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

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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) octahedral sites.
- The impact of the microstructure 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 at high rates.

29 Abstract

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Layered oxides showing edge-sharing octahedra are promising negative electrode materials 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 microstructure on material and electrochemical properties. An arsenal of characterization techniques has been used to investigate these three types of particles using X-Ray Diffraction (XRD), electron microscopy, but also by associating mass spectroscopy to thermogravimetric analyses (TGA). Their ability to intercalate lithium has been compared, showing interesting and very similar specific capacities for solid-state and sol-gel synthesis (> 100 mAh.g⁻¹ at 0.5 A.g⁻¹). In addition, it was shown that the the synthesis giving rise to nanosheet (NS) led to lower performance due to the presence of organic molecules in the interlayer spacing of the 2D lamellar structure. Lastly, *in situ* XRD evidenced a solid-solution reaction for HTiNbO₅, with an initial and irreversible phase change leading to the formation of Li_{0.4}HTiNbO₅. Moreover, *ex situ* ¹H MAS NMR measurements highlight the essential role of the proton in the charge storage mechanism of HTiNbO₅. Thus, this paper demonstrates the interest of HTiNbO₅ as a fast negative electrode material for high-power Li-ion batteries as well as the predominant role that the proton can play in the diffusion of lithium ions inside a confined interlayer space.

63 Introduction

64 The climate change forces people to use cleaner energies, *i.e.* releasing less
65 greenhouse gases. Thus, renewable energies must be deployed as well as vehicles powered
66 by electric energy thanks to electrochemical storage and conversion devices (batteries
67 and/or fuel cells). In this regard, the batteries need to be charged faster to allow a larger
68 deployment of this technology. It seems necessary to replace the negative graphite
69 electrode in order to charge these electrochemical systems within a few minutes.¹⁻⁴ The
70 capacity of graphite is lower during a fast charge (>C) because the insertion of lithium is
71 largely limited by their diffusion in the interlayer space between graphene layers.⁵ In
72 addition, graphite inserts lithium ions at a potential that can go below 0.1 V vs Li⁺/Li. This
73 electrochemical property which allows to achieve high energy density can also lead to the
74 formation of lithium metal in the form of dendrites by lithium plating, resulting in possible
75 short circuits and thermal runaway.^{5,6}

76 Regarding this quest for more powerful devices, different types of materials have
77 been proposed. Among them, niobium and titanium oxides seem to be of interest for such
78 applications.⁷⁻¹⁰ The hexagonal form of niobium oxide (T-Nb₂O₅) exhibits a capacity of 130
79 mAh.g⁻¹ for a 6 minutes charge while titanium dioxide presents a high theoretic capacity of
80 335 mAh.g⁻¹ for one electron exchanged per transition metal.¹⁰ Even if it is still challenging to
81 achieve high specific capacities, different strategies have been developed to reach the
82 theoretical capacity of TiO₂, like the creation of cationic vacancies, fluorine doping, or the
83 reduction of the particle size to improve the ionic and electrical conductivity.^{7,8,11,12} Another
84 strategy is to synthesize a metastable form of TiO₂, called TiO₂(B). After an ionic exchange
85 reaction from K₂Ti₄O₉ to H₂Ti₄O₉, TiO₂(B) is synthesized by a topotactic dehydration reaction
86 of H₂Ti₄O₉.^{13,14} This material presents edge-sharing octahedra which seems to be an
87 interesting crystallographic feature for fast charging applications.¹⁵ Moreover, it proposes
88 relatively high capacities for fast charging without the need to obtain nanometric particles.⁷
89 In a recent study, Fleischmann *et al.* investigate the electrochemical characteristics of the
90 different intermediate oxides during the dehydration of H₂Ti₄O₉ leading to TiO₂(B).¹⁶ They
91 demonstrate that partial deprotonation of this oxide offers the highest capacities over a
92 broad range of current densities. Their work sheds light on the impact of protons and water
93 molecules located between the sheets in the charging mechanism of titanium oxides.

94 During the 1960s and 1970s, Raveau *et al.* studied the ion exchange properties of
95 various niobium, titanium and/or tungsten based multicationic oxides.^{17–24} In most cases, the
96 studied materials present interesting intercalation properties. Our previous study proposed
97 the ion exchange of $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$ and the use of the protonated material as an interesting
98 host matrix for lithium intercalation.²⁵ $\text{H}_2\text{TiNb}_6\text{O}_{18} \cdot 2\text{H}_2\text{O}$ exhibited significantly higher
99 capacities than $\text{Rb}_2\text{TiNb}_6\text{O}_{18}$ as well as a very low ($\sim 1\%$) volume expansion during lithium ion
100 insertion. Among the materials presented by the group of Raveau, KTiNbO_5 also offers
101 interesting features. It is a lamellar oxide with 2×2 units of edge-sharing octahedra. These
102 blocks form $(\text{TiNbO}_5)_n$ layers by corner sharing. Between these layers are located potassium
103 ions. First described by Wadsley²⁶, KTiNbO_5 crystallizes with an orthorhombic lattice in the
104 *Pnma* space group. The material is then described as lamellar along the *c* direction with cell
105 parameters equal to 6.459 Å, 3.792 Å, 18.742 Å for *a*, *b* and *c* respectively. The titanium ions
106 are mainly located on the internal octahedra of the layers because these are less distorted.
107 Moreover, KTiNbO_5 is subject to interesting ion exchange properties. The protons are not
108 surrounded by water molecules. In fact, they are necessary for the stability of the interlayer
109 through the formation of hydrogen bonds with the oxygen atoms in the $(\text{TiNbO}_5)_n$ layers.^{22,26}

110 Thanks to the use of HTiNbO_5 , we propose to combine the double strategy of using a
111 material based on titanium and niobium having 2×2 units of edge-sharing octahedra but also
112 an oxide offering ionic exchange properties (and so, proton which can help lithium
113 insertion). Several groups have studied this material as a negative electrode for Li-ion
114 batteries. First, in 2008, J-F Colin *et al.* studied lithium intercalation properties of HTiNbO_5 .
115 They showed the possible insertion of 2 Li^+ per formula unit giving rise to $\text{Li}_2\text{HTiNbO}_5$
116 between 1.0V and 3.0V vs Li^+/Li , resulting in a capacity of $\sim 240 \text{ mAh.g}^{-1}$. A modification of
117 the orientation of the layers is observed in a very similar way to LiTiNbO_5 .²⁷ Moreover, the
118 authors proposed a phase change at the beginning of the first lithiation giving rise to
119 $\text{Li}_{0.4}\text{HTiNbO}_5$, which is irreversibly formed. Lastly, it has been shown that $\text{Li}_3\text{HTiNbO}_5$ can be
120 formed if this oxide is reduced down to a potential of 0V vs Li^+/Li leading to a rocksalt-like
121 structure with very low cyclability. The work of Y. Yuan *et al.* reports on the lithium insertion
122 properties of HTiNbO_5 at higher current densities as negative electrode in high-power Li-ion
123 battery.²⁸ HTiNbO_5 is presented as nanowires and exhibits a specific capacity of about 100
124 mAh.g^{-1} at 5C. An initial phase change is also observed and the following Li^+ insertion is

125 governed by a solid solution type mechanism. As this material can be exfoliated, a recent
126 study by J. Zhang *et al.* proposes a study of restacked HTiNbO₅ nanosheets in combination
127 with MXenes nanosheets.²⁹ Specific capacities higher than 100 mAh.g⁻¹ at 5 A.g⁻¹ have been
128 demonstrated. Nevertheless, no publication reports on the influence of morphologies on the
129 charge storage mechanism and capacities of this oxide. Moreover, no study on the influence
130 of proton in the interlayer on the storage ability of HTiNbO₅ has been achieved to date.

131 In the present paper, we study the lithium intercalation behavior of three different
132 microstructures of HTiNbO₅ (microparticles, nanoparticles and restacked nanosheets). A
133 systematic investigation of the relationship between the structural, chemical and
134 microstructural properties of the material and their electrochemical characteristics is
135 proposed. Thanks to the use of thermogravimetric analysis (TGA) combined with mass
136 spectroscopy (MS) as well as *in situ* XRD and *ex situ* ⁶Li MAS NMR, we propose a clear
137 understanding of the insertion properties of the different HTiNbO₅ samples. Moreover, *ex*
138 *situ* ¹H MAS NMR provides some clues on the understanding of the influence of protons in
139 the charge storage mechanism of this oxide.

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1. Experimental section

a. Synthesis method of HTiNbO₅

In this study, HTiNbO₅ powder was synthesized in a two-step procedure. First, KTiNbO₅ was produced as described below using sol-gel or solid-state route.

i. Synthesis of KTiNbO₅

In the solid-state synthesis method, Nb₂O₅ (Alfa Aesar, 99.9%), TiO₂ (Alfa Aesar, ≥ 99%), and K₂CO₃ (ACS Reagent, ≥ 99.0%) precursors were 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.

In the sol-gel synthesis method, 1.351 mg of NbCl₅ (Sigma Aldrich, 99%) was dissolved in 30 mL of ethanol. Separately, 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. Citric acid (Alfa Aesar, ≥ 99%) was then 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 stirring for 1 hour to ensure a complete dissolution of all species, the two solutions were mixed, then stirred and heated to 120 °C until forming a blackish gel. 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.

ii. Ion exchange HTiNbO₅ SS and SG

Ion exchange was performed to obtain HTiNbO₅ from KTiNbO₅. 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 at room temperature. The acidic solution was changed daily to ensure complete exchange of potassium cations by protons. The resulting suspension containing HTiNbO₅ powder was then centrifuged and rinsed with DI water until neutral pH of the wastewater was obtained.

181 iii. HTiNbO₅ nanosheets (NS)

182 The acid-base reaction of HTiNbO₅ SS with tetrabutylammonium (TBA⁺OH⁻) in
183 aqueous solution allows the exfoliation of (TiNbO₅)⁻ sheets which are then in suspension in
184 this aqueous solution. More precisely, 250mL of aqueous solution at pH=10 containing DI
185 water and TBAOH was prepared. Then, 1g of HTiNbO₅ SS powder is introduced for 14 days
186 and stirred. The solution containing suspended TiNbO₅ nanosheets is further recovered by
187 centrifugation. The solution contains about 2g.L⁻¹ of exfoliated particles in suspension.
188 Finally, the nanosheets are restacked by a progressive addition of 0.1M HCl in the solution
189 until complete restacking (pH~4). The obtained HTiNbO₅ NS powder was then centrifuged
190 and rinsed with DI water until neutral pH wastewater was obtained. HTiNbO₅ SG particles
191 have been exfoliated following similar experimental conditions. HTiNbO₅ NS from SG were
192 successfully obtained but the process exhibited an extremely low yield. We attributed this
193 lower reaction yield (in comparison to HTiNbO₅ SS particles) to the smaller size of the
194 particles involving defects on the surface that do not allow a good ionic exchange between
195 the bulky TBA⁺ cations and the protons. We therefore, do not include electrochemical results
196 concerning such material.

197 b. Characterization

198 i. Powder X-ray diffraction

199 X-ray diffraction (XRD) patterns were collected using a PANalytical X'Pert Pro
200 diffractometer (Malvern Panalytical, Almelo, Netherlands). X'Celerator detector with Cu-K_{α1}-
201 K_{α2} (λ = 1.54060, 1.54439 Å) radiation was used acceleration voltage and current were 40 kV
202 and 40 mA, respectively. With a step scan of 0.0167°, diffraction patterns have been
203 collected between 20° and 80° (2θ). Moreover, *in situ* XRD patterns have been collected
204 using homemade Leriche-like cell.³⁰ During charge-discharge experiment, a current of 0.02
205 A.g⁻¹ was applied during 60 min and relaxed during 30 min for XRD pattern acquisition.

206 ii. Electron microscopy

207 Scanning electron microscopy (SEM) images were obtained obtained using a Zeiss
208 MERLIN Instrument operated at 20 kV using in-Lens annular detector. Samples were
209 prepared by dispersing a small fraction of the powder on a piece of conducting carbon tape.
210 EDX spectra were collected at 8.0 mm working distance using an X-Max 50 mm² OXFORD
211 Instruments detector.

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

219 **iii. NMR**

220 For MAS NMR analysis, free-standing electrodes with about 5-10 mg.cm⁻² were polarized for
221 10h at different states of charge after performing a cyclic voltammogram (CV) at 0.1 mV.s⁻¹.
222 After disassembling the Swagelok in a glove box, electrodes were rinsed with a few drops of
223 DMC and then dried overnight under *vacuum* in a Büchi oven at 60°C. Then, the electrolyte-
224 free electrode was placed in a 2.5 mm-diameter zirconia rotor for MAS NMR experiments.
225 ⁷Li, ⁶Li and ¹H MAS NMR spectra were acquired on a Bruker Avance 200 spectrometer (B₀ =
226 4.7 T, Larmor frequencies ν_0 (⁷Li = 77.78 MHz, ⁶Li = 29.45 MHz and ¹H = 200.15 MHz) at RT. A
227 Bruker MAS probe with a cylindrical 2.5 mm (o.d) zirconia rotor spun at a frequency of 30
228 kHz was used. ⁷Li Spectra were obtained by applying a single pulse sequence with a recycle
229 delay (D1) of 3s. ⁶Li Spectra were obtained by applying a synchronized echo sequence with a
230 recycle delay of 3s. ¹H Spectra were obtained by applying a single pulse sequence with a
231 recycle delay of 30s. D1 values were chosen to ensure the acquisition of quantitative
232 spectra. Integrated intensities were determined by using spectral simulation (DMFit
233 Software).³¹ The resulting integrated intensities were normalized with respect to the mass of
234 the sample contained in the NMR rotor, the number of scans, and the receiver gain.

235 **iv. Electrochemistry**

236 To shape the material, self-supported electrodes were fabricated by mixing, with a small
237 amount of ethanol, 75%wt HTiNbO₅, 15%wt of conductive carbon (Carbon Black by Superior
238 Graphite, Chicago, IL, USA) to increase electronic conductivity and 10%wt poly (1,1,2,2-
239 tetrafluoroethylene dissolved in water (PTFE, Sigma Aldrich) to form a homogeneous paste.
240 This mixture was mixed in a mortar to homogenize the solution and then cold-rolled until
241 the obtention of electrodes with a weight of about 5-10 mg.cm⁻² according to the

242 requirements enabling the determination of reliable gravimetric values.³² Using Swagelok
243 cells, electrochemical measurements were performed by separating positive electrode and
244 metallic lithium (99.9%, Aldrich) with a 675 μm thick glass fiber membrane (10 mm diameter,
245 GF/D Whatman) soaked with 1M LiPF_6 dissolved in 1:1 %wt. EC/DMC (Solvionic, France,
246 battery grade purity). The cells were assembled in a glove box containing less than 0.1 ppm
247 of O_2 and H_2O . A VMP3 potentiostat (Biologic operated under ECLab software version
248 V11.36) was used for electrochemical measurements.

249 **2. Results and discussion**

250 **a. Materials characterization**

251 In this work, three different HTiNbO_5 samples are presented: HTiNbO_5 synthesized by
252 solid-state route (called HTiNbO_5 SS), restacked HTiNbO_5 nanosheet particles obtained by
253 the exfoliation of HTiNbO_5 SS particles (designated as HTiNbO_5 NS), and a sample called
254 HTiNbO_5 SG synthesized by sol-gel process using the Pechini method. This nomenclature will
255 be used throughout the entire paper.

256 As described in the introduction for its analog KTiNbO_5 and in Figure 1, HTiNbO_5 is a
257 lamellar oxide with 2x2 units of edge-sharing octahedra. The presence of protons as well as
258 the strong O-H bonds allow this oxide to be considered as an acid.²⁴ It is the reason why
259 insertion of basic organic molecules by acid-base reaction is possible, such as butylamine as
260 explained in Supplementary Information.³³⁻³⁵ Moreover, due to the decrease of the
261 interlayer distance after the ion exchange (from $c = 18.742 \text{ \AA}$ for KTiNbO_5 to $c = 16.656 \text{ \AA}$ for
262 HTiNbO_5), an O-H-O bond is formed between two $(\text{TiNbO}_5)_n$ layers.²⁴ This strengthens the
263 lamellar structure of this material. To confirm these assessments extracted from literature
264 data^{22,24}, XRD patterns were obtained for this material. As shown in Figure 2.A, the oxides
265 HTiNbO_5 SS and HTiNbO_5 SG exhibits similar diffraction pattern that are consistent with
266 those proposed in the literature.^{22,24} Thus, these materials will be considered as pure phases
267 with a complete ion exchange due to the absence of peaks corresponding to KTiNbO_5 .
268 Moreover, EDX analyses confirm the presence of negligible amount of potassium in HTiNbO_5
269 SS and SG (< 1%). Since HTiNbO_5 NS was obtained from HTiNbO_5 SS, this material can also be
270 considered as pure. Nevertheless, HTiNbO_5 NS exhibits different pattern than SS and SG, due
271 to the exfoliation-stacking process. Despite the presence of the (002) peak, the absence of
272 (004) and (008) peaks proves the low ordering of (TiNbO_5) layers in this sample. Moreover,

273 the average interlayer distance for this microstructure can be calculated from the (002)
274 peak. In this respect, we determine a value of the c parameter equal to 16.62 Å, ~18.20 Å,
275 and ~22.21 Å for SS, SG, and NS respectively. These c parameters have been calculated from
276 the (002) peak using the Bragg law (Figure 2.B.). The value for SS is very close to the
277 literature data^{22,24} thus confirming the interlayer distance decrease after ion exchange
278 process. The different value found for HTiNbO₅ SG will be further discussed in the following
279 part concerning thermogravimetric analyses coupled with mass spectroscopy. Moreover, for
280 HTiNbO₅ NS, the c parameter is also very close to the literature data and can be explained by
281 the disorder created during restacking which results in larger interlayer distance.³⁶⁻³⁸

282 To corroborate the observations made from XRD patterns, SEM and TEM images of
283 HTiNbO₅ SS, SG and NS are shown in Figure 3. A clear lamellar microstructure is observed for
284 the micro size particles of HTiNbO₅ SS with a preferential growth along the
285 \vec{c} direction (Figure 3.A-B-C). In the case of HTiNbO₅ SG, smaller spherical particles of about
286 50 nm are observed as shown in Figure 3.(D-E-F). The particles are agglomerated as often
287 observed in the case of sol-gel synthesis using the Pechini method.³⁹⁻⁴¹ Interestingly, for
288 HTiNbO₅ NS, the random stacking of HTiNbO₅ sheets is observed by SEM. The SEM/TEM
289 images presented in Figure 3.(G-H-I) demonstrate this assumption although they are also
290 depicting some kind of organization of the nanosheets along the \vec{c} direction which explains
291 the (002) peak presence in the corresponding XRD pattern. Moreover, the high intensity of
292 the (002) diffraction peak compared to the other peaks in the case of HTiNbO₅ SS is
293 explained by a preferential growth of particles along the c -axis, unlike what is observed for
294 HTiNbO₅ SG.

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

303 For a better understanding of the difference in the (002) peak position between
304 HTiNbO₅ SS, SG and NS, TGA combined with MS has been performed. The TGA analyses show
305 a large difference between SS, SG and NS with respect to mass loss as shown in Figure 5.A.
306 For HTiNbO₅ SS, a mass loss of about 1% is observed before 300°C. It can be assigned to the
307 loss of water molecules adsorbed at the surface, and possibly a small amount of structural
308 water. Then, between 300°C and 550°C, a transition from HTiNbO₅ to Ti₂Nb₂O₉ causes an
309 additional 4% mass loss.⁴³ This mass loss corresponds to one water molecule (H₂O) per
310 chemical formula. *A contrario*, HTiNbO₅ SG loses 4% of its mass before the transition to
311 Ti₂Nb₂O₉ after 300°C. This higher mass loss is attributed to the presence of about one water
312 molecule per protons in the interlayer. This observation, together with the observed
313 difference in crystallinity, explains the difference between the *c* parameters of SS and SG.
314 The case of HTiNbO₅ NS is more complex to analyze because of the almost linear decrease of
315 the mass loss during the analysis. At the end of the experiment (550°C), about 11% of the
316 total mass is lost.

317 Moreover, mass spectroscopy has been combined to TGA at *m/z* = 18 to investigate
318 in more details water molecule evaporation (Figure 5.B) and at *m/z*= 40 to know about CO₂
319 evolution (Figure 5.C). Thanks to these experiments, in the case of HTiNbO₅ NS, the mass loss
320 is both related to the evaporation of water molecules (chemisorption, physisorption, and
321 transition to Ti₂Nb₂O₉) but also to the loss of CO₂. This CO₂ emission shows the presence of
322 organic molecule and more precisely of TBAOH used for the exfoliation in the interlayer
323 spacing. This observation helps to highlight one reason why the interlayer distance is higher
324 in HTiNbO₅. Lastly, as previously mentioned, we notice that the transition to Ti₂Nb₂O₉ occurs
325 around 250-300°C which demonstrates the strength of the O-H bond and the important role
326 of protons to insure the stability of the crystallographic structure.

327 **b. Electrochemistry**

328 To characterize the potential lithium ion insertion in these materials and compare
329 them, charge-discharge experiments at different current densities have been carried out and
330 are displayed in Figure 6. All electrodes were tested between 1.0V and 3.0V vs Li⁺/Li to
331 ensure the stability of the materials all over the cycling experiments. Various current
332 densities from 0.02 A.g⁻¹ to 2.0 A.g⁻¹ were used to evaluate the potential use of these
333 different materials in power applications. At low current density (0.02 A.g⁻¹), the first cycle

334 shows a specific capacity of 204, 318 and 250 mAh.g⁻¹ for HTiNbO₅ SS, SG and NS
335 respectively (Figure 6(A-B-C)). However, low coulombic efficiency in the first cycle is
336 observed specifically for HTiNbO₅ SG and NS, which leads to a decrease in capacity (Figure
337 S1). Thus, during the 3rd cycle at 0.02 A.g⁻¹, a specific capacity of 225, 204 and 113 mAh.g⁻¹ is
338 observed for HTiNbO₅ SS, SG and NS respectively. Such differences between HTiNbO₅ NS and
339 the others (SS and SG) can be explained by the steric effect due to the presence of TBAOH
340 molecules in the interlayer space of HTiNbO₅ NS which considerably reduces the number of
341 available lithium site even if the interlayer spacing is larger than for SS and SG. Moreover,
342 the low coulombic efficiency of the first cycle indicates that a significant amount of lithium
343 cations is not deinserted, thus impeding the further intercalation of lithium during the
344 subsequent cycles.

345 Concerning the shape of the charge-discharge curve, we observe in the case of
346 HTiNbO₅ SS a pronounced plateau at 1.6 V vs Li⁺/Li. For HTiNbO₅ SG, the insertion of lithium
347 cations takes place in a wider potential range (mostly between 1.7V and 1.3V vs Li⁺/Li) with a
348 lower average potential than for HTiNbO₅ SS. In contrast to the other two microstructures,
349 HTiNbO₅ NS exhibits a charge-discharge plot almost linear between 1.7 V and 1.0 V vs Li⁺/Li.
350 The charge storage mechanism that governs lithium insertion in HTiNbO₅ will be discussed in
351 more details below, at the light of *in situ* XRD analyses and *ex situ* solid-state MAS NMR.
352 When increasing the current density, a similar decrease of the specific capacity is observed
353 for HTiNbO₅ SS and SG, which are exhibiting very similar specific capacities at each current.
354 Despite the supposedly good diffusion of lithium ions in between the exfoliated HTiNbO₅
355 sheets, a lower capacity is observed for HTiNbO₅ NS based electrode as shown Figure 6.C. To
356 better visualize the differences between each sample, Figure 6.D indicates their specific
357 capacities as a function of the cycle number at different current densities and for the three
358 different microstructures. Except for the first few cycles, comparable specific capacities are
359 determined for SS and SG electrodes. For example, specific capacities of 149 mAh.g⁻¹ at 0.10
360 A.g⁻¹ and 82 mAh.g⁻¹ at 1.0 A.g⁻¹ are reported for HTiNbO₅ SS that represented respectively
361 65% and 35% of its specific capacity at 0.02 A.g⁻¹. For the same currents, HTiNbO₅ NS shows
362 specific capacity of only 63 and 25 mAh.g⁻¹ respectively. From these observations, we can
363 conclude that the architecture of the nanosheets particles (HTiNbO₅ NS) is not adequate as a

364 fast charging/discharging electrode for high power Li-ion batteries. These low capacities can
365 be assigned to the presence of organic molecule in the nanosheets.

366 To prove this assumption, the intercalation of organic molecule was performed on
367 HTiNbO₅ SS as described in Supplementary Information. Figure S3.A demonstrates the
368 effective presence of butylamine in the interlayer space of HTiNbO₅ by comparing the XRD of
369 the material before and after mixing with butylamine. Moreover, Figure S3.B demonstrates
370 that even if the electrode achieves a higher capacity at very low current in the case of
371 butylamine-HTiNbO₅, a rapid decrease of the capacity is observed due to the steric effect
372 caused by the presence of these very large organic molecules.⁴⁴ These results are in line with
373 the observations made on HTiNbO₅ NS. Moreover, Figure S3 displays the poor
374 electrochemical behavior of KTiNbO₅ SS showing the non-insertion of lithium due to the
375 presence of the large K⁺ ions in the interlayer spacing confirming the influence of the
376 intercalated species between the (TiNbO₅) layers on electrochemical behavior of the
377 corresponding electrode.

378

379 c. *In situ* XRD

380 To better understand the charge storage mechanism that governs HTiNbO₅ according
381 to the different morphologies, we performed *in situ* XRD for HTiNbO₅ SS, SG, and NS. These
382 results are presented in Figure 7. It can be noted that for the HTiNbO₅ SS, the preferential
383 growth of the grains only enables the detection of (00l) peaks.⁴³ Thus, it is not possible to
384 trace the volume change in these materials. However, it is still possible to understand the
385 mechanisms that govern lithium intercalation in HTiNbO₅ as well as the differences
386 according to the various microstructures. On one hand, for HTiNbO₅ SS we observe an initial
387 phase change during the first lithiation. Li_{0.4}HTiNbO₅ phase is irreversibly formed and then
388 the material shows a solid solution type lithiation mechanism during the subsequent
389 charging and discharging steps.²⁸ This is highlighted by the reversible shift of the (002) peak
390 as shown in Figure 7.A. Moreover, the c parameter decreases during the insertion of lithium
391 ions due to coulombic attraction between the positively charged cations in the interlayer
392 and the negatively charged layers (TiNbO₅)_n. On the other hand, when lithium ion are
393 extracted during discharge, the c parameter reversibly increases. Interestingly, HTiNbO₅ SG

394 shows a very similar behavior, with a phase change occurring at the beginning of the first
 395 lithiation as shown in Figure 7.B. Indeed, the (011) peak initially at 24° disappears leaving
 396 place to another peak at 25.5°. The latter shows the formation of Li_{0.4}HTiNbO₅ phase
 397 (Equation 1). As for HTiNbO₅ SS, after this initial step and irreversible formation of
 398 Li_{0.4}HTiNbO₅, a solid-solution reaction takes place during the following cycles (Equation 2).

399



402

403 The (002) peak shift in HTiNbO₅ SG electrode is more easily visible thanks to the top
 404 view presented in Figure S4.D. Thus, by comparing the variation of the (002) peak between
 405 HTiNbO₅ SS and HTiNbO₅ SG, we notice that the variation of the c parameter is very similar
 406 with an initial change followed by a progressive shift. In the case of HTiNbO₅ NS, due to the
 407 low crystallinity of the material, it is more complex to trace the Li ion insertion mechanism
 408 by *in situ* XRD (Figure 7.C). Nevertheless, we notice that smaller peak shifts are observed
 409 during lithiation/delithiation. The (002) peak shows an irreversible shift at the end of the first
 410 cycle as seen in Figure 7.C and Figure S4.(E-F). This explains the low coulombic efficiency
 411 determined for this material. Also, a gradual decrease of the intensity of the peaks seems to
 412 demonstrate a decrease of the crystallinity of the structure which could result in a
 413 disorganization of the (TiNbO₅)_n layers, which in turn could hinder lithium ion diffusion
 414 between the (TiNbO₅) sheets. To summarize, these *in situ* XRD experiments demonstrate, in
 415 the case of HTiNbO₅ SS and SG, the formation of a phase described as Li_{0.4}HTiNbO₅ during
 416 the first lithiation. This phase reversibly inserts lithium ions through a solid solution
 417 mechanism. In the case of NS, a disorganization of the layers leads to an amorphization and
 418 a decrease of the interlayer distance that, in turn, result in a low coulombic efficiency and
 419 low specific capacities.

420

421 d. *Ex situ* solid-state MAS NMR

422 *Ex situ* solid-state MAS NMR was performed on HTiNbO₅ SS at several charge and
423 discharge potentials to follow the evolution of lithium and protons local environments upon
424 cycling (Pristine state, 1.5V, 1.0V and 3.0V vs Li⁺/Li). Related CV are shown in Figure 8.A.
425 Indeed, several groups have demonstrated the importance of solid-state MAS NMR.⁴⁵⁻⁴⁹
426 This technique allows to better understand the redox mechanisms, to monitor different
427 lithiation sites population and distribution as well as to evidence the changes in the physico-
428 chemical properties of electrodes for batteries and supercapacitors during charging and
429 discharging processes. Here, ⁷Li and ⁶Li *ex situ* MAS NMR give some insight on lithium local
430 environments as well as the reversibility of the process. ¹H *ex situ* MAS NMR allows a better
431 understanding of the role of the proton as well as how the proton local environment is
432 altered during the insertion of lithium ions during the solid solution mechanism.

433 As shown in Figure 8.B, for each potential, the ⁷Li MAS NMR spectrum displays a
434 relatively broad signal close to 0 ppm. These signals are assigned to lithium ions inserted into
435 the material, based on their relative integrated intensities with respect to the state of
436 charge. Compared to 1.5V, the peak at 1.0V is broader, thus suggesting possible differences
437 in lithium mobility within the material or the existence of a slightly different distribution of
438 lithium local environments. The integrated intensity at 1.5V corresponds to 70% of that at
439 1.0V. Interestingly, the lithiation-delithiation process is not fully reversible with the presence
440 of a peak for the sample recovered after one cycle (3.0V) corresponding to 14% of the
441 lithium present at 1.0V as calculated in Figure S5. This observation is in good agreement with
442 the results obtained by electrochemistry and by *in situ* XRD where we noticed that part of
443 the lithium inserted at the beginning of the first reduction process is consumed to
444 irreversibly form Li_{0.4}HTiNbO₅.

445 In an attempt to obtain more information on the lithiation sites in this material, ⁶Li
446 solid-state NMR was performed on HTiNbO₅ with the same cycled electrodes. Thanks to
447 Figure 8.C, we can notice that at 3.0V (after one cycle) the material shows two distinct
448 resonances. A first one at 1 ppm, very sparsely populated and another one at -0.5 ppm more
449 populated. *A contrario*, at 1.5V and 1.0V, only an intense non-symmetrical resonance can be
450 observed with a maximum close to 1 ppm. This resonance increases clearly during the
451 lithiation process from 1.5 to 1.0 V. This result indicates that the related lithium local
452 environment corresponds to the main lithiation site. In addition, the signals observed at 1.0

453 and 1.5 V seem to include a shoulder at approx. -0.5 ppm. This information suggests that the
454 major resonance remaining after delithiation at 3.0V is already present during the lithiation
455 process. We then tentatively assign the resonance at -0.5 ppm to the Li site populated upon
456 the irreversible formation of the $\text{Li}_{0.4}\text{HTiNbO}_5$ phase during the initial lithiation. The peak at
457 0.5 ppm could also correspond to lithium in the SEI layer. However, we thought this
458 hypothesis less probable as the electrode never goes below a potential of 1V. The potential
459 at which the SEI starts to form is about 0.8V vs Li^+/Li . Furthermore, ^{19}F MAS NMR spectrum
460 appear to indicate that the amount of LiF (a typical SEI component) is only very weakly
461 observed at 1.0V and even less at 3.0V (Figure S6). In addition, at 3.0V, the less populated
462 site (at 1 ppm) could correspond to lithium that did not deintercalate during the oxidation
463 but different from the 0.4 lithium of $\text{Li}_{0.4}\text{HTiNbO}_5$. Thus, we can conclude that when the first
464 site (-0.5 ppm) is completed, giving rise to the phase change, the lithium ions that are further
465 intercalated go into a different site (1ppm).

466 Based on these observations, ^1H MAS NMR was also performed on the same
467 electrodes to understand changes in proton local environment in the interlayer space as a
468 function of the amount of associated lithium. In 2004, Takagaki *et al.* reported ^1H MAS NMR
469 experiments on HTiNbO_5 nanosheet.⁵⁰ They assigned a resonance at 12 ppm to the proton in
470 the interlayer space. As shown in Figure 8.D, the pristine HTiNbO_5 SS also shows a peak at 12
471 ppm corresponding to an -OH group of the interlayer space, in agreement with previously
472 reported results. An additional small proton resonance, barely visible, is also superimposed
473 on the empty rotor signal at 7 ppm and is attributed to -OH outside the layers (at the surface
474 of the particles). Interestingly, on electrodes reduced to 1.5V and 1.0V, the 12 ppm
475 resonance peak disappears completely while a new signal at 3.4 ppm appears. This indicates
476 that the local environment of all protons present in the interlayer space has changed. The
477 displacement to lower chemical shifts and the narrowing of the resonance indicates more
478 acidic and more mobile protons, respectively. Thus, the lithiation process implies a
479 movement and reorganization of the interlayer protons, due to the insertion of lithium ions.
480 The higher mobility of the protons suggests that the insertion of lithium in the interlayer
481 space leads to a greater instability of the protons in the structure. After one full cycle of the
482 material to 3V, two signals corresponding to protons are observed (Figure 8.D). The
483 resonance at 12 ppm reappears and indicates the presence of protons with a local

484 environment very similar to the pristine material. This resonance is nevertheless much less
485 intense compared to the case of the pristine material, consistent with a partial reversibility
486 of the redox reaction. Another resonance at 5.6 ppm, wider and more intense than the one
487 at 12 ppm, implies the presence of protons that are more acidic than those in the pristine
488 material but less mobile than the protons in the samples lithiated to 1.5 and 1.0V, suggesting
489 an intermediate state of local environment. Overall, these observations also seem to confirm
490 the irreversible phase change observed by *in situ* XRD. Lastly, ^1H MAS NMR on the pristine
491 HTiNbO_5 SG has been performed (Figure S7). It shows very similar properties (acidity and
492 mobility) of protons that the HTiNbO_5 SS. This provides an additional argument to explain
493 the observed electrochemical similarities between HTiNbO_5 SS and HTiNbO_5 SG.

494

495 **Conclusion**

496 This work reports on the synthesis and the characterizations of different
497 microstructures of HTiNbO_5 with special care to their electrochemical properties.
498 Microparticles (SS), nanoparticles (SG) as well as restacked nanosheets (NS) present different
499 amounts of water in the interlayer space according to XRD and TGA coupled with MS. The
500 similar electrochemical behavior of nano- and microparticles is explained by the very close
501 charge storage mechanism with an initial and irreversible phase change to form
502 $\text{Li}_{0.4}\text{HTiNbO}_5$, followed by continuous solid-solution reaction during subsequent cycles. ^1H
503 solid state MAS NMR on HTiNbO_5 SS highlights the importance of proton in the interlayer
504 spacing for the fast charging abilities of this oxide. In fact, change in the proton properties
505 seems to help the Li ion intercalation by being more mobile and more acidic. In contrast,
506 nanosheet microstructure shows a very poor electrochemical activity because of the organic
507 molecule in its interlayer space. An exfoliation process of HTiNbO_5 without the use of organic
508 molecule as exfoliation agent can be of interest to increase the electrochemical performance
509 of HTiNbO_5 nanosheet (NS). Nevertheless, several insightful conclusions can be extracted
510 from this work. First, in contrast to $\text{Ti}_2\text{Nb}_2\text{O}_9$, nanosizing the structure does not seem to be
511 useful and effective to achieve higher specific capacity at high rate.⁴³ This is explained by the
512 main role that protons are playing in the charge storage mechanism. Subsequently, it can be
513 interesting to complete this type of study on other materials made up of protons to
514 generalize the assumptions proposed here. More globally, layered materials presenting

515 protons in their interlayer spaces can be materials of choice as negative electrode for next
516 generation of high rate Li-ion batteries.

517

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522 great advices on intercalation of organic molecule in layered inorganic materials as HTiNbO₅.
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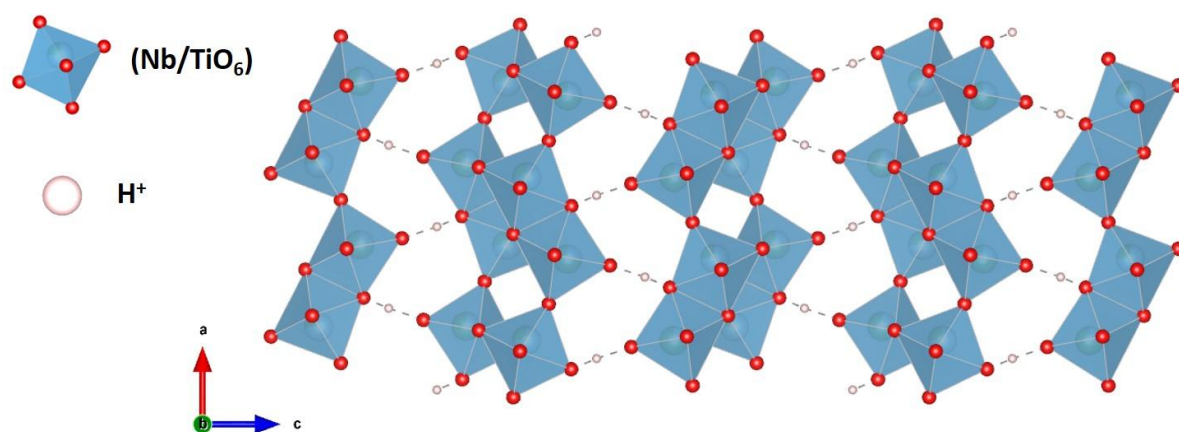
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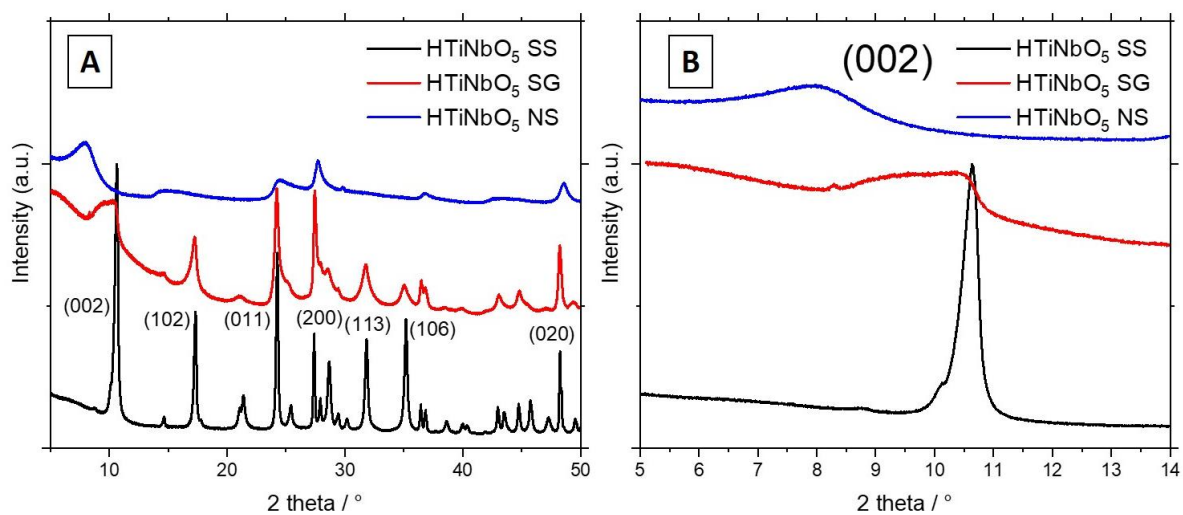
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Figures



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

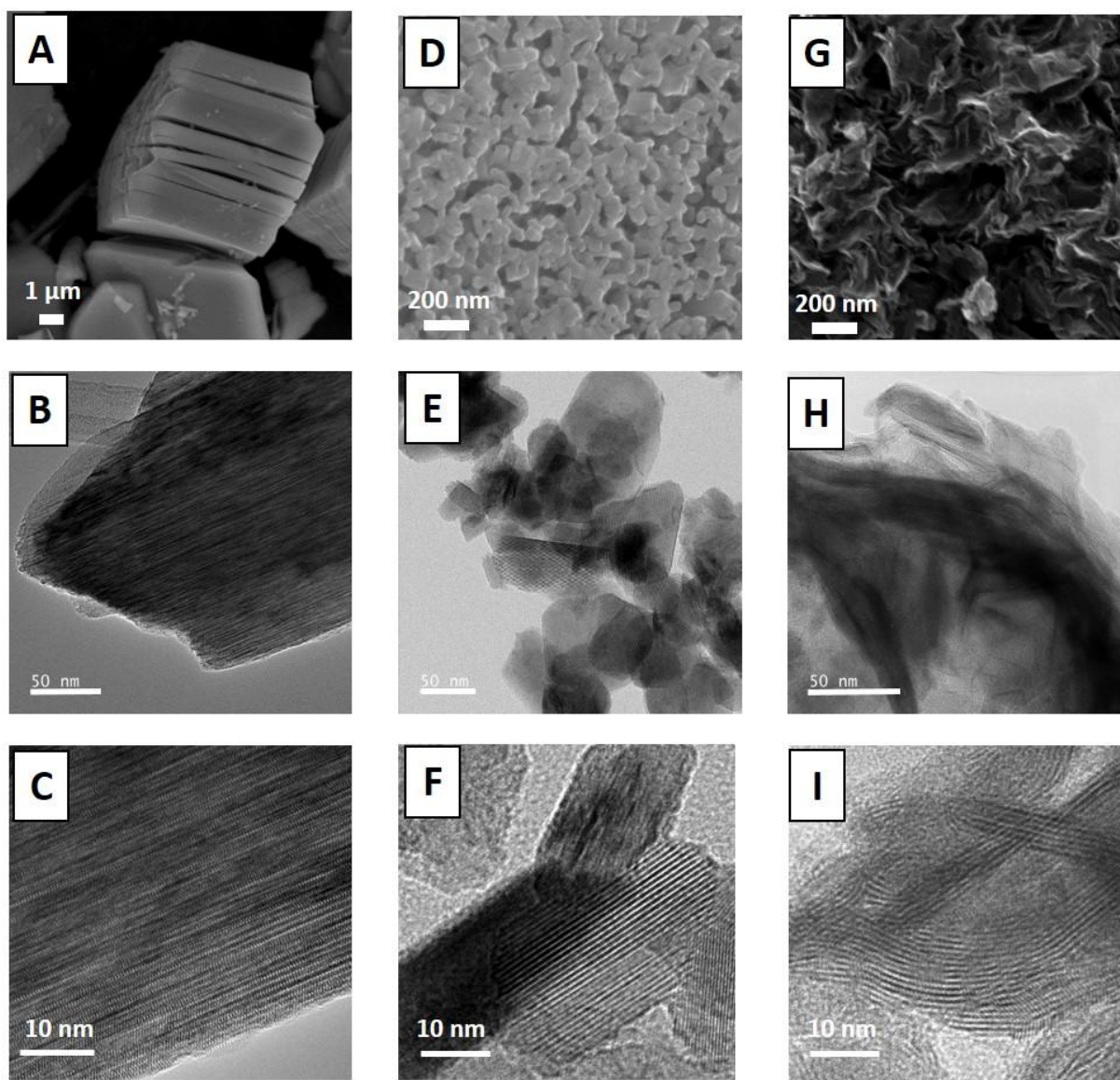


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566 **Figure 2. XRD pattern of HTiNbO₅ for the three different morphologies (SS/SG/NS) between (A) 5-**
 567 **50° and (B) 5-14° 2θ angles. XRD patterns highlight the difference in the interlayer distance thanks**
 568 **to the (002) peak shift.**

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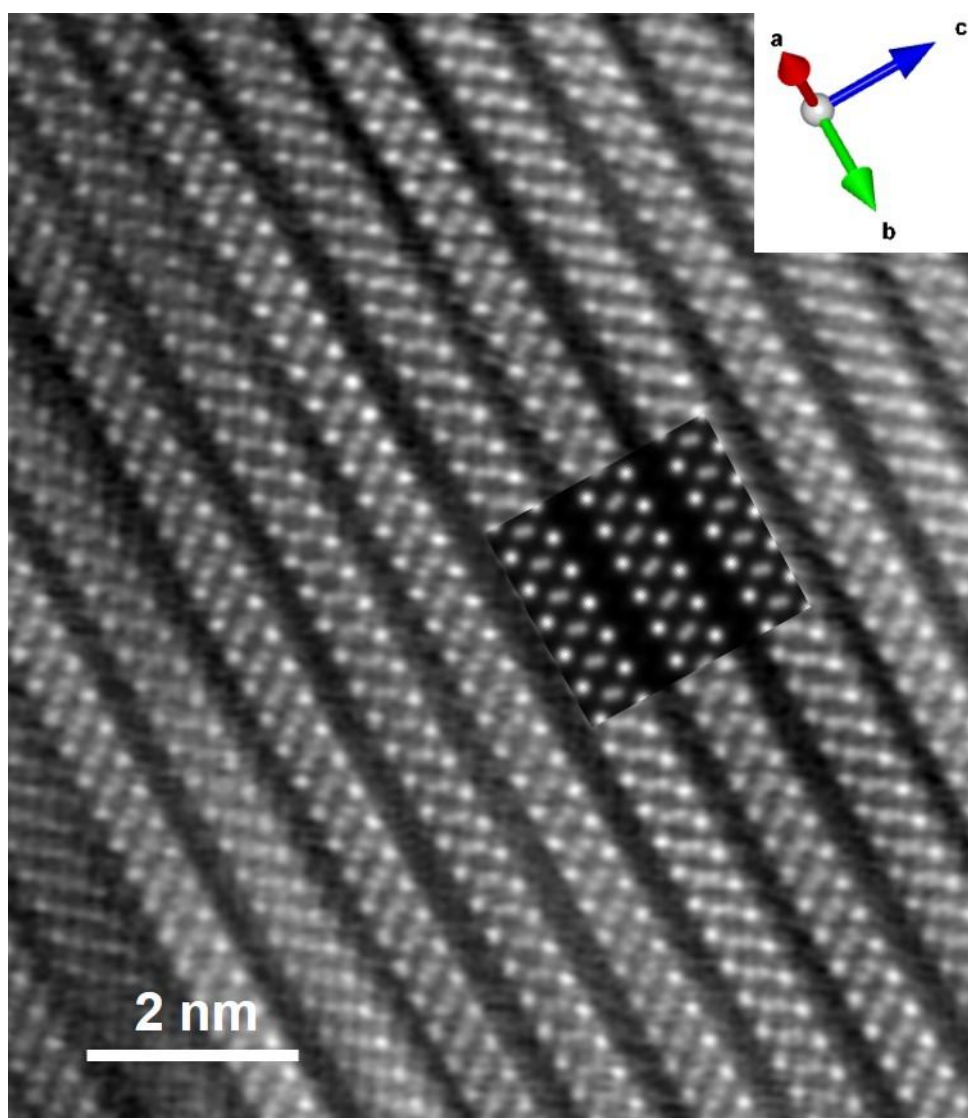
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 572 **Figure 3. SEM and TEM images of (A-B-C) HTiNbO₅ solid-state (SS) (D-E-F) HTiNbO₅ sol-gel (SG) (G-H-**
 573 **I) HTiNbO₅ nanosheets (NS).**

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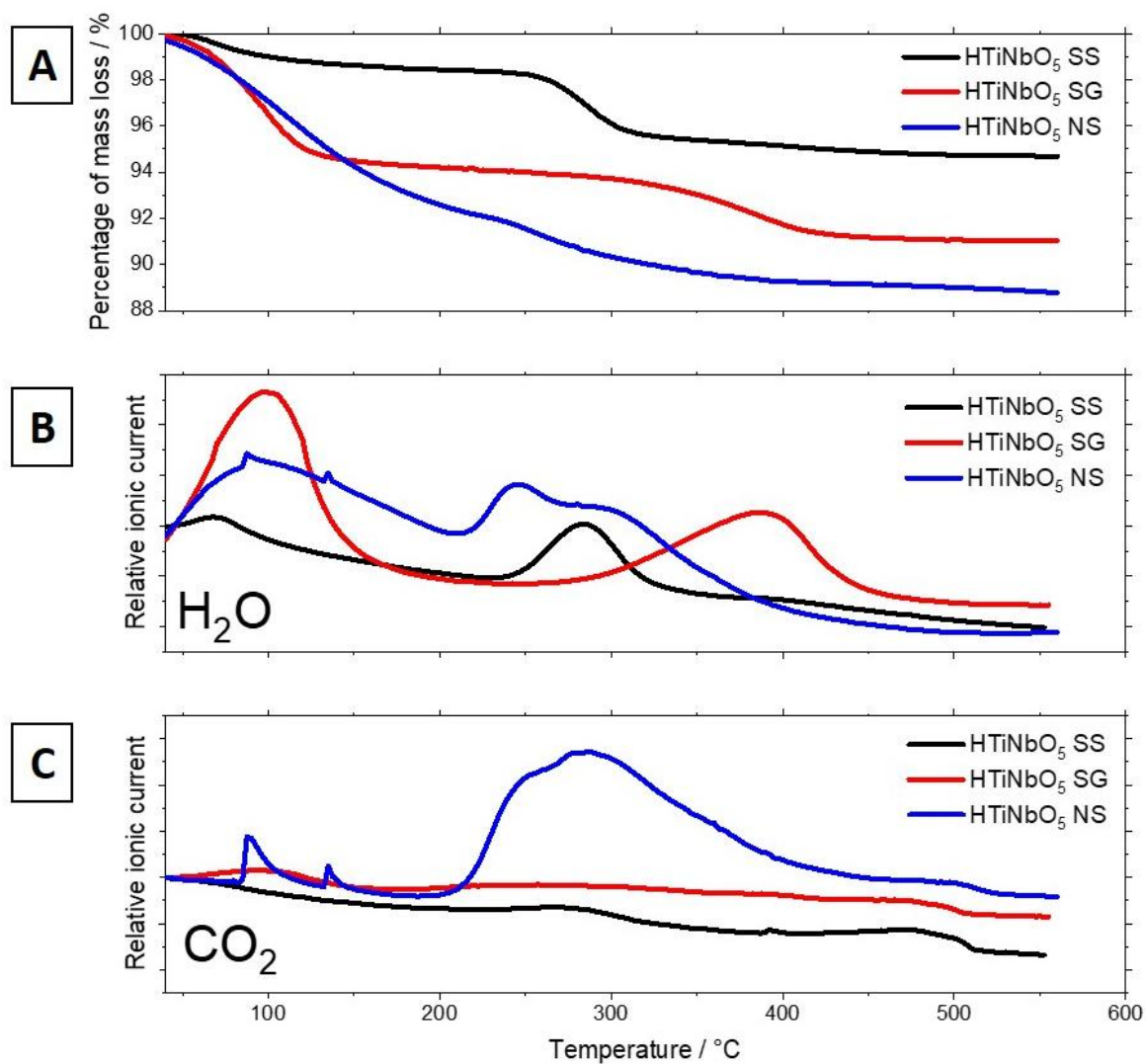
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577 **Figure 4. Experimental HAADF-STEM image (Radial Wiener Filtered) of HTiNbO₅ SS viewed along**
578 **[110] (scale bar: 2 nm). Inset : simulated HAADF image (Dr Probe⁵², using ICSD file #31797²⁴ as**
579 **input structure).**

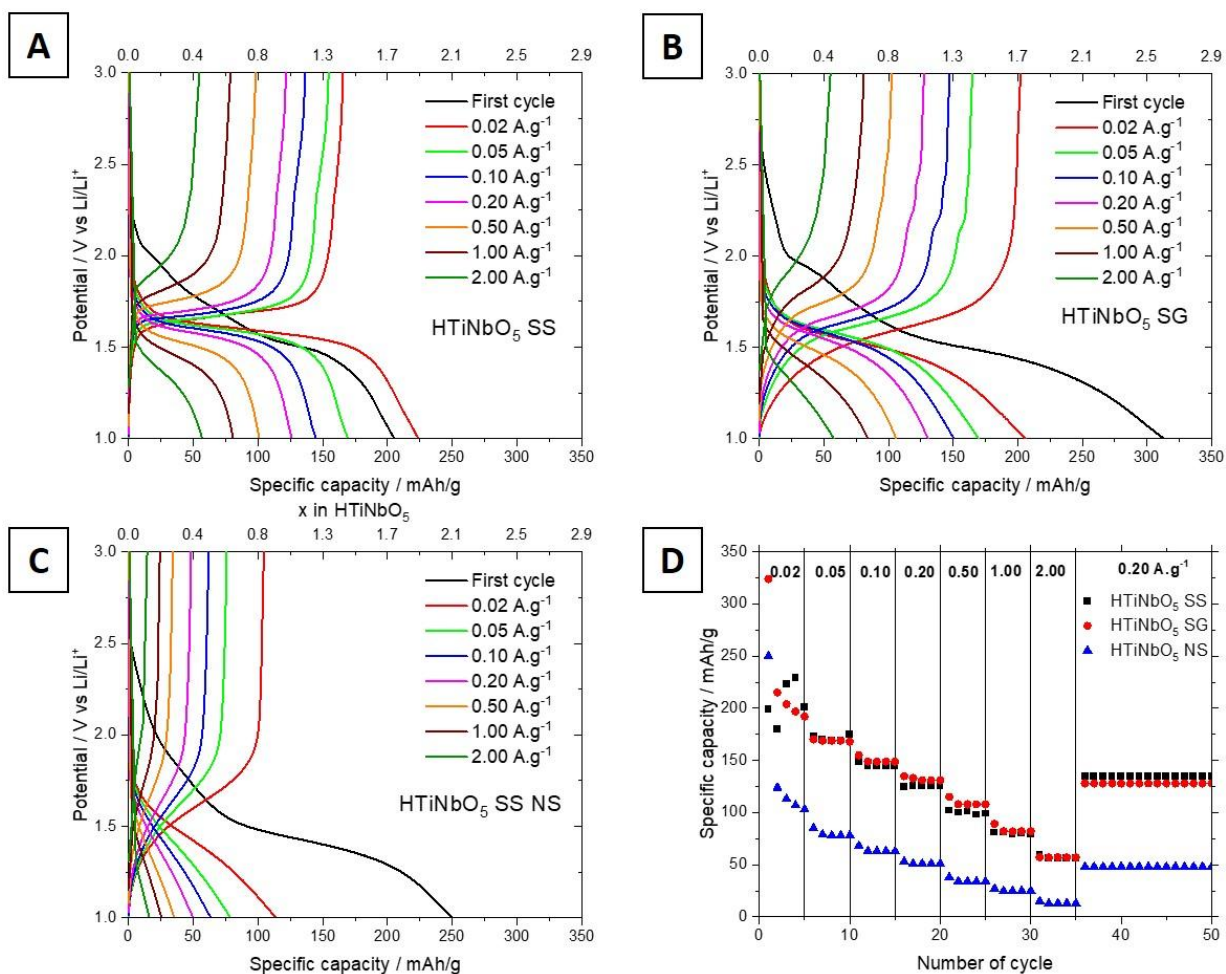
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582 **Figure 5. (A) Thermogravimetric analysis of the three different morphologies (SS/SG/NS) coupled**
 583 **with corresponding mass spectroscopy following different species (B) H₂O (m/z=18) and (C) CO₂**
 584 **(m/z=40)**

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586

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

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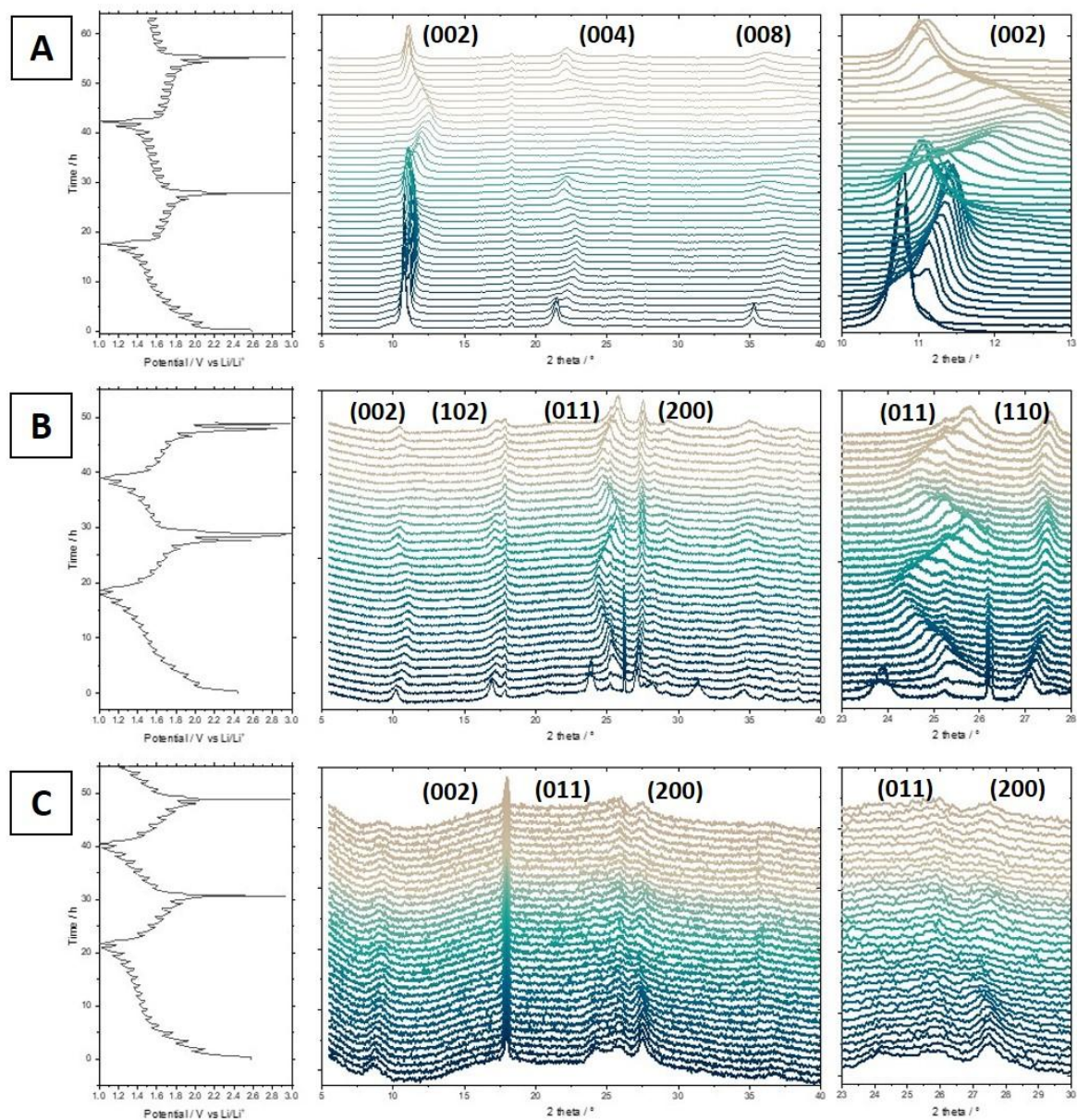
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603 **Figure 7. *In situ* XRD patterns at a current density of 0.02 A.g⁻¹ between 1.0V and 3.0V vs Li⁺/Li of**
 604 **(A) HTiNbO₅ solid-state (SS) (B) HTiNbO₅ sol-gel (SG) (C) HTiNbO₅ nanosheets (NS) with**
 605 **corresponding voltage-time curves.**

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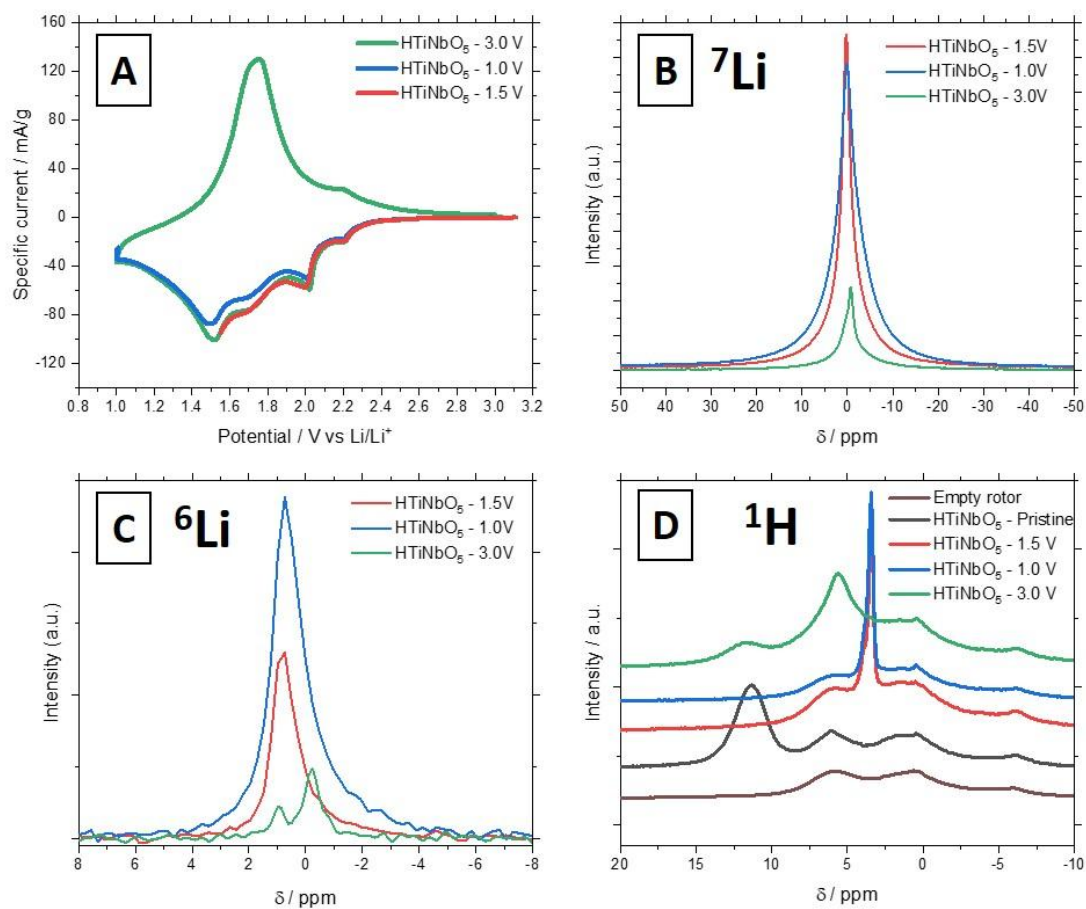
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613 **Figure 8. (A) CV of HTiNbO₅ solid-state (SS) at different potential (1.5V/1.0V/3.0V vs Li⁺/Li).**
 614 **(B) *ex situ* ⁷Li MAS NMR normalized spectra of HTiNbO₅ solid-state (SS) at different potential.**
 615 **(C) *ex situ* ⁶Li MAS NMR normalized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

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