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# Revisiting $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$ as electrode materials for energy storage devices

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## ABSTRACT

In the search of new materials for the future generation of Li-ion batteries, a look into the past has brought the multicationic oxide  $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$  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  $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$  and the obtained proton exchanged analogues  $\text{H}_2\text{TiNb}_6\text{O}_{18}$  when used as negative electrode materials is depicted in terms of both structure and electrochemical behavior. Interestingly, while only a negligible  $\text{Li}^+$  insertion is evidenced in the rubidium phase, the  $\text{H}_2\text{TiNb}_6\text{O}_{18}$  exhibits a much higher lithium intercalation between 1 V and 3 V vs  $\text{Li}/\text{Li}^+$ . A specific capacity of  $118 \text{ mAh}\cdot\text{g}^{-1}$  is reported when cycled at  $0.02 \text{ A}\cdot\text{g}^{-1}$ . A solid solution type mechanism has been revealed by *in situ* 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  $372 \text{ mAh}\cdot\text{g}^{-1}$  for graphite based electrodes, the reduction of  $\text{Li}^+$  to  $\text{Li}^0$  can occur at a potential down to 0 V vs.  $\text{Li}/\text{Li}^+$  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  $\text{Li}^+$  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  $\text{Li}^+$  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  $\text{Li}^+$  insertion occurs at a potential far

away from the thermodynamic reduction of  $\text{Li}^+$  (i.e., E greater than 1.0 V vs.  $\text{Li}/\text{Li}^+$ ) 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  $\text{Li}/\text{Li}^+$ . [7,8,10,11] In this case, a classic example is  $\text{T-Nb}_2\text{O}_5$  which show reversible  $\text{Li}^+$  intercalation between 1.0 V and 2.0 V vs  $\text{Li}/\text{Li}^+$  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.,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Tl}^+$ ) 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 ( $\text{H}^+$ ,  $\text{Li}^+$ , ...) can liberate part of the accessible volume within the hexagonal channels, without triggering any phase change in the material.

$\text{Rb}_2\text{Nb}_6\text{TiO}_{18}$ , exhibits an interconnected bronze-like tunnel structure, as well as the presence of possible  $\text{Nb}^{5+}$  and  $\text{Ti}^{4+}$  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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Rb<sub>2</sub>Nb<sub>6</sub>TiO<sub>18</sub> and consequent electrochemical characterization as LIB negative electrode material are reported. Both structural and electrochemical differences between Rb<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub> and H<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub> are discussed in the following parts of this communication.

## 2. Experimental section

### 2.1. Synthesis of Rb<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub> / H<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub>

High-temperature solid state methods were used to synthesize Rb<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub>. Stoichiometric amounts of Nb<sub>2</sub>O<sub>5</sub> (Alfa Aesar, 99.9% metal basis), TiO<sub>2</sub> and 10% excess Rb<sub>2</sub>CO<sub>3</sub> (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 °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 Rb<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub>.

### 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 ( $K\alpha_1 = 1.5406 \text{ \AA}$ ,  $K\alpha_2 = 1.5444 \text{ \AA}$ ) and K<sub>β</sub> filter (Nickel) in the Bragg-Brentano reflection geometry. Data was collected from 10 to 90° 2θ. *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<sup>-1</sup> with 30 min at open circuit voltage for XRD pattern collection.[18] All XRD were collected in ~ 0.008° 2θ steps. Structure refinement has been performed using FullProf Suite. Preliminary values of this refinement have been taken from the literature.<sup>14</sup>

#### 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<sup>-1</sup> 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 mm<sup>2</sup> OXFORD Instruments detector. TEM observations were performed using a 200 kV JEOL F200 Cold FEG Transmission Electron Microscope, fitted with a ± 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 H<sub>2</sub>O) 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 μm 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<sup>-2</sup>, 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 O<sub>2</sub>, H<sub>2</sub>O) using a single lithium (Li) electrode as both reference and counter (99.9%, Sigma

Aldrich), glass fiber separator (Whatman) and 200 μL of 1 M LiPF<sub>6</sub> 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<sup>-1</sup>. 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<sup>-1</sup>. The charge–discharge curves presented in the respective figures correspond always the third charge/discharge curve out of the five.

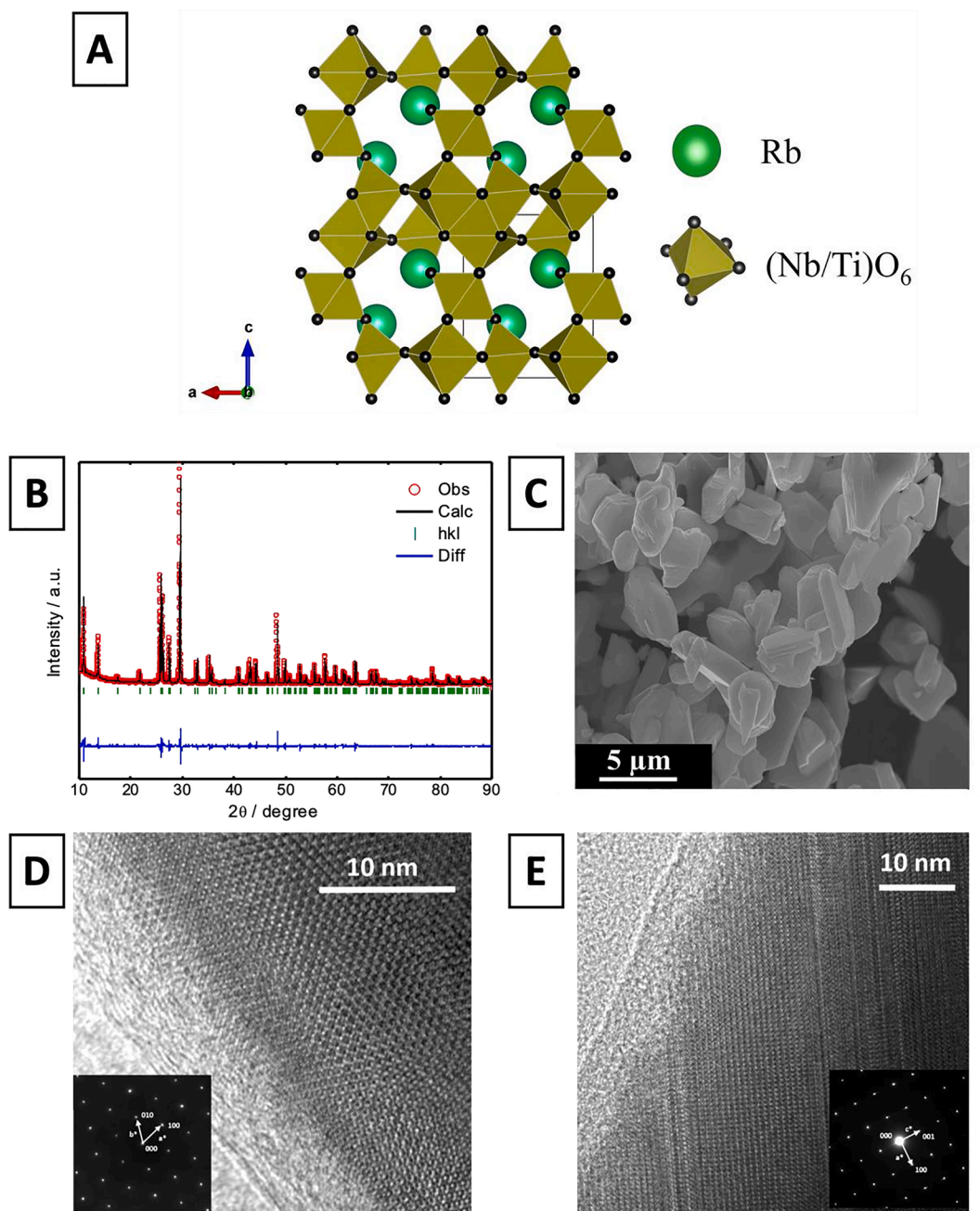
## 3. Results & discussion

The crystallographic structure of Rb<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub> is presented in Fig. 1. A. The material crystallizes in the hexagonal system, with a P $\bar{3}$ m1 space group. The structure is composed of two types of distorted (Nb/Ti)O<sub>6</sub> octahedra sharing corners and edges. More precisely, Rb<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub> are formed by the intergrowth of (M<sub>6</sub>O<sub>15</sub>)<sub>n</sub> and (MO<sub>3</sub>)<sub>n</sub> layers which creates the 3D structure and cages. As previously reported<sup>20</sup>, Ti cations seem to be preferentially located in the (MO<sub>3</sub>) sites due to a lower distortion of these octahedra. Rb<sup>+</sup> is located within large O<sub>21</sub> cages (158.7 Å<sup>3</sup>) 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  $a = 7.5323(5) \text{ \AA}$  and  $c = 8.2002(6) \text{ \AA}$ , 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 μm 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 (1 1 0) and (1 0 1) planes. While large homogenous domains are observed on (1 1 0) plane, some defects are visible along (1 0 1). This observation might be a result of Ti deficiency located in the (MO<sub>3</sub>) sites, causing some irregularities in the stacking sequence of the layers and then local rearrangement of the structure. Nevertheless, the HRTEM images along with (1 1 0) and (1 0 1) planes highlight the presence of cages along these directions.

The substitution of Rb<sup>+</sup> ions by H<sup>+</sup> 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 Rb<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub> and H<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub> 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. H<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub> shows slightly smaller parameters because of the replacement of bulky Rb<sup>+</sup> 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 crystallinity.[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 H<sub>2</sub>O molecule per proton is inserted in H<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub>·2H<sub>2</sub>O

To investigated the electrochemical activity of both Rb<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub> and H<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub>·2H<sub>2</sub>O, CVs were performed at 2 mV.s<sup>-1</sup> between 3 V and 1 V vs Li/Li<sup>+</sup>. As shown in Fig. 3.A, Rb<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub> 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<sup>-1</sup>. In fact, due to the steric gene created by the presence of the bulky and not mobile Rb<sup>+</sup> ions, no insertion of Li<sup>+</sup> ions in the O<sub>21</sub> cages are possible. In contrast to his Rb<sup>+</sup> analogue, H<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub>·2H<sub>2</sub>O has a clear faradic electrochemical signature. A broad wave between 2.6 and 1.5 V vs. Li/Li<sup>+</sup> probably arises from the combination of



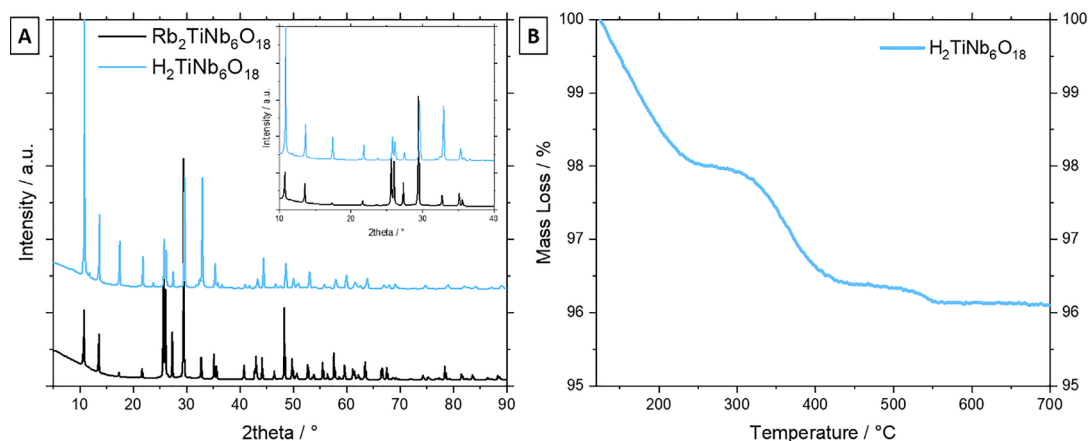
**Fig. 1.** A. Crystal structure of  $2 \times 2$   $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$  unit cell. (space group  $P\bar{3}m1$ ) B. Full pattern matching refinement of  $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$ .  $R_{wp} = 37.5\%$  /  $\chi^2 = 13.6$ . C. SEM image of  $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$ . D. (110) plane of  $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$  observed by TEM. E. (101) plane of  $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$  observed by TEM.

several superimposed redox activities, such as the irreversible reduction of structural water, and the reduction of Nb and/or Ti upon  $\text{Li}^+$  insertion. Similarly, a final wave below 1.3 V vs.  $\text{Li}/\text{Li}^+$  suggests a further reduction of the metal hosts at this lower potential. After 5 cycles, the remaining specific capacity is  $100 \text{ mAh.g}^{-1}$  at  $2 \text{ mV.s}^{-1}$ . The reversible reduction of the  $\text{Nb}^{5+}/\text{Nb}^{4+}$  and/or  $\text{Ti}^{4+}/\text{Ti}^{3+}$  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.

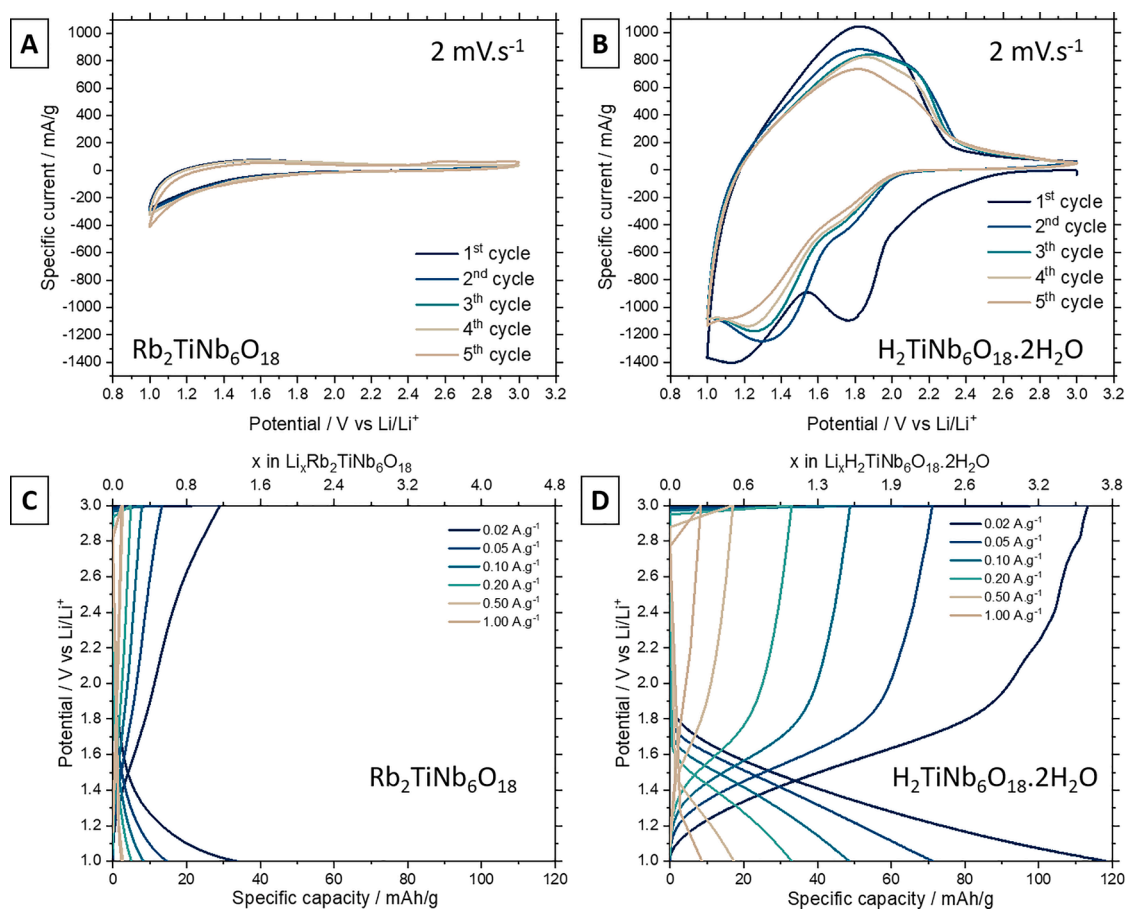
Based on the obvious differences in CV between  $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$  and  $\text{H}_2\text{TiNb}_6\text{O}_{18} \cdot 2\text{H}_2\text{O}$ , the rate capability of these two materials was investigated by GCPL cycling at increasing current densities. Results are shown in Fig. 3(C-D). As expected, the  $\text{Li}^+$  insertion in the  $\text{O}_{21}$  cages is

very low for  $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$  at every measured current density. Once again, in contrast,  $\text{H}_2\text{TiNb}_6\text{O}_{18} \cdot 2\text{H}_2\text{O}$  presents a reversible specific capacity of  $118 \text{ mAh.g}^{-1}$  at  $0.02 \text{ A.g}^{-1}$ , which corresponds to more than  $3.55 \text{ Li}^+$  inserted/unit cell. It is 4 times higher than the capacity observed for  $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$  in the same conditions.  $\text{H}_2\text{TiNb}_6\text{O}_{18} \cdot 2\text{H}_2\text{O}$  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  $\text{Li}^+$  insertion rate between 1.8 and 1.0 V vs  $\text{Li}/\text{Li}^+$ . Further study of the electrochemical behavior of the electrode is under progress.

Nevertheless, when the current density is increased, the specific capacity of  $\text{H}_2\text{TiNb}_6\text{O}_{18} \cdot 2\text{H}_2\text{O}$  sharply decreases. At  $0.2 \text{ A.g}^{-1}$ , a specific capacity of  $32 \text{ mAh.g}^{-1}$  is observed which represented 27 % of the capacity at  $0.02 \text{ A.g}^{-1}$ . This relatively poor electrochemical behavior at



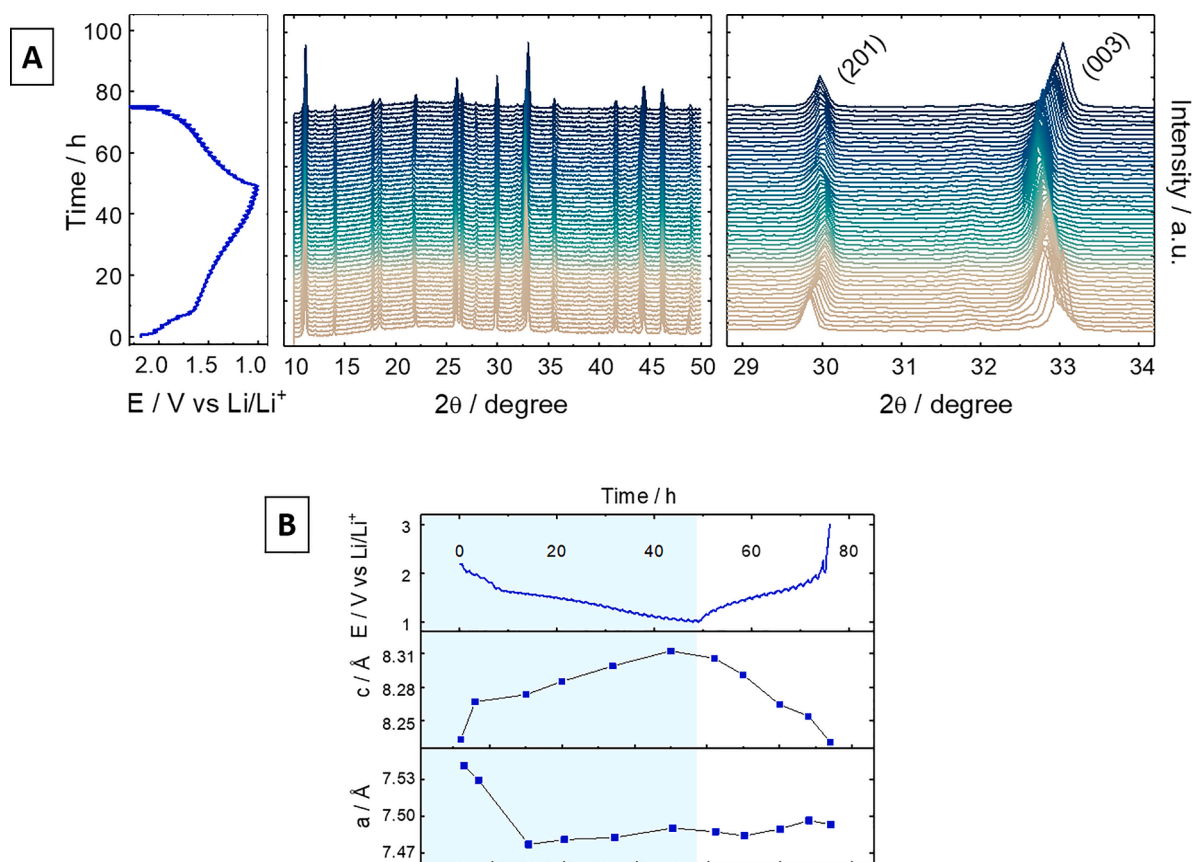
**Fig. 2.** A. X-ray diffraction patterns of  $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$  and  $\text{H}_2\text{TiNb}_6\text{O}_{18}$  indexed in  $P\bar{3}m1$  space group. B. TGA curves between 40 °C and 700 °C of  $\text{H}_2\text{TiNb}_6\text{O}_{18}$  showing the number of structural water molecule (one water molecule per proton).



**Fig. 3.** A-B. Cyclic Voltammetry at  $2 \text{ mV}\cdot\text{s}^{-1}$  of  $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$  and  $\text{H}_2\text{TiNb}_6\text{O}_{18}$  respectively. C-D. Charge and discharge curves at different current densities of  $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$  and  $\text{H}_2\text{TiNb}_6\text{O}_{18}$  respectively.

high rate is probably due to the not favorable  $\text{Li}^+$  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  $0.1 \text{ mV}\cdot\text{s}^{-1}$  to  $20 \text{ mV}\cdot\text{s}^{-1}$ ) 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. 4** shows *in situ* XRD data collected during the first GCPL cycle of  $\text{H}_2\text{TiNb}_6\text{O}_{18}\cdot 2\text{H}_2\text{O}$ . 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



**Fig. 4.** A. *In situ* XRD of  $\text{H}_2\text{TiNb}_6\text{O}_{18}$  cycled between 3.0 and 1.0 V at  $0.005 \text{ A.g}^{-1}$ . Charge /discharge and two  $2\theta$  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  $\text{H}_2\text{O}$  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 ( $\text{TiNb}_6\text{O}_{18}$ ) 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 exemplified by the shifting behavior of the (003) reflection towards lower angles. Upon de-lithiation, a contraction in the *c* dimension 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,  $\text{Rb}_2\text{Nb}_6\text{TiO}_{18}$  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  $\text{Rb}_2\text{Nb}_6\text{TiO}_{18}$  with  $\text{H}_3\text{O}^+$  was reported. Electrochemical measurements of  $\text{Rb}_2\text{Nb}_6\text{TiO}_{18}$  electrode show a weak

electrochemical activity, while Li ion insertion is clearly depicted in the protonated phase  $\text{H}_2\text{Nb}_6\text{TiO}_{18} \cdot 2\text{H}_2\text{O}$ . A specific capacity of  $118 \text{ mAh.g}^{-1}$  is reported at  $0.02 \text{ A.g}^{-1}$  between 3 V and 1 V vs  $\text{Li/Li}^+$ . This impressive difference between  $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$  and  $\text{H}_2\text{TiNb}_6\text{O}_{18} \cdot 2\text{H}_2\text{O}$  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,  $\text{H}_2\text{Nb}_6\text{TiO}_{18} \cdot 2\text{H}_2\text{O}$  exhibits a minor volume expansion (1%) over  $\text{Li}^+$  insertion along (001).

#### CRediT authorship contribution statement

**Jerónimo 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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## References

- [1] A.M. Colclasure, A.R. Dunlop, S.E. Trask, B.J. Polzin, A.N. Jansen, K. Smith, Requirements for Enabling Extreme Fast Charging of High Energy Density Li-Ion Cells While Avoiding Lithium Plating, *J. Electrochem. Soc.* 166 (8) (2019) A1412–A1424, <https://doi.org/10.1149/2.0451908jes>.
- [2] A. Burnham, E.J. Dufek, T. Stephens, J. Francfort, C. Michelbacher, R.B. Carlson, J. Zhang, R. Vijayagopal, F. Dias, M. Mohanpurkar, D. Scofield, K. Hardy, M. Shirik, R. Hovsapien, S. Ahmed, I. Bloom, A.N. Jansen, M. Keyser, C. Kreuzer, A. Markel, A. Meintz, A. Pesaran, T.R. Tanim, Enabling Fast Charging – Infrastructure and Economic Considerations, *J. Power Sources* 367 (2017) 237–249, <https://doi.org/10.1016/j.jpowsour.2017.06.079>.
- [3] M. Li, M. Feng, D. Luo, Z. Chen, Fast Charging Li-Ion Batteries for a New Era of Electric Vehicles, *Cell Rep. Phys. Sci.* 1 (10) (2020), 100212, <https://doi.org/10.1016/j.xcrp.2020.100212>.
- [4] C. Choi, D.S. Ashby, D.M. Butts, R.H. DeBlock, Q. Wei, J. Lau, B. Dunn, Achieving High Energy Density and High Power Density with Pseudocapacitive Materials, *Nat. Rev. Mater.* 5 (1) (2020) 5–19, <https://doi.org/10.1038/s41578-019-0142-z>.
- [5] M. Armand, J.-M. Tarascon, Building Better Batteries, *Nature* 451 (7179) (2008) 652–657, <https://doi.org/10.1038/451652a>.
- [6] M.M. Thackeray, K. Amine, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> Spinel Anodes, *Nat. Energy* 6 (6) (2021) 683, <https://doi.org/10.1038/s41560-021-00829-2>.
- [7] K.J. Griffith, K.M. Wiaderek, G. Cibir, L.E. Marbella, C.P. Grey, Niobium Tungsten Oxides for High-Rate Lithium-Ion Energy Storage, *Nature* 559 (7715) (2018) 556–563, <https://doi.org/10.1038/s41586-018-0347-0>.
- [8] V. Aravindan, J. Sundaramurthy, A. Jain, P.S. Kumar, W.C. Ling, S. Ramakrishna, M.P. Srinivasan, S. Madhavi, Unveiling TiNb<sub>2</sub>O<sub>7</sub> as an Insertion Anode for Lithium Ion Capacitors with High Energy and Power Density, *ChemSusChem* 7 (7) (2014) 1858–1863, <https://doi.org/10.1002/cssc.201400157>.
- [9] D. Butts, J. Schoiber, C. Choi, G.J. Redhammer, N. Hüsing, S. Donne, B. Dunn, Fe-Substituted Sodium B''-Al<sub>2</sub>O<sub>3</sub> as a High-Rate Na-Ion Electrode, *Chem. Mater.* 33 (15) (2021) 6136–6145, <https://doi.org/10.1021/acs.chemmater.1c01680>.
- [10] K.J. Griffith, I.D. Seymour, M.A. Hope, M.M. Butala, L.K. Lamontagne, M. B. Preefer, C.P. Koçer, G. Henkelman, A.J. Morris, M.J. Cliffe, S.E. Dutton, C. P. Grey, Ionic and Electronic Conduction in TiNb<sub>2</sub>O<sub>7</sub>, *J. Am. Chem. Soc.* 141 (42) (2019) 16706–16725, <https://doi.org/10.1021/jacs.9b06669>.
- [11] A.S. Prakash, P. Manikandan, K. Ramesha, M. Sathiya, J.-M. Tarascon, A.K. Shukla, Solution-Combustion Synthesized Nanocrystalline Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> As High-Rate Performance Li-Ion Battery Anode, *Chem. Mater.* 22 (9) (2010) 2857–2863, <https://doi.org/10.1021/cm100071z>.
- [12] V. Augustyn, J. Come, M.A. Lowe, J.W. Kim, P.-L. Taberna, S.H. Tolbert, H. D. Abruna, P. Simon, B. Dunn, High-Rate Electrochemical Energy Storage through Li<sup>+</sup> Intercalation Pseudocapacitance, *Nat. Mater.* 12 (6) (2013) 518–522.
- [13] K.J. Griffith, A.C. Forse, J.M. Griffin, C.P. Grey, High-Rate Intercalation without Nanostructuring in Metastable Nb<sub>2</sub>O<sub>5</sub> Bronze Phases, *J. Am. Chem. Soc.* 138 (28) (2016) 8888–8899, <https://doi.org/10.1021/jacs.6b04345>.
- [14] G. Desgardin, C. Robert, D. Groult, B. Raveau, Une Nouvelle Famille Structurale: Les Titanoniobates et Titanotantalates A<sub>2</sub>Nb<sub>6</sub>TiO<sub>18</sub> et A<sub>2</sub>Ta<sub>6</sub>TiO<sub>18</sub>, *J. Solid State Chem.* 22 (2) (1977) 101–111, [https://doi.org/10.1016/0022-4596\(77\)90026-3](https://doi.org/10.1016/0022-4596(77)90026-3).
- [15] C. Michel, A. Guyomarc'h, B. Raveau, Nouveaux Echangeurs Cationiques Avec Une Structure a Tunnels Entrecroises: Les Oxydes A12M33O90 et al2M33O90, 12H2O, *J. Solid State Chem.* 22 (4) (1977) 393–403, [https://doi.org/10.1016/0022-4596\(77\)90016-0](https://doi.org/10.1016/0022-4596(77)90016-0).
- [16] C. Michel, A. Guyomarc'h, B. Raveau, Nouveaux Échangeurs Cationiques Avec Une Structure à Tunnels Entrecroisés: Les Niobates et Tantalates A10M29.2O78 et a10M29.2O78-10H2O, *J. Solid State Chem.* 25 (3) (1978) 251–261, [https://doi.org/10.1016/0022-4596\(78\)90110-X](https://doi.org/10.1016/0022-4596(78)90110-X).
- [17] G. Desgardin, C. Robert, B. Raveau, Etude Du Comportement Du Thallium Dans de Nouvelles Structures a Tunnels Entrecroises : Les Oxydes Ti<sub>2</sub>Nb<sub>6</sub>TiO<sub>18</sub> et Ti<sub>2</sub>Ta<sub>6</sub>TiO<sub>18</sub>, *Mater. Res. Bull.* 13 (6) (1978) 621–626, [https://doi.org/10.1016/0025-5408\(78\)90187-3](https://doi.org/10.1016/0025-5408(78)90187-3).
- [18] J.B. Leriche, S. Hamelet, J. Shu, M. Morcrette, C. Masquelier, G. Ouvrard, M. Zerrouki, P. Soudan, S. Belin, E. Elkaim, F. Baudelet, An Electrochemical Cell for Operando Study of Lithium Batteries Using Synchrotron Radiation, *J. Electrochem. Soc.* 157 (5) (2010) A606, <https://doi.org/10.1149/1.3355977>.
- [19] Y. Gogotsi, P. Simon, True Performance Metrics in Electrochemical Energy Storage, *Science* 334 (6058) (2011) 917, <https://doi.org/10.1126/science.1213003>.
- [20] T.-Y. Chen, E.R. Maddrell, N.C. Hyatt, J.A. Hriljac, A Potential Wasteform for Cs Immobilization: Synthesis, Structure Determination, and Aqueous Durability of Cs<sub>2</sub>TiNb<sub>6</sub>O<sub>18</sub>, *Inorg. Chem.* 55 (24) (2016) 12686–12695, <https://doi.org/10.1021/acs.inorgchem.6b01826>.
- [21] M. Sato, J. Abo, T. Jin, M. Ohta, Structure and Ionic Conductivity of MLaNb<sub>2</sub>O<sub>7</sub> (M= K, Na, Li, H), *J. Alloys Compd.* 192 (1–2) (1993) 81–83.
- [22] J.-F. Colin, V. Pralong, M. Hervieu, V. Caignaert, B. Raveau, New Titanoniobates (Li, H<sub>2</sub>TiNb<sub>6</sub>O<sub>5</sub> and (Li, H)<sub>3</sub>TiNb<sub>6</sub>O<sub>5</sub>: Synthesis, Structure and Properties, *J. Mater. Chem.* 18 (26) (2008) 3121–3128.
- [23] Y.u. Yuan, H. Yu, X. Cheng, W. Ye, T. Liu, R. Zheng, N. Long, M. Shui, J. Shu, H<sub>0.92</sub>K<sub>0.08</sub>TiNbO<sub>5</sub> Nanowires Enabling High-Performance Lithium-Ion Uptake, *ACS Appl. Mater. Interfaces* 11 (9) (2019) 9136–9143, <https://doi.org/10.1021/acsami.8b21817>.
- [24] C. Bohnke, O. Bohnke, J.L. Fourquet, Electrochemical Intercalation of Lithium into LiLaNb<sub>2</sub>O<sub>7</sub> Perovskite, *J. Electrochem. Soc.* 144 (4) (1997) 1151.
- [25] O.A. Drozhzhin, V.V. Grigoryev, A.M. Alekseeva, R.R. Samigullin, D.A. Aksyonov, O.V. Boytsova, D. Chernyshov, V.V. Shapovalov, A.A. Guda, A.V. Soldatov, K. J. Stevenson, A.M. Abakumov, E.V. Antipov, Revisited Ti<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> as an Anode Material for Advanced Li-Ion Batteries, *ACS Appl. Mater. Interfaces* 13 (47) (2021) 56366–56374.
- [26] J.E.B. Randles, A Cathode Ray Polarograph. Part II.—The Current-Voltage Curves, *Trans Faraday Soc* 44 (0) (1948) 327–338, <https://doi.org/10.1039/TF9484400327>.
- [27] A. Ševčík, Oscillographic Polarography with Periodical Triangular Voltage, *Collect. Czechoslov. Chem. Commun.* 13 (1948) 349–377.
- [28] S. Fleischmann, J.B. Mitchell, R. Wang, C. Zhan, D. Jiang, V. Presser, V. Augustyn, Pseudocapacitance: From Fundamental Understanding to High Power Energy Storage Materials, *Chem. Rev.* 120 (14) (2020) 6738–6782, <https://doi.org/10.1021/acs.chemrev.0c00170>.
- [29] J. Come, V. Augustyn, J.W. Kim, P. Rozier, P.-L. Taberna, P. Gogotsi, J.W. Long, B. Dunn, P. Simon, Electrochemical Kinetics of Nanostructured Nb<sub>2</sub>O<sub>5</sub> Electrodes, *J. Electrochem. Soc.* 161 (5) (2014) A718–A725, <https://doi.org/10.1149/2.040405jes>.
- [30] X. Yu, H. Pan, W. Wan, C. Ma, J. Bai, Q. Meng, S.N. Ehrlich, Y.-S. Hu, X.-Q. Yang, A Size-Dependent Sodium Storage Mechanism in Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> Investigated by a Novel Characterization Technique Combining in Situ X-Ray Diffraction and Chemical Sodiation, *Nano Lett.* 13 (10) (2013) 4721–4727, <https://doi.org/10.1021/nl402263g>.
- [31] L. Zhao, H.-L. Pan, Y.-S. Hu, H. Li, L.-Q. Chen, Spinel Lithium Titanate (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>) as Novel Anode Material for Room-Temperature Sodium-Ion Battery, *Chin. Phys. B* 21 (2) (2012) 028201, <https://doi.org/10.1088/1674-1056/21/2/028201>.