), TiO_2 and 10% excess Rb_2CO_3 (ACROS Organics 99%) were thoroughly mixed using an agate mortar and pestle. The powdered mixture was heated at 900 °C for 6 h followed by re-grinded and a final calcination at 1150 °C using a platinum crucible for 12 h. The phase purity of the resulting materials was checked by X-ray diffraction and Le Bail refinement.

Protonated substituted phases were obtained by introducing the powder samples in 3 M HCl (Fisher bioreagent, analytical reagent grade) for 3 days upon stirring. Substitution was performed at 100 $^{\circ}$ C, by regularly add the 3 M HCl solution. Substitution amounts were estimated by EDX by means of comparing experimental Nb/Rb ratios to the theoretical one of Rb₂TiNb₆O₁₈.

2.2. Characterization

2.2.1. Powder X-ray diffraction

Powder XRD data was collected using a PANalytical X'Pert Pro diffractometer with using a Cu source (K $\alpha_1 = 1.5406$ Å, K $\alpha_2 = 1.5444$ Å) and K_β filter (Nickel) in the Bragg-Brentano reflection geometry. Data was collected from 10 to 90° 20. *In situ* electrochemical cycling XRD was obtained using a lab-produced cell, close to "Letiche cell" using a Beryllium window and by cycling the cell at 0.005 A.g $^{-1}$ with 30 min at open circuit voltage for XRD pattern collection.[18] All XRD were collected in $\sim 0.008^\circ$ 20 steps. Structure refinement has been performed using FullProf Suite. Preliminary values of this refinement have been taken from the literature.¹⁴

2.2.2. Thermogravimetric analysis (TGA)

TGA was performed using a TA 449 F3 Jupiter device. Samples (50–100 mg) were stabilized at 50 °C for 20 min followed by 3 °C.min⁻¹ temperature ramp from 50 to 700 °C in argon-flow mode.

2.2.3. SEM and TEM

SEM micrographs were obtained at 20 kV using a Zeiss MERLIN Instrument using in-Lens annular detector. Samples were prepared by dispersing a small fraction of the powder on a piece of conducting carbon tape. EDX was collected at 8.0 mm working distance using an X-Max 50 mm² OXFORD Instruments detector. TEM observations were performed using a 200 kV JEOL F200 Cold FEG Transmission Electron Microscope, fitted with a \pm 35° double tilt sample holder and a EDX JEOL centurion XL (Energy Dispersive X-ray detector).

2.2.4. Electrochemistry

Electrodes were prepared by thoroughly grinding active material, conducting carbon (Superior graphite) and polyvinylidene fluoride (PTFE) binder (Sigma-Aldrich, 60 wt% dispersion in H₂O) in a 75:15:10 wt ratio, with about 2 mL of ethanol, until a paste was obtained. The paste was rolled out to a thickness of ~ 150 μ m using a glass cylinder. Electrodes were dried at 60 °C overnight before cutting them into 12 mm diameter disks using a manual electrode puncher. Resulting electrodes ranged between 5 and 10 mg·cm⁻², consistent with reasonable mass loading metrics.[19] Electrochemical experiments were performed using Swagelok cells in a 2-electrode configuration. Cells were mounted inside an Argon-filled glovebox (<0.1 ppm O₂, H₂O) using a single lithium (Li) electrode as both reference and counter (99.9%, Sigma

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Aldrich), glass fiber separator (Whatman) and 200 μ L of 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC) 1:1 v/v (Solvionic, 99.9% purity, electrochemistry grade) as the electrolyte.

All electrochemical studies were performed using a MPG2 BioLogic Potentiostat/Galvanostat controlled by EC-Lab Software. Cyclic voltammetry (CV) were collected at 2 mV·s⁻¹. Galvanostatic cycling with potential limitation (GCPL) cycling was performed in series of 5 cycles at 0.02, 0.05, 0.10, 0.20, 0.50, 1.00 A·g⁻¹. The charge–discharge curves presented in the respective figures correspond always the third charge/discharge curve out of the five.

3. Results & discussion

The crystallographic structure of Rb₂TiNb₆O₁₈ is presented in Fig. 1. A. The material crystallizes in the hexagonal system, with a P $\overline{3}$ m1 space group. The structure is composed of two types of distorted (Nb/Ti)O₆ octahedra sharing corners and edges. More precisely, Rb₂TiNb₆O₁₈ are formed by the intergrowth of (M₆O₁₅)_n and (MO₃)_n layers which creates the 3D structure and cages. As previously reported²⁰, Ti cations seem to be preferentially located in the (MO₃) sites due to a lower distortion of these octahedra. Rb⁺ is located within large O₂₁ cages (158.7 Å³) which is formed in the bronze-like hexagonal tunnels interconnected along [1 0 0], [0 1 0] and [1 1 0] directions.

The purity of the phase was confirmed by Le Bail refinement shown in Fig. 1.B. Unit cell parameters were determined as a = 7.5323(5) Å and c = 8.2002(6) Å, showing a very small difference with the previously reported values. [14,20] A SEM micrograph in Fig. 1.C shows that large particles of ~ 10 um were obtained, as expected from the high-temperature conditions of the synthesis process. HR-TEM micrographs in Fig. 1.(D-E) reveal some differences between (110) and (101) planes. While large homogenous domains are observed on (110) plane, some defects are visible along (101). This observation might be a result of Ti deficiency located in the (MO₃) sites, causing some irregularities in the structure. Nevertheless, the HRTEM images along with (110) and (101) planes highlight the presence of cages along these directions.

The substitution of Rb⁺ ions by H⁺ ions, as described in the experimental part, was checked by EDX. A ratio of 1 for 40 between Rb and Nb allows us to assume that a nearly complete substitution by protons is achieved. Meanwhile, a Nb/Ti ratio remains at a value close to 6, as expected, before and after proton exchange. Diffractograms of both Rb₂TiNb₆O₁₈ and H₂TiNb₆O₁₈ are shown in Fig. 2.A. Interestingly, no phase change is observed and both materials get very close cell parameters. A small decrease from 7.5323(5) to 7.5126(5) Å for the a parameter and from 8.2002(6) to 8.1807(7) Å for the c parameter is observed. H₂TiNb₆O₁₈ shows slightly smaller parameters because of the replacement of bulky Rb⁺ by a smaller cation. Nevertheless, as reported in some similar substitutions[15,16], the proton is inserted into the structure accompanied by a water molecule with no difference in terms of particle size nor cristallinity.[21-24] Subsequently, a TGA was performed and the associated results are shown in Fig. 2.B. About 4% of the mass is lost between 50 °C and 700 °C which corresponds to 2 water molecules per cell unit, as observed in the literature [14-16]. Thus, we can conclude that during the ionic exchange, about one H2O molecule per proton is inserted in H2TiNb6O18·2H2O

To investigated the electrochemical activity of both $Rb_2TiNb_6O_{18}$ and $H_2TiNb_6O_{18}$ ·2H₂O, CVs were performed at 2 mV·s⁻¹ between 3 V and 1 V vs Li/Li⁺. As shown in Fig. 3.A, Rb₂TiNb₆O₁₈ shows a weak electrochemical signature within the investigated potential range, only a weak double layer capacitance is observed corresponding to a capacity of about 13 mAh.g⁻¹. In fact, due to the steric gene created by the presence of the bulky and not mobile Rb⁺ ions, no insertion of Li⁺ ions in the O₂₁ cages are possible. In contrast to his Rb⁺ analogue, H₂TiNb 6O₁₈·2H₂O has a clear faradic electrochemical signature. A broad wave between 2.6 and 1.5 V vs. Li/Li⁺ probably arises from the combination of

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Fig. 1. A. Crystal structure of $2x2 Rb_2TiNb_6O_{18}$ unit cell. (space group P $\overline{3}$ m1) B. Full pattern matching refinement of $Rb_2TiNb_6O_{18}$. Rwp = $37.5 \% / Chi^2 = 13.6$. C. SEM image of $Rb_2TiNb_6O_{18}$. D. (110) plane of $Rb_2TiNb_6O_{18}$ observed by TEM. E. (101) plane of $Rb_2TiNb_6O_{18}$ observed by TEM.

several superimposed redox activities, such as the irreversible reduction of structural water, and the reduction of Nb and/or Ti upon Li⁺ insertion. Similarly, a final wave below 1.3 V vs. Li/Li⁺ suggests a further reduction of the metal hosts at this lower potential. After 5 cycles, the remaining specific capacity is 100 mAh.g⁻¹ at 2 mV·s⁻¹. The reversible reduction of the Nb⁵⁺/Nb⁴⁺ and/or Ti⁴⁺/Ti³⁺ redox couples is most probably at the origin of the charge transfer observed in this material upon cycling, as described in the literature.[25] We can conclude from CV experiments that substitution of rubidium by protons give to this oxide the ability to significantly store more lithium ions into its structure.

Based on the obvious differences in CV between $Rb_2TiNb_6O_{18}$ and $H_2TiNb_6O_{18}$ ·2H₂O, the rate capability of these two materials was investigated by GCPL cycling at increasing current densities. Results are shown in Fig. 3(C-D). As expected, the Li⁺ insertion in the O_{21} cages is

very low for Rb₂TiNb₆O₁₈ at every measured current density. Once again, in contrast, H₂TiNb₆O₁₈·2H₂O presents a reversible specific capacity of 118 mAh.g⁻¹ at 0.02 A.g⁻¹, which corresponds to more than 3.55Li⁺ inserted/unit cell. It is 4 times higher than the capacity observed for Rb₂TiNb₆O₁₈ in the same conditions. H₂TiNb₆O₁₈·2H₂O inserts its lithium ions between 1.8 V and 1.0 V with a linear slope. This "pseudo-capacitive like" signature can be linked to the presence of various insertion sites with different activation energies in the structure which allows a practically constant Li⁺ insertion rate between 1.8 and 1.0 V vs Li/Li⁺. Further study of the electrochemical behavior of the electrode is under progress.

Nevertheless, when the current density is increased, the specific capacity of $H_2TiNb_6O_{18}\cdot 2H_2O$ sharply decreases. At 0.2 A.g⁻¹, a specific capacity of 32 mAh.g⁻¹ is observed which represented 27 % of the capacity at 0.02 A.g⁻¹. This relatively poor electrochemical behavior at

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Fig. 2. A. X-ray diffraction patterns of $Rb_2TiNb_6O_{18}$ and $H_2TiNb_6O_{18}$ indexed in P $\overline{3}$ m1 space group. B. TGA curves between 40 °C and 700 °C of $H_2TiNb_6O_{18}$ showing the number of structural water molecule (one water molecule per proton).



Fig. 3. A-B. Cyclic Voltammetry at 2 mV.s⁻¹ of $Rb_2TiNb_6O_{18}$ and $H_2TiNb_6O_{18}$ respectively. C-D. Charge and discharge curves at different current densities of $Rb_2TiNb_6O_{18}$ and $H_2TiNb_6O_{18}$ and $H_2TiNb_6O_{18}$ respectively.

high rate is probably due to the not favorable Li⁺ diffusion between cages which limited the capacity at high current but also due to the large particles size which increases the diffusion length. Calculation of *b* value from CV at different scan rates (from 0.1 mV.s⁻¹ to 20 mV.s⁻¹) reveals a value close to 0.5 which seems to indicate that a diffusion-controlled process is controlling the insertion of ions in this type of structure [4,26–28]. For this reason, the synthesis of nanoparticles *via* soft chemistry can be an option to lower the diffusion length and increase the capacity of this type of structure at a higher cycling rate.

Fig. 4Ashows in situ XRD data collected during the first GCPL cycle of $H_2TiNb_6O_{18}$ ·2H₂O Note that the relative intensity of the peaks is different from that of the raw powder material, likely due to the preferential alignment of the anisotropic particles during electrode assembly. The absence of additional peak formation in Fig. 4.A. demonstrates that no phase change occurs upon electrode operation. Alternatively, a gradual shift of the peaks supports a solid solution mechanism, consistent with the linear GCPL profile observed before [29,30]. Additionally, the relatively small shift of the peaks indicates small volume variations

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Fig. 4. A. In situ XRD of $H_2TiNb_6O_{18}$ cycled between 3.0 and 1.0 V at 0.005 $A.g^{-1}$. Charge /discharge and two 2 θ ranges curves are shown. B. Evolution of cell parameters as a function of time during charge/discharge process.

[30,31]. This shift arises from a gradual change in the distances between atoms due to changes in the oxidation state of Nb and/ or Ti. Additionally, a more scrupulous observation shows the shifting of (00 *l*) reflections, while others remain almost constant, indicating a preferential lithium insertion along [0 0 1] direction.

Fig. 4B shows the unit cell evolution over the first discharge cycle. As calculated from Full Pattern Matching refinements, an initial pronounced decrease in the *a* parameter is observed. This effect is coincident with the removal of H₂O from the crystal structure at the beginning of the first reductive polarization. In fact, the water molecules have an influence on the stability of the structure as well as on electrostatic force of the protons with respect to the (TiNb₆O₁₈) skeleton. A hypothesis may be that the *a* parameter is modified to compensate the water molecule removal during the first cycle. After this initial change, no significant volume changes occur in the *a* parameter. Alternatively, a continuous increase in the *c* dimension over lithiation was determined, which is observed, while *a* stays relatively constant. Overall, the effect of volume expansion/contraction during the first cycle does not exceed 1%.

4. Conclusion

The motivation to find new negative electrode material for LIBs inspired the examination of unstudied structures previously reported in the literature. Here, $Rb_2Nb_6TiO_{18}$ was selected as a potential candidate based on its hexagonal tunnel structure, as well as the high amount of edge sharing octahedra. The investigation by Le Bail refinement and TEM has allowed a clear description of the materials. Moreover, for the first time, cationic exchange of $Rb_2Nb_6TiO_{18}$ with H_3O^+ was reported. Electrochemical measurements of $Rb_2Nb_6TiO_{18}$ electrode show a weak

electrochemical activity, while Li ion insertion is clearly depicted in the protonated phase $H_2Nb_6TiO_{18}$ · $2H_2O$ A specific capacity of 118 mAh.g⁻¹ is reported at 0.02 A.g⁻¹ between 3 V and 1 V vs Li/Li⁺. This impressive difference between $Rb_2TiNb_6O_{18}$ and $H_2TiNb_6O_{18}$ · $2H_2O$ capacity highlights the importance of the nature of the cations in the ability to insert alkali ions in this type of structure. *In situ* XRD measurement showed no phase changes, indicating a solid-solution charge storage mechanism. Additionally, $H_2Nb_6TiO_{18}$ · $2H_2O$ exhibits a minor volume expansion (1%) over Li⁺ insertion along (001).

CRediT authorship contribution statement

Jeronimo Miranda: Investigation, Methodology, Writing – review & editing. Etienne Le Calvez: Investigation, Methodology, Writing – review & editing. Richard Retoux: TEM images. Olivier Crosnier: Conceptualization, Methodology, Supervision, Writing – review & editing. Thierry Brousse: Conceptualization, Methodology, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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2. Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄

Charge storage mechanism insight the hexagonal tungsten bronze: the case of $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$.

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Charge storage mechanism insight the hexagonal tungsten bronze: the case of H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄

Etienne Le Calvez^{1,2}, Julio César Espinosa-Angeles^{1,2}, Eric Gautron¹, Eric Quarez¹, Olivier Crosnier^{1,2}, and Thierry Brousse^{1,2}*

¹ Nantes Université, CNRS, Institut des Matériaux Jean Rouxel, IMN, F-44000 Nantes, France ² Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR 3459, 33 rue Saint Leu, 80039 Amiens Cedex, France

Abstract

Oxides derived from the ReO₃ structure, such as bronzes or Wadsley-Roth phases, have reemerged from the past as they offer very attractive properties as negative electrodes for high power Li-ion batteries. Here we revisit the hexagonal bronze $C_{80,5}Nb_{2,5}W_{2,5}O_{14}$ and its protonated $H_{0,25}C_{80,25}Nb_{2,5}W_{2,5}O_{14}$ phase obtained after ion exchange. A characterisation by HAADF-STEM, EDX and XRD revealed a specific cation ordering in the material and a preferential ion exchange in the heptagonal tunnels of this oxide. When used as Li-ion battery electrodes, $H_{0,25}C_{80,25}Nb_{2,5}W_{2,5}O_{14}$ exhibits higher specific capacities as well as wider capacity retention at high currents than $C_{80,5}Nb_{2,5}W_{2,5}O_{14}$. The protonated phase provide specific capacities of 132 mAh.g⁻¹ and 111 mAh.g⁻¹ at respectively, 0.02 A.g⁻¹ and 0.2 A.g⁻¹. Kinetic analysis reveals that the good capacity at high rate is due to favourable diffusion of lithium ions into $H_{0,25}C_{80,25}Nb_{2,5}W_{2,5}O_{14}$. In addition, *in situ* XRD and *ex situ* HAADF-STEM were employed to reveal the solid solution mechanism happening during lithium insertion as well as the different lithiation sites of the material.

Introduction

For a swift development of electric vehicles, it is critical that the battery systems used can be charged fast without losing range, safety, and life span.¹ The chemistry of the materials involved in here takes the spotlight. The aim is to develop electrodes that can electrochemically store a large amount of charges within a short time.² Therefore, the target would be the design of a Li-ion battery which can be charged only in a few minutes.^{3,4} Thus, various solutions have been proposed to improve the charging speed of these batteries, particularly the replacement of the negative graphite electrodes, which limits the full potential of this feature. Indeed, Li⁺ ions are inserted into graphite at a potential close to the one of the redox couple Li⁺/Li.⁵ This characteristic, for the case of rapid charging, can be detrimental to the battery. An higher rate

of charging can lead to a potential below 0 V *vs*. Li⁺/Li and thus lead to the growth of lithium dendrites at the electrode, which will cause malfunctioning of the system attempting to the safety of the device.^{6–8} Moreover, considering that the charge storage mechanism dominating in graphite is intrinsically limited by the diffusion of lithium ions, it will translate to a low capacity at rapid charging. Therefore, this will reduce the energy delivered by the system.¹

The most promising approach to replace graphite appears to be the use of transition metal oxides operating at a potential above 0.8-1.0V *vs*. Li⁺/Li. They not only prevent the growth of lithium dendrites but also the formation of SEI, which drains lithium ions from the electrolyte. Lithium ion depletion would damage the ionic conductivity of the electrolyte, which is an important feature to take into account for fast charging devices.⁹ Nowadays, oxides such as Li₄Ti₅O₁₂ are marketed as negative electrodes in power batteries.^{10–12} However, the low relative specific capacity offered by Li₄Ti₅O₁₂ has led researchers to look elsewhere. Both electronic and ionic conductivity are key attributes to enhance these electrodes power performance.

Reducing the particle size increases the electronic and ionic conductivity, but decreases the volumetric density of the batteries due to the lower real density.^{13–16} The creation of cationic vacancies and fluorine or chlorine doping are also promising ways to increase power density.¹⁷⁻ ¹⁹ On the other hand, finding new materials with intrinsic good ionic and electronic conductivity seems interesting. In this sense, Goodenough's group proposed TiNb₂O₇ in 2011.²⁰⁻²² This is a so-called Wadsley-Roth material because it has blocks of octahedra (MO₆) organised similarly as ReO₃, and these blocks share their edges forming a 3D structure. These type of blocks are promising to provide fast lithium ion transport.^{23–26} As early as 1983, R.J. Cava had identified the potential of these materials in several papers describing the insertion of lithium ions into the so-called Wadsley-Roth materials.^{27–29} More recently, Griffith et al. propose two materials with exciting electrochemical properties for fast charging. A Wadsley-Roth oxide (Nb₁₆W₅O₅₅) and a tetragonal bronze (Nb₁₈ $W_{16}O_{93}$) both showing extraordinary electrochemical properties.³⁰ In the early 1950s, Magnéli et al. studied the crystallography of tungsten bronzes and quickly realized the tremendous variety of crystallographic forms that exist.^{31–33} Bronzes can have tetragonal, hexagonal tunnels, or both in the case of materials with intergrowths.^{34–37} They can also be made of different transition atoms (W, Nb, Ta, Ti, Mo, V...).³⁸⁻⁴² This large family of materials has been less studied than the Wadsley-Roth oxides as negative electrodes for fast charging batteries.

For all the reasons presented here, this paper reports on the study of a never before investigated hexagonal tungsten bronze as a negative electrode for Li-ion batteries, Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄. This oxide is examined in the form of micrometric particles in order to maintain a good volumetric energy density. In addition, ion exchange was studied for the first time on this material to exchange cesium ions with protons. This method has proven to be an effective way to obtain better-performing electrode materials.⁴³ The characterization of the material before and after ion exchange by HAADF-STEM, EDX, and powder XRD shows a selective exchange of certain cesium. The electrochemical characteristics of these materials were studied by galvanostatic and CV measurements. Finally, *in situ* XRD and IDPC HAADF-STEM measurements have conducted an analysis of the charge storage mechanism and on the different lithiation sites, respectively.

3. Experimental section

a. Synthesis of Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄ and H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄

 $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ was synthesized by mixing Cs_2CO_3 , Nb_2O_5 , and WO_3 in a stoichiometric ratio. After grinding the compounds for 10 minutes to ensure a good mix of particles, the resulting powder is introduced into a platinum crucible and calcined at 1000°C for 48h. To obtain the $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ phase, 1 g of the $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ powder is placed in 200 mL of an aqueous solution of 3M HNO₃ for three days. The acidic solution is changed daily to promote a favorable ionic exchange.

b. Characterization i. Powder X-ray diffraction

X-ray diffraction (XRD) pattern was collected using a PANalytical X'Pert Pro diffractometer (Malvern Panalytical, Almelo, Netherlands). X'Celerator detector with Cu-K_{α 1}-K_{α 2} (λ = 1.54060, 1.54439 Å) radiation was used acceleration voltage and current were 40 kV and 40 mA, respectively. With a step scan of 0.0167°, diffraction patterns were collected between 20° and 90° (20). Le Bail refinements were performed with using a Pseudo-Voigt function for the peak profile.⁴⁴ *In situ* XRD patterns were collected using a homemade Leriche-like cell.⁴⁵ During charge-discharge experiments, a current of 0.02 A.g⁻¹ was applied for 60 minutes and then stopped for 30 minutes for XRD pattern acquisition.⁴⁵

ii. Scanning electron microscopy

Scanning electron microscopy (SEM) images were obtained using a Zeiss Merlin instrument and chemical analysis with EDX using X-max, detector 50 mm² at a working distance of 8 mm on the same device.

iii. Scanning/Transmission electron microscopy

Scanning/Transmission electron microscopy (S/TEM) was performed to characterize the structural changes of the phases $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ and $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$. Powders were dispersed in ethanol and then deposited on a holey carbon film coated copper grid before insertion in a probe-corrected S/TEM Themis Z G3 (Thermo Fisher Scientific). TEM micrographs were collected at 300 kV using a OneView CMOS camera (Gatan).High-angle annular dark-field (HAADF-STEM) images were acquired at 300 kV, with 20 mrad convergence angle and 39-200 mrad collection angles.

iv. Electrochemistry

To assess the electrochemical behavior of the materials, self-supported electrodes were prepared by mixing, in a small amount of ethanol, 75% w/w $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ (or $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$), 15% w/w of conductive carbon (Carbon Black by Superior Graphite, Chicago, IL, USA) to increase electronic conductivity and 10% w/w poly 1,1,2,2-tetrafluoroethylene dissolved in water (PTFE, Sigma Aldrich) to form a homogeneous paste. Then, the mixture was placed into a mortar to homogenize the composite paste and then cold-rolled until the obtention of electrodes with a mass loading of about 5-10 mg.cm⁻² according to previous recommendations.⁴⁶ Using Swagelok [®] cells, electrochemical measurements were performed by separating working electrode, and metallic lithium (99.9%, Aldrich) with a glass fiber membrane (70 mm, 10 mm diameter, GF/D Whatman) soaked with 1 M LiPF₆ dissolved in 1:1 % wt. EC/DMC (Solvionic, France, battery grade purity). The Swagelok cells were assembled in a glove box containing less than 0.1 ppm of O₂ and H₂O. VMP3 potentiostat (from Biologic run under ECLab software version V11.36) was used for electrochemical measurements.

4. Materials characterization

 $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ shows a hexagonal tungsten bronze structure, as it can be seen in Figure 1. Derived from the ReO₃ structure, this oxide is formed by (MO₆) octahedra connected

via their corners. In the center of a tunnel created by five octahedra (MO_6), a metal cation forms a pentagon bipyramidal (MO_7), shown in violet in Figure 1. The edge-sharing connection between the octahedra and the pentagon bipyramidal forms a compact structure frequently observed for Nb-W oxides.³⁶ Such as skeleton forms 6-sided hexagonal and 7-sided heptagonal tunnels where alkali Cs⁺ cations can be located.^{47–49} Around the five octahedra creating the pentagon bipyramidal, the 6- and 7-sided tunnels are arranged successively in the order 6-7-6-7-7. One distorted (MO_6) octahedron connects two 7-sided tunnels. Moreover, 3-sided octahedral tunnels are formed. However, they are too small to accommodate Cs⁺ inside.



Figure 1. Crystal structure of Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄ showed with four unit cells projected along c axis. It is built from (MO₆) octahedra and (MO₇) pentagon bipyramidal creating hexagonal and heptagonal tunnels. Crystal structure is shown with the use of VESTA.⁵⁰

 $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ was introduced into an aqueous solution containing 3M HNO₃, as described in the experimental section. The ion exchange for $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ has been reported previously, although without a clear characterization of the resulting crystal structure or the amount of cesium cations exchanged.⁵¹ Considering that the structure of $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ was solved for the first time by electronic microscopy³⁸, HAADF-STEM was used to verify the ion exchange feasibility of this phase.



Figure 2. (A-C) Experimental HAADF-STEM image (Radial Wiener Filtered) of $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ and $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ respectively, viewed along [001] (scale bar: 1 nm). Inset : simulated HAADF image (Dr Probe⁵², using ICSD file #110708⁴⁸ as input structure. (B-D) EDX map of Cs_{0.5}Nb_{2.5}W_{2.5}O_{14} and H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14} respectively. These figures show the replacement of Cs⁺ by H⁺ in the heptagonal tunnel when Cs⁺ stay in the hexagonal tunnel. In the green square, the calculated images based on literature data can be observed.

Figure 2.C shows the HAADF-STEM images of $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ after the ion exchange. It is observed that the skeleton of the structure remains unchanged with both octahedra (MO₆) and pentagon bipyramidal (MO₇). However, we can distinct the absent of some Cs cations in the heptagonal tunnels, on the contrary, those located in the hexagonal tunnels seem to remain in the structure. According to our understanding, if Cs⁺ located in octahedral tunnels cannot be exchanged easily, consequently they are more anchored to the structure and its stability. No experiments under more drastic conditions (such as a higher temperature) were performed to verify whether it is possible to exchange these Cs⁺ ions. Therefore, the question remains opened. Moreover, protons replace half of the cesium ions,

possibly accompanied by one or more water molecules. The new oxide corresponds to the chemical formula $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$. EDX images captured from the same spot confirms the absence of cesium ions in the heptagonal tunnels and their presence in the hexagonal tunnels. The niobium/tungsten distribution seems to be conserved giving another evidence that ion exchange only modify the amount of cesium in the phase. SEM images before and after ion exchange in Figure S3 show that the ion exchange does not cause any cracking or delamination as particles size and morphology are very similar.

Hence, Figure 2.A shows HAADF-STEM image of Cs0.5Nb2.5W2.5O14 powder before ion exchange. This image confirms the structure proposed in the literature. Indeed, the green square in Figure 1.A corresponds to the refined calculated structure already reported by Weirich et al. and it fits well with our image.⁴⁸ The hexagonal bronze skeleton with tunnels formed by 6 or 7 octahedra can be clearly seen. Moreover, we can demonstrate the presence of Cs⁺ thanks to the whitish contrast of the spheres observable inside both hexagonal and heptagonal tunnels.⁴⁹ To better understand the possible cation ordering of Nb⁵⁺ and W⁶⁺, EDX on the HAADF-STEM image was performed for the first time (Figure 2.B). There is no doubt that niobium cations (in red) appear to be located at specific sites. The cation in the center of the pentagon bipyramidal is predominantly niobium. In addition, the octahedra separating the two heptagonal tunnels contain also a niobium atom. Tungsten ions appear to be preferentially located on octahedra that are less distorted, as those forming pentagonal units. Although it is complicated to determine with accuracy the ratio of Cs⁺ ions in each tunnel, the EDX image shows that both sites are indeed occupied and equally filled with Cs⁺. Moreover, in the case of tungsten bronzes but also of the so-called Wadsley-Roth structures, many publications report the observation by HRTEM of inter-growth of different phases.^{36,37,53,54} In the case, and as it can be seen in the enlarged HAADF-STEM image Figure S1, a considerable continuity of the crystal lattice can be observed without obvious intergrowth with different bronze phases.

To further characterize this new material ($H_{0.25}Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$) and more precisely, to quantify the amount of water inserted found with protons, thermogravimetric analysis (TGA) was carried out. As it is shown in Figure S3, different mass losses are observed between $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ and $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ in the range of 100° to 900°C. Considering that the initial mass loss is due to chemisorbed water molecules, we found a different mass loss of 0.51% at 700°C. Furthermore, the molar mass ratio of 0.25 water molecule per $H_{0.25}Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}, 0.25 H_2O$ (4.5/953.6 g.mol⁻¹) is 0.47%. These results provide the

evidence that each proton are inserted with approximately one water molecule into the heptagonal cages as already reported in the case of close structures.⁴³



Figure 3. Le Bail refinement of (A) Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄ (Rp = 3.71 %, wRp = 6.73 %) and (B) H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄ (Rp = 4.18 %, wRp = 6.48 %).

Lastly, powder X-ray diffraction (XRD) patterns were collected to compare crystallographic structure of both Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄ and H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄. As expected from the small difference observed in the HAADF-STEM images, two almost identical patterns were obtained (see Figure S5.(A-B)). Moreover, Le Bail refinement was performed. Initially, to represent their new phase, Lundberg and Sundberg used the orthorhombic $P2_12_12$ space group (n° 18). ³⁸ More recent studies consider that more symmetric space group (Pbam, n°55) can better describe the unit cell symmetry.^{47,48} For our refinements, P2₁2₁2 space group was used to describe both Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄ and H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄. The initial refinements in the Pbam space group led, in both cases, to significantly worse agreement factors. These incorrect refinements are mainly due to the poor fit of the diffraction peak around $2\theta = 28^{\circ}$. This peak can be adequately fitted by the 501 reflection which is forbidden by the Pbam space group but allowed by the $P_{2_12_12}$ space group. The refinements were therefore performed in the P2₁2₁2 space group, and led to a better fit to the experimental data. Results of Le Bail refinements made from Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄ and H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄ patterns are presented in Figure 3 with the corresponding cell parameters and volume. Interestingly, cell parameters and volume are found to be extremely close with 0.06% of volume difference between the two compounds. This result confirms the observations from HAADF-STEM, the ion exchange carried out only replace the cesium from heptagonal tunnels without changing the crystallographic structure of the materials in contrast with the layered materials like KTiNbO₅

or KLaNb₂O₇,where a significant decrease of the interlayer distance is observed, due to the exchange.^{55,56}

5. Electrochemistry

Then, the electrochemical behavior of $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ and $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ was first evaluated by galvanostatic experiments at different current densities between 1.0V and 3.0V vs Li⁺/Li. Figure 4.A shows the results obtained in the case of $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$, and Figure 4.B displays the protonated $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ phase. A similar charge profile is observed for both phases, at the first lithiation with a small plateau at 1.8V followed by a constant decrease of the electrode potential as a function of the capacity. The small additional and irreversible plateau at 1.6V only observed in the case of $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ could be attributed to irreversible water reduction. A low coulombic efficiency is noticed during the first cycle. 70% and 78% capacity retention between the first charge and the first discharge is seen in the case of $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ and $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ respectively. This feature is often observed for materials with similar crystallographic structures^{30,43,57}. Interestingly, despite the irreversible water reduction, a higher coulombic efficiency is observed in the case of $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$. This demonstrates a more reversible process during the first reduction for $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$.



Figure 4. Galvanostatic charge-discharge curves at different current densities in potential range of 3.0V to 1.0V for vs Li⁺/Li (A) $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ and (B) $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$. (C) Specific capacity *vs* cycle number at different current densities for both $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ and $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$.

The real difference between the two materials is to be found in the capacity values observed at low and high current densities. Indeed, at low current (0.02 A.g^{-1}), the capacities extracted for $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ and $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ are 101 and 132 mAh.g⁻¹ respectively. For a relatively high current such as 0.2 A.g^{-1} , the difference in capacity increases even more with 68 mAh.g⁻¹ compared to 111 mAh.g⁻¹, in the case of $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$.

Relatively speaking, the differences increase again when considering the extremely high current density case. At 2.0 A.g⁻¹, a capacity of 61 mAh.g⁻¹ for H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄ is obtained, contrarily to the only 15 mAh.g⁻¹ of the same material before the ion exchange. Figure 4.C shows then the capacities of these two materials at all density currents applied, where the large differences in specific capacity are clearly noticeable. Due to their very close molar mass, the theoretical capacities of the two powders are very close, 134 and 136 mAh.g⁻¹ for Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄ and H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄, respectively. These calculations were made considering the exchange of one electron per transition metal (TM), Nb and W. Thus, when Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄ inserts only 0.75 e⁻/TM, almost 1e⁻/TM is introduced in the protonated oxide at 0.02A.g⁻¹. The reason why the proton phase exhibits higher specific capacities is due to the absence of cesium in the heptagonal tunnels that allows more lithium ions to be inserted inside the host material. In addition, lithium ions seem to diffuse easily into the heptagonal cages, as the proton might play a role in this mechanism.⁵⁸

Being the protonated phase ($H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$) the more appealing one among the two already seen, we decided to keep exploring such a phase to better understand the different insertions mechanisms in this material. Therefore, we began performing cyclic voltammetry (CV) at different scan rate. Although it is a simple technique; it is widely used to understand kinetic phenomena of similar materials.^{59,60} Figure 5A shows a CV where an extremely broad peak between 1.0 V and 2.0 V *vs.* Li⁺/Li is observed, corresponding to a very common CV for those insertion materials containing niobium as an electroactive cation.^{60,61}



Figure 5. (A) CV at different scan rate between 1.0V and 3.0V vs Li⁺/Li for $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14.}$ (B) Specific capacity vs scan rate at different current densities for $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14.}$ (C) Specific current in function of scan rate and the corresponding linear fit for determination of b value for $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14.}$

Moreover, one can observed the very similar quasi-rectangular shape for both 0.1 mV/s and 2 mV/s sweep rates without exhibiting any resistive behavior. In addition, a relative small

capacity loss of 27% is observed between 0.1 mV.s⁻¹ and 2 mV.s⁻¹ (20 times faster), see Figure 5.B, with 33% capacity retention at 20 mV/s (200 times faster the rate). We can take advantage of such experiments and calculate the b-value using the Equation. 1, as already reported several times by Dunn *et. al.* ^{1,59,60} providing a better idea of the lithium diffusion in the bulk of the oxide. Figure 5.C shows the result of our calculation and as it is shown the calculated b-value approaches to 0.94 and, according to the literature the closer the b-value is to 1 the closer to the electrochemical behavior of a "capacitor", meaning a very weak influence of ion diffusion in the material involved. Because of the b-value calculated in the phase presented in here is in fact closer to 1, we can attribute a charge storage mechanism of a "pseudocapacitive intercalation" phenomenon, which actually explains both the peaks involved in the CV as well as the "rectangular" shape.^{1,59,62}

$i = a. v^b$

Equation 1

where i is the intensity of reduction/oxidation peak, v the corresponding scan rate, a and b are constant values.

To shed more light on the charge storage mechanism of the protonated phase, and moreover establishing a possible lithium insertion into the material we decided to perform *in situ* XRD to follow the structural changes over the charge/discharge cycles. The experiment was carried out at 0.02 A.g⁻¹ and the result of the first two cycles is depicted in Figure 6. It is worth mentioning that the relative intensity of the peaks is found to be different when compared to the XRD of the raw powder, most likely due to the preferential alignment of the anisotropic particles over the electrode preparation.



Figure 6. In situ XRD patterns of H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄ at a current of 0.02 A.g⁻¹ between 1.0V and 3.0V vs Li⁺/Li with (A) voltage-time curve, (B) in situ XRD patterns at corresponding potential in range of 20° - 50° and 25° - 30° .

During the first lithiation there is not further changes in the initial reflections. Since no new reflections seem to appear, it is consistent with a solid solution mechanism where the lithiation does not lead to any phase changes. However, one must notice the shift of the peaks in the patterns, which actually confirms the insertion of lithium cations into the open tunnels of the protonated powder. The new arriving cations will cause the pristine structure to swell. This shifting appears to be reversible, thus, to confirm such a reversibility Le Bail refinements were carried out in all *in situ* patterns. These results are shown in Figure 7.(A-B), where the evolution of the cell parameters and volume upon charge/discharge of the first cycle is displayed. It is observed that such swelling only takes place along the *ab* plane, where both *a* and *b* increase slightly whereas along the *c* direction does not change at all. This shows the anisotropic insertion of lithium in the structure. Details of the refinements of the pristine materials, fully reduced to 1.0V vs Li⁺/Li and re-oxidised to 3.0V vs Li⁺/Li are available in Figure S6.



Figure 7. Variation of (A) cell parameters and (B) unit cell volume during the first charge and discharge process in H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄ electrode.

Between the pristine electrode and the electrode at 1.0V, the change in parameters a, b and c is about 2.5%, 2.3% and 0.1% respectively. The insertion of lithium ions will slightly extend the size of the tunnels in the *ab* plane, increasing the parameters *a* and *b* but the parameter *c*, which is the average size of two opposite corners of an octahedron (≈ 4 Angstroms), remains practically unchanged. An almost constant increase in cell volume results in a reasonable growth of ~5% of cell volume. This is consistent with the percentage reported for the bronze phases and Wadsley-Roth materials.^{30,63} Interestingly, a good reversibility of the structure is observed upon oxidation up to 3V and during the following cycle in $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ (Figure S6.A-C).

Conclusion

In summary, this work examines for the first time the result of ion exchange on acidic media performed on $C_{s_{0.5}Nb_{2.5}W_{2.5}O_{14}}$. HAADF-STEM has shown that despite the presence of cesium ion in the hexagonal and heptagonal sites prior to ion exchange, only half of the cesium are extracted, those in the heptagonal tunnels. The resulting material is then $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$. In addition, the use of the same technique revealed some cation ordering in the Nb and W sites. When niobium ions are predominantly present in the bipyramidal pentagons, tungsten ions take their place in the less distorted octahedra, those forming the hexagonal tunnels. Le Bail refinement reveals that the structure of the both, $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ and $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$, are almost similar with extremely close cell parameters.

On the contrary, a major difference in Li^+ insertion properties is observed between the two materials. $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ provides much higher specific capacities than its equivalent before ion exchange. Specific capacities of 132 and 111 mAh.g⁻¹ are found for $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ at respectively 0.02 and 0.2 A.g⁻¹. This better electrochemical behavior is mainly attributed to the size difference between cesium ions and protons enabling the formation of a larger number of lithiation sites as well as an enhanced ionic diffusion within the heptagonal tunnels. Also, the mechanism governing charge storage was revealed through the use of *in situ* XRD. During the whole lithiation/delithiation process, a solid solution mechanism is involved resulting in a relatively small increase of the cell volume of about 5%.

The authors consider that it is of interest to revisit this type of material with known crystallographic structures to rediscover oxides of interest for future generations of Li-ion batteries. In addition, a study of materials such as W₃Nb₂O₁₄, a tetragonal bronze, may be of great benefit to understand the influence of structure and the presence of alkali ions and/or protons on the charge storage of this family of materials.

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Figure S1. HAADF-STEM images of $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ at lower magnification showing the absence of defects in the crystal arrangement.

Supporting Information (SI)



Figure S2. Crystallographic structure of H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄



Figure S3. SEM images of (A) Cs0.5Nb2.5W2.5O14 and (B) H0.25Cs0.25Nb2.5W2.5O14



Figure S4. TGA of Cs0.5Nb2.5W2.5O14 and H0.25Cs0.25Nb2.5W2.5O14



Figure S5. (A-B) XRD pattern of both Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄ and H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄ showing the small difference between the two patterns (before and after ion exchange).



Figure S6. Le Bail refinement of (A) pristine electrode $H_{0.25}Cs_{0.25}Nb_{2.5}Wb_{2.5}O_{14}$, (B) $H_{0.25}Cs_{0.25}Nb_{2.5}Wb_{2.5}O_{14}$ electrode after first reduction at 1.0V vs Li/Li⁺ and (C) $H_{0.25}Cs_{0.25}Nb_{2.5}Wb_{2.5}O_{14}$ electrode after first oxidation at 3.0V vs Li/Li⁺

III. Conclusion et perspective

Ce dernier chapitre nous a permis de mettre en lumière deux structures cristallographiques originales qui permettent après un échange ionique d'insérer des ions lithium dans leurs tunnels respectifs.

Pour la première fois, nous avons démontré l'échange ionique total du rubidium dans Rb₂Nb₆TiO₁₈. Ainsi, il est possible d'échanger les deux ions rubidium de la structure par des protons accompagnés par des molécules d'eau donnant lieu au matériau H2Nb6TiO18. Ce matériau peut insérer environ 3.6 $Li^+/H_2Nb_6TiO_{18}$ à une densité de courant de 0.02 A.g⁻¹ quand son analogue au rubidium n'insère qu'1.2 Li⁺ à densité de courant égale. Durant le processus de lithiation/délithiation, la variation du volume dans H₂Nb₆TiO₁₈ est seulement de 1%. Ceci est expliqué par la forte compacité du squelette (TiNb₆O₁₈) ainsi que la large taille des tunnels qui permettent une lithiation du matériau n'engendrant pas de fortes modifications de la structure des octaèdres (NbO₆) et (TiO₆). Les matériaux ne présentant pas ou un très faible changement de volume durant la lithiation sont appelés « zero strain materials » et sont considérés comme d'intérêt pour des applications dans les batteries de puissance et dans les batteries tout-solide. Cependant, les capacités gravimétriques de H2Nb6TiO18.2H2O, que ce soit à faible ou à fort courant de charge/décharge sont largement plus faibles que Ti₂Nb₂O₉ ou encore HTiNbO₅ malgré un échange ionique et une structure prometteuse. Par exemple, à 0.02 A.g⁻¹, HTiNbO₅ SS et Ti₂Nb₂O₉ SG proposent des capacités spécifique de 225 mAh.g⁻¹ et 230 mAh.g⁻¹ respectivement, quand H₂Nb₆TiO₁₈ possède une capacité spécifique de 118 mAh.g⁻¹.

D'autre part, les propriétés d'échanges ioniques du matériau de Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄ ont été étudiées pour la première fois. Ainsi, il a été démontré une substitution partielle des ions Cs⁺ par des protons. Les images HRTEM démontrent que les ions césium sont principalement extraits dans les sites formés par des cages heptagonales. Par EDX, il a été estimé qu'environ la moitié des ions césium ont été remplacés par des protons accompagnés de molécules d'eau donnant lieu au matériau H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄.0.25 H₂O. De manière similaire à Rb₂Nb₆TiO₁₈, la phase protonée propose une plus large capacité spécifique et une meilleure rétention de capacité pour des charges rapides. Dans le cas de H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄, des capacités spécifiques de 164 mAh.g⁻¹ et 78 mAh.g⁻¹ à respectivement 0.02 A.g⁻¹ et 0.5 A.g⁻¹ tandis que des capacités plus faibles de 145 mAh.g⁻¹ et 27 mAh.g⁻¹ sont observées pour Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄ aux mêmes densités de courant. Il a également été démontré que le matériau propose un *b value* (paramètre b) proche de 1, ce qui semblerait indiquer un mécanisme de charge faiblement limité par la diffusion des ions dans les tunnels du matériau (*pseudocapacitive intercalation*). Dernièrement, une analyse par DRX *in situ* explicite un mécanisme de lithiation par solution solide avec un changement de volume entre la phase lithiée et la phase initiale d'environ 8%.

Plusieurs autres méthodes d'analyses vont être utilisées sur ces matériaux pour mieux comprendre les mécanismes de lithiation dans ces phases méconnues dans la littérature. Ainsi, l'utilisation de *ex situ MAS NMR* au ⁶Li ainsi que du *ex situ HRTEM* vont permettre de mettre en lumière les différents sites de lithiation dans ces phases.

IV. Ouverture

Une grande chance m'a été donnée de pouvoir travailler dans le laboratoire du Prof. Bruce Dunn pendant 2 mois (25 Avril 2022 – 21 Juin 2022). Dans le cadre de ce séjour, j'ai travaillé en étroite collaboration avec un doctorant, sur le développement de matériaux à base de niobium, de tungstène mais également de molybdène. Nous avons développé deux familles de matériaux ayant des propriétés électrochimiques intéressantes.

Une famille de bronze tetragonaux a été synthétisée ($M_3Nb_2O_{14}$ (M= Mo, W, $Mo_{0.5}W_{0.5}$)) ainsi qu'une famille d'oxydes de Wadsley-Roth ($M_3Nb_1AO_{44}$ (M= Mo, W, $Mo_{0.5}W_{0.5}$)). Ces deux familles de matériaux dénotent des précédents matériaux étudiés car ils ne possèdent pas d'ions alcalins pouvant être échangés. Cependant, les stœchiométries du bronze hexagonal $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ et des bronzes tetragonaux $M_3Nb_2O_{14}$ autorisent une comparaison qui permet de mettre en lumière l'influence des Cs^+ et des H_3O^+ dans les mécanismes de stockage de charge impliqués dans ce type de matériau. La communion des savoir-faire et de la connaissance entre l'IMN et UCLA a permis de partager un grand nombre de techniques de caractérisations. Ainsi, la DRX *in situ*, la calorimétrie *operando*, la mesure du potentiel entropique, des mesures XANES *operando* ou bien encore de la RMN *ex situ* a permis de comprendre dans son ensemble les mécanismes de stockage de charge et l'influence des techniques. Ces résultats obtenus dans le cadre de ce séjour à UCLA seront présentés lors de ma soutenance.

V. Bibliographie

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Conclusion générale

Pour permettre le déploiement de batterie se chargeant en quelques minutes et présentant une densité d'énergie relativement élevée, il semble essentiel de trouver de nouveaux matériaux pour remplacer le graphite et les oxydes à base de cobalt et de nickel commercialement très répandus dans les batteries Li-ion actuelles. Durant cette thèse, différentes stratégies ont été mises en place pour proposer des matériaux pouvant potentiellement remplacer les actuelles électrodes positives et négatives, notamment pour les batteries de puissance.

Ainsi, le premier chapitre se concentre sur le remplacement de l'électrode positive par une électrode composite présentant un matériau non lithié utilisé comme matériau actif (Ag₂V₄O₁₁) ainsi qu'une molécule organique lithiée et sacrificielle (Li₂DHBN). Une preuve de concept du fonctionnement de ce genre de système a été établie.

Ensuite, ce travail de thèse s'est tourné vers les oxyde de niobium pour remplacer l'électrode négative. En collaboration avec le Prof. Bruce Dunn spécialiste des oxydes de niobium pour les batteries de puissance, la substitution partielle des ions argent par des ions lanthane dans une structure pérovskite a permis la formation de lacunes cationiques. Des sites de lithiation sont alors créés dans le matériau. Le matériau Ag_{1-3x}La_{x□2x}NbO₃, synthétisé par voie sol-gel, a été proposé comme matériau modèle pour le stockage rapide des ions lithiums.

Dans un but similaire à la formation de lacunes par substitution cationique, des échanges ioniques dans les matériaux KTiNbO₅, $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$ et $Rb_2Nb_6TiO_{18}$ permettent le remplacement des ions alcalins par des protons ou des H_3O^+ donnant respectivement lieu aux matériaux HTiNbO₅, $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$, $H_2Nb_6TiO_{18}$. Ces derniers proposent une capacité plus élevée comparativement à leurs analogues possédant des ions alcalins (K⁺, Rb⁺, Cs⁺). Cette stratégie s'est montrée concluante dans le cas de matériau lamellaire (KTiNbO₅) comme reporté précédemment dans la littérature mais également pour des matériaux plus compacts présentant des structures tunnellaires ($H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ et $H_2Nb_6TiO_{18}$.). Dernièrement, la déshydratation de HTiNbO₅ a permis la formation d'un matériau possédant des tunnels pentagonaux, Ti₂Nb₂O₉, qui démontre d'excellentes propriétés électrochimiques quand il est synthétisé par voie sol-gel.



(A) Capacité spécifique et (B) capacité relativement à la capacité à 0.02 A.g⁻¹ en fonction du courant imposé pour les principaux matériaux d'électrode négative développés dans le cadre de cette thèse.

Comme indiqué dans la Figure ci-dessus, une comparaison des principaux matériaux d'électrode négative développés est proposée comme un résumé non exhaustif de cette thèse. On remarque dans le graphe de gauche (A) que le matériau présentant la capacité spécifique la plus importante à n'importe quel courant est le matériau Ti₂Nb₂O₉ (synthétisé par voie sol-gel). A fort courant, HTiNbO₅ et H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄ montrent des capacités relativement élevées et similaires. Cependant, la densité plus élevée de H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄ permet d'obtenir des capacités volumiques supérieures comparativement à HTiNbO₅ mettant en avant l'intérêt des matériaux ayant une forte compacité pour le stockage électrochimique de l'énergie. Enfin, le graphe de droite (B) confirme que malgré les faibles capacités spécifiques des oxydes Ag_{1-3x}La_{x□2x}NbO₃, l'impressionnante rétention de capacité qu'ils démontrent semble confirmer leurs intérêts comme matériaux modèles pour les électrodes de batteries Li-ion de puissance.

Le grand nombre de matériaux proposés dans cette thèse permet également de mettre en avant la difficulté d'obtenir des matériaux combinant une haute densité d'énergie et une forte densité de puissance. L'objectif majeur qui est de trouver des matériaux pouvant stocker rapidement un nombre maximum de charge est limité par le compromis intrinsèque qui semble exister entre la puissance et l'énergie dans les systèmes électrochimiques tels que des batteries, les supercondensateurs ou encore les *Li-ion capacitors*. Cependant, l'étude de l'ensemble de ces matériaux montre que c'est en passant par la chimie du solide, c'est-à-dire le design d'un

matériau proposant les meilleurs propriétés d'un point de vue cristallographique, que de futures applications dans les batteries de puissance pourront réellement se développer.

D'un autre point de vue, le grand nombre de techniques de caractérisation avancées utilisées durant cette thèse, a permis de mieux comprendre les différents mécanismes de stockage de charge. Par exemple, l'utilisation pour un même matériau de la DRX *in situ* dans ce laboratoire en combinaison avec des mesures de potentiel entropique et de génération de chaleur à UCLA a permis de mieux comprendre l'origine des différences électrochimique dans les différentes synthèses de Ti₂Nb₂O₉. Aussi, l'utilisation de la RMN *ex situ* a mis en avant l'intérêt du proton dans le stockage de charge de HTiNbO₅ ou encore la microscopie électronique à transmission haute résolution qui nous a permis de visualiser l'échange ionique dans H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄ ainsi que la structure cristallographique complexe de cet oxyde.

Plus généralement, cette thèse a permis de créer une nouvelle voie de recherche dans le groupe supercondensateurs de l'équipe ST2E de Nantes. En effet, la recherche de nouveaux matériaux de puissance pour les batteries permet d'imaginer de potentielles applications dans l'industrie mais pourrait également permettre de mieux comprendre la nouvelle vision scientifique proposant une continuité entre les différents mécanismes de charges (EDLC, pseudocapacité, intercalation pseudocapacitive, intercalation classique).⁸

A travers le projet DISCUS, cette thèse a été également l'occasion de renforcer la collaboration entre l'Institut des Matériaux de Nantes Jean Rouxel (plus particulièrement le groupe supercondensateurs) et l'*University of California at Los Angeles*, ce qui était l'un des objectifs de ce projet. De fait, de nombreux spécialistes des batteries de puissance comme Prof. Sarah Tolbert, Prof. Laurent Pilon ainsi que le Prof. Bruce Dunn ont été impliqués dans ces travaux de recherche et ont permis d'apporter leurs expertises sur ce travail de thèse. Il serait hors-sujet de détailler l'ensemble des partenaires et thèses du projet DISCUS (Developing Innovative Integrated Solutions for Sustainable Communities and Urban Systems), mais les avancées de ce travail s'inscrivent dans le développement de solutions innovantes, intégrées et

⁸ Fleischmann, S.; Zhang, Y.; Wang, X.; Cummings, P. T.; Wu, J.; Simon, P.; Gogotsi, Y.; Presser, V.; Augustyn, V. Continuous Transition from Double-Layer to Faradaic Charge Storage in Confined Electrolytes. *Nat. Energy* **2022**, *7* (3), 222–228.

durables répondant à l'interdépendance critique des aliments, de l'énergie et de l'eau dans les systèmes urbains.

Perspectives et point de vue critique sur ce travail de thèse

Dans ces dernières pages, plus personnelles et subjectives, seront développées les perspectives qu'offrent mes travaux de thèse ainsi qu'un point de vue critique et personnel sur ces derniers. Comme à l'accoutumé, au fil de cette thèse tandis que certaines questions ont été élucidées, de nombreuses autres ont pu être posées et mériteraient une attention toute particulière. Les commentaires ci-dessous essayeront de les pointer du doigt.

Les travaux présentés dans le Chapitre II vis-à-vis de l'association d'Ag₂V₄O₁₁ et Li₂DHBN amènent intrinsèquement à se poser de nombreuses questions car d'autres expériences aurait méritées d'être réalisés pour comprendre les défaillances du système. Le manque de temps, des résultats préliminaires peu prometteurs ainsi qu'une envie collective de regarder ailleurs (vers les oxydes de niobium) expliquent le manque d'opiniâtreté dont nous avons fait preuve durant cette étude. Comme largement expliqué dans la publication associée à ce chapitre, une étude plus large des problèmes de lithiation et de délithiation du graphite aurait pu être menée grâce à la caractérisation de l'interface du graphite (SEI) durant le cyclage (XPS, MEB, EDX, XRF) ainsi que la dissolution et le transport des ions vanadium. Nous espérons que de futurs travaux par notre groupe ou d'autres groupes de recherche se pencheront sur ces questions permettant l'amélioration du système proposé.

Le premier oxyde de niobium présenté dans le Chapitre III, $Ag_{1-3x}La_x\square_{2x}NbO_3$ a été un premier matériau modèle pour la compréhension des mécanismes de charge résultant d'une substitution cationique du site A d'une pérovskite. Bien d'autres études pourraient être menées pour mettre en avant l'intérêt de cette approche et la généraliser à d'autres oxydes D'autres oxydes vont être étudiés par le laboratoire. La substitution du site A et/ou B sur des pérovskites présentant déjà des propriétés redox comme par exemple SrVO₃ sont à l'étude. Malgré l'intérêt de ce matériau comme modèle vis-à-vis de l'insertion d'ion lithium dans une structure fermée de type pérovskite, la méthode de formation de lacunes doit être appliquée à des matériaux présentant déjà des propriétés électrochimiques si elle veut être considérée comme prometteuse pour de potentielles applications industrielles.

Comme démontré dans le cas de la famille KTiNbO₅ durant le Chapitre IV, la présence de protons peut permettre une amélioration des caractéristiques électrochimiques d'un matériau. Finalement, par synthèse céramique (qui permet de comparer les propriétés intrinsèques d'un matériau), HTiNbO5 présente des capacités spécifiques plus élevées que Ti₂Nb₂O₉. La présence de protons permet-elle toujours une amélioration des capacités observées ? Les travaux présentés dans cette thèse ne peuvent prétendre répondre à cette question. Le seul cas de la famille KTiNbO₅ ne pouvant pas faire office de juge de paix. Cependant, la comparaison des différents matériaux de cette famille nous permet de pointer l'intérêt du proton sur le mécanisme de charge ainsi que les propriétés électrochimiques observées. D'autres travaux sur des oxydes similaires comme HNb₃O₈, H₂TiNb₆O₁₈, HLaNb₂O₇ pourraient permettre d'obtenir des conclusions plus générales sur l'influence du proton dans les oxydes de niobium pour des applications dans les batteries Li-ion dites de puissance. Aussi, la comparaison de matériau proche comme H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O₁₄ avec des oxydes comme $W_3Nb_2O_{14}$ pourrait permettre de mieux apprivoiser le rôle du proton dans ce type d'oxyde. Dans ce but, durant les 2 mois passés dans le laboratoire du Pr. Bruce Dunn, j'ai développé différents matériaux présentant des structures de types bronzes de tungstène (W₃ Nb₂O₁₄, Mo₃ Nb₂O₁₄, Mo_{1.5}W_{1.5}Nb₂O₁₄). Ils possèdent des sites de lithiation clairs et présentent donc des caractéristiques électrochimiques intéressantes. Cependant, ils ne disposent pas d'ions alcalins pouvant être échangés par des protons. Une étude de ces composés et des différences avec $H_{0.25}Cs_{0.25}Nb_{2.5}W_{2.5}O_{14}$ est en cours.

Sur un tout autre sujet, les questions vis-à-vis de l'impact environnemental des oxydes présentés dans ces travaux n'ont malheureusement pas pu être soulevées dans le cadre de cette thèse, par manque de temps mais aussi par manque de compétence. Ces questions, qui taraudent nombre de jeunes doctorants travaillant dans le domaine de la chimie des matériaux, nécessitent l'étude du cycle de vie des matériaux synthétisés. L'impact multifactoriel sur l'environnement de l'extraction des métaux (ici le niobium, le titane, le tungstène et le molybdène), leur purification, leur transport, l'empreinte énergétique des méthodes de synthèses sont des facteurs

primordiaux si l'on veut développer des technologies propres qui permettrons de respecter les accords de Paris du point de vue de la hausse des émissions de CO₂. La « criticité » des matériaux utilisés doit également être pris en compte. Le niobium, le tungstène et le lithium sont considérés par l'Union Européenne comme des matériaux critiques, c.à.d. qu'il y a un ou plusieurs problèmes sur leurs disponibilités sur Terre, leurs répartitions géographiques et/ou leur rareté et donc leur prix.⁹ Aussi, les conditions d'extractions dans les pays miniers doivent être prises en compte. On peut prendre l'exemple du niobium qui est partiellement extrait en République Démocratique du Congo (RDC) dans des mines illégales de coltan présentant des risques d'effondrements. La plupart du temps, des enfants sont exploités pour extraire cette roche. La vente de ces minerais permettant l'achat d'armes menant à des guérillas dans tout le pays. Le manque de données et d'informations vis-à-vis de tous ces problèmes appelle à une grande précaution du point de vue de la possible industrialisation des oxydes de niobium/tungstène/molybdène comme matériaux d'électrodes négatives. Ainsi, une étude de l'impact environnemental et humain en vue de l'utilisation industrielle de ce type de matériaux est nécessaire.

⁹ Hofmann, M.; Hofmann, H.; Hagelüken, C.; Hool, A. Critical Raw Materials: A Perspective from the Materials Science Community. *Sustain. Mater. Technol.* **2018**, *17*, e00074. https://doi.org/10.1016/j.susmat.2018.e00074.



NantesUniversité

Titre: Matériaux et dispositifs de stockage de l'énergie électrique pour des bâtiments et des transports propres.

Mots clés: Batteries Li-ion, matériau à charge rapide, oxyde de niobium, formation de site d'insertion, mesures *in situ/operando*

Résumé: Les batteries Li-ion sont des dispositifs de stockage de l'énergie ayant envahi le marché de l'électronique portatifve ainsi que celui des voitures électriques. Elles proposent une densité d'énergie relativement haute mais possèdent l'inconvénient d'une recharge lente principalement à cause de l'électrode négative composée de graphite. Pour obtenir des temps de charge plus rapides, les oxydes de niobium ont émergé en raison de leurs structures cristallographiques particulières permettant l'insertion des ions Li⁺ grâce à de bonnes propriétés de diffusion ionique dans le matériau.

Ainsi, dans le but d'augmenter la densité de puissance des batteries Li-ion, cette thèse a entrepris la synthèse et la caractérisation d'oxydes possédant des structures cristallographiques complexes principalement à base de niobium mais également composées d'argent, de vanadium, de titane, de tungstène ou encore de molybdène.

La formation de lacunes par substitution de l'argent par du lanthane dans la pérovskite AgNbO₃ a permis d'obtenir un premier matériau modèle vis-à-vis de l'insertion rapide. Ensuite, les propriétés d'échange ionique d'une série de matériaux (KTiNbO₅, $Cs_{0.5}Nb_{2.5}W_{2.5}O_{14}$, $Rb_2TiNb_6O_{18}$) ont été étudiées dans le but de remplacer les ion K⁺, Cs⁺, Rb⁺ par des protons ou des H₃O⁺. Chaque oxyde protoné présentant des propriétés d'insertion bien supérieures à leurs analogue possédant des ions alcalins.

Aussi, durant l'ensemble de ce travail de thèse, un large panel de méthodes de caractérisation a été utilisé dans le but de définir les propriétés physico-chimique et électrochimiques des matériaux synthétisés. D'une part, des caractérisations structurales grâce à l'utilisation de la diffraction des rayons X (DRX) et de la microscopie électronique à transmission ont permis de comprendre la structure cristallographique de ces oxydes. D'autre part, les mécanismes d'insertion ont été résolus grâce à l'utilisation de méthodes originales telles que la DRX *in situ*, la mesure du potentiel entropique ou encore par l'utilisation de la calorimétrie *operando*.

Title: Electric energy storage materials and devices for zero net energy buildings and clean transportation.

Keywords: Li-ion batteries, fast charging material, niobium oxide, insertion site formation, *in situ/operando* measurements

Abstract: Li-ion batteries are energy storage devices that have invaded the market for portable electronics and electric cars. They offer a relatively high energy density but have the disadvantage of slow charging due to the negative electrode based on graphite. To achieve shorter charging times, niobium oxides have emerged due to their particular crystallographic structures allowing the insertion of Li+ ions without limiting the diffusion of these ions in the material. With the same aim of increasing the power density of Li-ion batteries, this thesis undertook the synthesis and characterisation oxides with complex of crystallographic structures mainly based on niobium but also composed of Ag, V, Ti, W, and Mo.

The formation of vacancies by substitution of silver by lanthanum in the perovskite AgNbO₃ allowed obtaining a first model material for fast insertion.

Next, the ion exchange properties of a series of materials (KTiNbO₅, Cs_{0.5}Nb_{2.5}W_{2.5}O₁₄, Rb₂TiNb₆O₁₈) were investigated with the aim of replacing K⁺, Cs⁺, Rb⁺ ions with protons or H₃O⁺. Each protonated oxide exhibits much better insertion properties than its alkali ion analogue.

A wide range of characterisation methods was used to define the physico-chemical and electrochemical properties of the synthesised materials. On the one hand, structural characterisation using X-ray diffraction and transmission electron (XRD) (HRTEM) has provided microscopy а good understanding of the crystallographic structure of oxides. On the other hand insertion these mechanisms have been solved by using original methods such as in situ XRD, entropy potential measurement or operando calorimetry.