



Article Design of Sodium Titanate Nanowires as Anodes for Dual Li,Na Ion Batteries

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Abstract: The bottleneck in the implementation of hybrid lithium-sodium-ion batteries is the lack of anode materials with a desired rate capability. Herein, we provide an in-depth examination of the Li-storage performance of sodium titanate nanowires as negative electrodes in hybrid Li,Na-ion batteries. Titanate nanowires were prepared by a simple and reproducible hydrothermal method. At a low reaction pressure, the well-isolated nanowires are formed, while by increasing the reaction pressure from 2 to 30 bar, the isolated nanowires tend to bundle. In nanowires, the local coordinations of Na and Ti atoms deviate from those in Na₂Ti₃O₇ and Na₂Ti₆O₁₃ and slightly depend on the reaction pressure. During the annealing at 350 °C, both Na and Ti coordinations undergo further changes. The nanowires are highly defective, and they easily crystallize into Na₂Ti₆O₁₃ and Na₂Ti₃O₇ phases. The lithium storage properties are evaluated in lithium-ion cells vs. lithium metal anode and titanate electrodes fabricated with PVDF and carboxymethyl cellulose (CMC) binders. The Li-storage by nanowires proceeds by a hybrid capacitive-diffusive mechanism between 0.1 and 2.5 V, which enables to achieve a high specific capacity. Sodium titanates accommodate Li⁺ by formation of mixed lithium-sodium-phase $Na_{2-x}Li_xTi_6O_{13}$, which is decomposed to the distinct lithium phases Li_{0.54}Ti_{2.86}O₆ and Li_{0.5}TiO₂. Contrary to lithium, the sodium storage is accomplished mainly by the capacitive reactions, and thus the phase composition is preserved during cycling in sodium ion cells. The isolated nanowires outperform bundled nanowires with respect to rate capability.

Keywords: sodium-ion batteries; hybrid Li,Na-ion batteries; lithium intercalation; capacitive energy storage; layered sodium titanates; tunnel-type sodium titanates; lithium titanates; synthesis; structure characterization

1. Introduction

Hybrid lithium-sodium-ion batteries (LNBs) are a new class of batteries that combine the advantages of single lithium and sodium ones (i.e., high power and low cost) by avoiding their disadvantages (cycling stability and rate capability) [1]. The implementation of hybrid LNBs relies on the choice of electrode materials, which are able to intercalate both Li⁺ and Na⁺ ions [1,2]. As cathode materials, a large variety of polyanionic compounds (such as Na₃V₂(PO₄)₃, Na₃V₂(PO₄)₂F₃, Na₃V_{2-x}Fe_x(PO₄)₃, Na₄Fe₃(PO₄)₂P₂O₇, etc.) and layered alkali transition metal oxides (P3-Na_{2/3}Ni_{1/2}Mn_{1/2}O₂, P3/P2-Na_{2/3}Ni_{1/4}Mn_{3/4}O₂, Na_{0.34}K_{0.5}CoO₂, NaKNi₂TeO₆, etc.) can be used due to their diversity of flexible structures, offering suitable sites for accommodation of different ions at potentials higher than 2.0 V [1,2]. In contrast to cathode materials, there are few examples of anode materials operating at potentials lower than 2.0 V [1,2].

Searching for negative electrodes, two groups of high-power and low-cost materials, that preserve their structural integrity during the electrochemical reactions, need to be highlighted [3]. These are bio-carbon- and Ti-based materials. Bio-carbons appear in most perspectives since they are able to store high amounts of sodium and lithium ions at a voltage approaching that of pure sodium/lithium metal, as well as having a low cost with



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). a small environmental impact [4,5]. The enhanced storage performance is a consequence of their complex mechanisms, including adsorption, intercalation, and pore-filling reactions [6]. However, their low cycling stability, high first irreversible capacity, and worse rate capability impede the feasible utilization of hard carbons in LNBs [2,4,5]. Ti-based materials operate at a broader voltage range thanks to the Ti⁴⁺/Ti³⁺ redox couple, thus preventing the formation of sodium dendrites during cycling [7,8]. In addition to the intercalation mechanism, the Ti-based materials store energy through intrinsic pseudocapacitive reactions, which enable them to reach a high-rate performance [9,10]. However, their poor electrical conductivity hinders the implementation of Ti-based electrodes in rechargeable batteries [7]. Therefore, the state-of-the-art research is, nowadays, focused on the improvement of electrical conductivity of titanates [7,8]. There are two approaches. The first approach aims to functionalize the titanates on the highly conductive materials, such as multi-walled carbon nanotubes, carbon nanotube and graphene, N-doped carbon hollow spheres, titanium peroxide, carbon coating, PEDOT coating, etc. [11–17]. The second approach consists in the manipulation of particle dimensions and morphology, resulting in development of nanorods, nanoplatelets, and nanosheets of Na₂Ti₃O₇, nanowires, nanotubes, 3D micro-flowers, exfoliated Na₂Ti₃O₇, restacked oxides, etc. [18–22]. In general, the morphology consisting of nanowires seems to be useful for electrodes since it enables to enlarge the interface between the electrolyte and the electrode due to the high surfaceto-volume ratios, to enhance the charge transport due to 1D electronic pathways, and to easily accept large volume expansion/contraction occurring during the repeatedly alkali ion insertion/extraction [23].

Among Ti-based materials, sodium titanates, having a general formula $Na_2Ti_xO_{2x+1}$ and diversity of structures, are most interesting from the electrochemical point of view [7,8]. The compound with the $Na_2Ti_3O_7$ composition exhibits a layered structure, which ensures suitable sites for fast Li^+ and Na^+ diffusion [24–26]. The unique property of $Na_2Ti_3O_7$ is its ability to intercalate 2 mol Na⁺ ions at extremely low potentials (i.e., of around 0.3 V vs. Na/Na^+ , theoretical capacity of 177 mAh/g) [25]. The layered $Na_2Ti_3O_7$ also intercalates 2 mol of Li⁺, but at higher potentials (i.e., in the voltage range of 1.5–2.0 V vs. Li/Li⁺) [27]. However, Na₂Ti₃O₇ possesses some drawbacks, one of them being its structural instability: even after oxide storage in a carbonate-based electrolyte solution (such as 1 M NaPF_{6} in EC/PC and 1 M NaClO₄ in EC/PC), the layered Na₂Ti₃O₇ is transformed to tunnel-like $Na_2Ti_6O_{13}$ [28]. Contrary to layered $Na_2Ti_3O_7$, tunnel $Na_2Ti_6O_{13}$ intercalates Na^+ ions at enhanced potentials (i.e., at 0.8 V vs. Na/Na⁺) [29,30]. Moreover, Na⁺ diffusion into tunnel $Na_2Ti_6O_{13}$ takes place faster than that of layered $Na_2Ti_3O_7$, resulting in an excellent cycling stability and rate performance [31]. Thus, the hybrid between layered $Na_2Ti_3O_7$ and tunnel Na₂Ti₆O₁₃ demonstrates improved Na-storage properties [32]. As in the case of Na₂Ti₃O₇, tunnel Na₂Ti₆O₁₃ intercalates Li⁺ ions in a broad potential range (i.e., lithiation at around 1.5 V together with charge storage below 1.2 V) [33]. The Li⁺ intercalation into Na₂Ti₆O₁₃ proceeds by only 2.75% volume expansion, thus resulting in an excellent cycling stability [33]. In comparison with layered $Na_2Ti_3O_7$ and tunnel $Na_2Ti_6O_{13}$, the higher potential of Na⁺ intercalation is achieved at Na₂Ti₄O₉, also having a tunnel-type structure (i.e., 1.1 V, 1.5 V, and 1.8 V vs. Na/Na⁺), while lithium intercalation is accomplished at around 1.4 V, 1.8 V, and 2.0 V vs. Li/Li⁺ [34]. In general, until now, intensive research has been carried out on the Na-storage performance of sodium titanates, while the studies on Li-storage performance are rare.

Herein, we provide an in-depth examination of the Li-storage performance of sodium titanate nanowires as negative electrodes in hybrid Li,Na-ion batteries. For the synthesis of nanowires, we adopt a simple and reproducible hydrothermal method, where the reaction pressure is varied between 2 and 30 bar. Structural and morphological peculiarities of sodium titanates are monitored by X-ray diffraction, Raman scattering, SEM, and TEM analyses. The lithium storage properties are evaluated in lithium-ion cells vs. lithium metal anode and titanate electrodes fabricated with PVDF and carboxymethyl cellulose (CMC) binders. Complementing the Li-storage properties, we also study the Na-storage ones. The

mechanism of Li-storage is discussed on the basis of CV experiments and ex situ X-ray diffraction and TEM analysis.

2. Materials and Methods

2.1. Materials

Sodium titanates were hydrothermally synthesized using a high-pressure laboratory reactor, Berghof, BR-100 (Berghof, Baden-Wuerttemberg, Germany). The reagents were TiO₂ (anatase, purris, Honeywell Fluka, Charlotte, NC, USA) and NaOH (p.a., Chem-Solutions GmbH, Dimitrovgrad, Bulgaria). Two grams of anatase powder was mixed with 75 mL of 10 M NaOH and stirred for 1 h. The prepared suspension was transferred into a 100 mL Teflon vessel, sealed in the autoclave, and heated at 150 °C for 48 h under stirring. To vary the reaction pressure, we used three procedures. In the first procedure, the reaction took place at the autogenic pressure, which was about 2 bar. The second procedure relied on the pumping of O₂ gas, so that the reaction pressure increased up to 30 bar by adding hydroxide, H₂O₂, to the reaction mixture of TiO₂ and NaOH. After cooling to room temperature, the resultant product was washed with H₂O until pH = 7 and dried at 60 °C for 12 h under a vacuum. Prior to the electrochemical characterization, the prepared sodium titanates will be denoted as NTO-2, NTO-5, and NTO-30, respectively.

For the sake of comparison, the Na₂Ti₃O₇ reference was obtained by solid-state reaction. Stoichiometric amounts of TiO₂ (anatase) and Na₂CO₃ were ball-milled for 5 h at 400 rpm (sample-to-ball weight ratio of 1 to 10). Then, the mixture was heated at 800 °C for 36 h under air. This method allowed to obtain Na₂Ti₃O₇ (SG P2₁/m) with the following lattice parameters: a = 8.5648(1) Å, b = 3.80185(4) Å, c = 9.1267(1) Å, and β = 101.603(2)°, which agree very well with the reference pattern (COD-96-231-0332).

2.2. Methods

Powder X-ray diffraction (Bruker Advance D8 diffractometer, Karlsruhe, Germany) with the LynxEye detector (CuK α radiation) was used to determine the structure of sodium titanates. The morphology of titanates was monitored by SEM (JEOL JSM 6390 microscope, Tokyo, Japan) and TEM analysis using a JEOL 2100 microscope (Tokyo, Japan) with a GATAN Orius 832 SC1000 camera (Plesantan, CA, USA). The chemical composition was evaluated by EDS analysis using an energy-dispersive X-ray spectrometer (Oxford INCA, Oxford Instruments, Abingdon, UK) integrated with a JEOL JSM 6390 microscope. The Raman spectra were recorded on a B&WTEK spectrometer (BTC665N-785S-SYS, Metrohm Group Newark, DE, USA) with laser excitation of 785 nm. The thermal stability of titanates was determined by simultaneous TG/DTA analyses (LABSYSTM Evo apparatus, SETARAM, Caluireet-Cuire, France) at a heating rate of 10 °C/min under Ar atmosphere.

For the electrochemical characterization, all electrodes were fabricated by the same procedure, including mixing of the active material with carbon black (Super C65, TiMCAL Ltd.—Bodio, Switzerland) and carboxymethyl cellulose (CMC, Merck, St. Louis, MO, USA) in a ratio of 80:10:10. The slurry was cast on aluminum foil, followed by drying at 80 °C overnight. The 10 mm disk electrodes were cut, pressed, and dried at 120 °C under a vacuum. The sodium and lithium cells of the Swagelok type were mounted in a glovebox (MB-Unilab Pro SP (1500/780), H₂O, and O₂ content < 0.1 ppm, MBraun, Garching, Germany). Clean sodium or lithium metal was used as a counter-electrode, while the electrolytes included 1 M NaPF₆ in PC (Sigma Aldrich, St. Louis, MO, USA) or 1 M LiPF₆ (EC/DMC 1:1 by vol., Sigma Aldrich, St. Louis, MO, USA). All electrochemical experiments were carried out on a 32-channel Biologic VMP-3e battery cycler (38170 Seyssinet-Pariset, France). Each electrochemical experiment was repeated at least twice, showing a rather high reproducibility. The capacity was calculated per gram of NTO. For the ex situ XRD and TEM experiments, the cells were dissembled in a glovebox, and the recovered electrodes were further analyzed.

3. Results and Discussions

3.1. Synthesis of Sodium Titanate Nanowires

Figure 1 displays the XRD patterns of the as-prepared Na–Ti-oxides. All XRD patterns consisted of few broad diffraction lines, which did not permit to unambiguously index them. It is of importance that the XRD profiles were the same irrespective of the reaction pressure, thus indicating a formation of sodium titanates with the same phase composition. For the sample treated at a lower pressure only, low-intensive diffraction lines due to unreacted anatase TiO₂ also appeared. For the sample treated at a higher pressure, these diffraction lines were hardly visible.



Figure 1. XRD patterns of NTO-2 (**A**), NTO-5 (**B**), and NTO-30 (**C**), as-prepared (a) and annealed at 350 $^{\circ}$ C (b). The XRD pattern of TiO₂ is also shown.

The main component of the as-prepared titanates is the water content. Between 50 and 200 °C, the titanates obtained at different reaction pressures lost around 12–15 wt.% of water (Figure 2A). The low temperature of the water release indicates that water appeared in a physisorbed state in the as-prepared Na-Ti-oxides. Hence, the as-prepared sodium titanates were annealed at 350 °C for 3 h in Ar atmosphere. After thermal annealing, the water content of all titanates decreased by more than 5 wt.%. However, the annealed titanates still evolved at around 5–8 wt.% of water (Figure 2B). This means that some water contamination still occurred in the annealed titanates. The occurrence of water contamination in annealed titanates shows their capability to easily adsorb water from the environment. In addition, after thermal annealing of titanates, the broad diffraction lines remained unchanged (Figure 1). This evidenced a preservation of the crystal structure of the titanates during the release of physisorbed water. In addition, the close examination of the DTA curve profiles revealed that NTO-2 demonstrated a low-intensive peak at around 645 °C, which we cannot ascribe to any previously known thermal reactions.

To rationalize the local coordination of Na and Ti atoms in the as-prepared and annealed titanates, Raman spectroscopy was undertaken (Figure 3). As a Raman reference for Ti-O and Na-O-Ti vibrations, we used Na₂Ti₃O₇, prepared by a solid-state reaction (Figure 3). In general, the Raman spectra of as-prepared and annealed titanates bore similar features, being more resolved for as-prepared titanates. In addition, the as-prepared titanates displayed more intensive Raman spectra than those of the annealed analogues. This indicates the different scattering properties of as-prepared and annealed titanates, which, in turn, is related to their different defect structures (see the discussion on HR-TEM images below). The comparison allowed to highlight the three most intensive bands appearing at around 675, 440, and 270 cm⁻¹, together with the less intensive bands at 910, 795, and 375 cm⁻¹. The band at around 270 cm⁻¹ can be assigned to Na–O–Ti vibrations.

The close inspection of the band profile allowed differentiating several positions for the asprepared titanates (i.e., at least two at 265 and 276 cm⁻¹), while only one band at 278 cm⁻¹ was visible for the annealed titanates. The band positions deviated from those observed for the reference Na₂Ti₃O₇: bands at 280 and 305 cm⁻¹ [35–37]. It is worth mentioning that the Na-coordination resembled that in Na₂Ti₆O₁₃, having a Raman band at 280 cm⁻¹ [38,39]. This evidenced a different Ti-coordination in hydrothermally prepared titanates and their analogues annealed at 350 °C in terms of the surrounding Na-ions.



Figure 2. Simultaneous TG/DTA/mass spectrometry curves of as-prepared (**A**) and annealed at 350 °C titanates (**B**) for NTO-2 (**a**), NTO-5 (**b**), and NTO-30 (**c**).



Figure 3. Raman spectra of as-prepared (**A**) and annealed at 350 °C (**B**) for NTO-2 (a), NTO-5 (b), and NTO-30 (c). The red lines correspond to the Raman spectrum of the $Na_2Ti_3O_7$ reference.

The bands that occurred in the range of $420-480 \text{ cm}^{-1} \text{ most}$ probably come from the bending modes of TiO₆ octahedra [39]. For the as-prepared titanates, two bands at 426 and 447 cm⁻¹ could be resolved, while for the annealed titanates these bands shifted at 438 and 475 cm⁻¹ and they rather resembled those observed for Na₂Ti₃O₇ (i.e., at 446 and 486 cm⁻¹). Furthermore, the bands that appeared between 580 and 750 cm⁻¹ enabled to distinguish between corner- and edge-sharing TiO₆ octahedra: the Ti-O-Ti stretches occurred in the region of 580–700 cm⁻¹ and around 750 cm⁻¹ for edge- and corner-sharing TiO₆, respectively [35,36]. For the as-prepared and annealed titanates, only bands in the region of 670–710 cm⁻¹ were observed, thus indicating a predominate existence of edge-sharing TiO₆. The band positions were different for as-prepared and annealed titanates: 672 and 705 cm⁻¹ vs. 668 and 710 cm⁻¹. Taking into account the Ti-O vibrational modes, this is a Raman sign for the different Ti-coordination (in terms of Ti-O bond lengths) in as-prepared and annealed titanates.

The band at around 910 cm⁻¹ is ambiguously interpreted in the literature: this band is assigned to short Ti–O bonds in highly distorted TiO₆ octahedra, in which all oxygen ligands are unshared, or it is due to overtone to the band at 450 cm⁻¹ [35,36,39,40]. This band was observed only for the titanates prepared under high pressure (i.e., NTO-30), where the band at 450 cm⁻¹ was also well-resolved. Based on the Raman observations, one may conclude that hydrothermally prepared sodium titanates exhibit local coordinations of Ti atoms that deviate from those in Na₂Ti₃O₇ and Na₂Ti₆O₁₃ and slightly depend on the reaction pressure used in the synthesis procedure. During the annealing at 350 °C, the geometry of the Ti-coordination underwent further changes.

The electron microscopy and diffraction analyses provided further information on the morphology and structure of the hydrothermally prepared titanates. The SEM images show that under a low reaction pressure, nanowires of sodium titanates were formed (Figure 4). By increasing the reaction pressure, the nanowires tend to stick to one another, thus forming a bundle of nanowires. Based on the EDS analysis, the ratio between Ti and Na slightly decreased with the increasing reaction pressure, i.e., the Ti-to-Na ratio was 2.1, 1.9, and 1.8 for titanates obtained under 2, 5, and 30 bar. These values are intermediate between those characteristic for Na₂Ti₃O₇ and Na₂Ti₆O₁₃ (i.e., between 1.5 and 3.0). It is worth mentioning that the morphology of Na₂Ti₃O₇ prepared by the solid-state reaction at 800 °C consisted of rods, but with bigger dimensions: length of 2–10 μ m and diameter up to 0.5 μ m (Figure S1, Supplementary Materials). The close morphology of the hydrothermally prepared titanates and Na₂Ti₃O₇ enabled to correctly compare their electrochemical properties.



Figure 4. SEM images at low (top) and high (bottom) magnifications of annealed NTO-2 (**a**), NTO-5 (**b**), and NTO-30 (**c**).

0.30 ni



The dimensions of the nanowires were calculated from the bright-field TEM images: NTO-2 reached a length of $0.5-0.70 \,\mu\text{m}$ and an average diameter of $0.05 \,\mu\text{m}$ (Figure 5a).

Figure 5. TEM images and SAED analysis of annealed NTO-2 ((a), top) and NTO-5 ((b), medium). The defects occurring for Na₂Ti₆O₁₃ and Na₂Ti₃O₇ nanowires are also shown (**bottom**).

The comparison showed that the dimensions of the nanowires were slightly changed after the enhancement of the reaction pressure, i.e., length of $0.3-0.5 \ \mu m$ and a diameter of 0.02 μm for NTO-5 (Figure 5b). The main difference was seen in the packing of nanowires: at a low reaction pressure, isolated nanowires predominately existed, while at a high reaction pressure, bundles of nanowires were clearly resolved (Figure 5). SAED analysis revealed that the titanates consisted of a mixture of Na₂Ti₆O₁₃ and Na₂Ti₃O₇ phases. Based on the 30–40 particle observations, the calculated phase composition was as follows: 75%of $Na_2Ti_6O_{13}$ and 25% of $Na_2Ti_3O_7$ for the sample obtained at a pressure of 2 bar, and 60% of $Na_2Ti_6O_{13}$ and 40% of $Na_2Ti_3O_7$ for the sample obtained at a pressure of 5 bar. The

calculated phase composition was consistent with the mean Ti-to-Na ratio determined from SEM–EDS: 2.6 and 2.4 composition vs. 2.1 and 1.9, respectively. The TEM observations of two distinct phases, Na₂Ti₆O₁₃ and Na₂Ti₃O₇, were not in contradiction with the Raman findings on specific coordination of Ti in hydrothermally prepared titanates. The close inspection of HR-TEM images revealed the formation of highly defective nanowires (Figure 5). Under an electron beam, these nanowires easily crystallized into Na₂Ti₆O₁₃ and Na₂Ti₃O₇ phases.

3.2. Sodium Storage Performance of Sodium Titanate Nanowires

The first step in the electrochemical characterization of titanates is the right choice of binder additives used for the electrode fabrication. In the case of titanates, we used two types of binders: the conventional PVDF dispersed in N-methyl-2-pyrrolidone (NMP) and water-soluble carboxymethyl cellulose (CMC). Using a conductive additive such as carbon black C65, Figure 6 compares the effect of the binders on the charge/discharge curves and the corresponding capacity of titanate electrodes in sodium-ion cells. The comparison showed that charge/discharge curve profiles retained their shape irrespective of the binder used. This is valid for both hydrothermally prepared titanates and the Na₂Ti₃O₇ reference. However, the CMC binder allowed to achieve a higher capacity than that of the PVDF binder used (i.e., more than 100 mAh/g). Considering that the titanates were discharged up to 0.1 V, the effect of the binder on the electrochemical properties could be related to the formation of solid electrolyte interphase (SEI) at low potentials, as it has been discussed in many previous studies [41]. The mechanism is still not clear, but experimentally, it has been established that $Na_2Ti_3O_7$ delivers a low capacity when PVDF binder is used [42]. Our results extend the above findings that both titanates obtained by solid-state and hydrothermal reactions are sensitive towards the used binder during electrode fabrication. It is interesting that, for Na₂Ti₃O₇, the capacity fading dramatically depends on whether PVDF or CMC binder was used, while for hydrothermally prepared titanates, this difference was mitigated (Figure 6). This implies that the CMC binder uniformly covered both Na₂Ti₃O₇ micron-sized rods and NTO nanowires, while the PVDF binder failed in this aspect. In addition, the PVDF binder displayed a high reactivity towards Ti-based oxides, as a result of which a dense fluoride layer was deposited on the electrode surface [43]. Based on the positive effect of the CMC binder on the storage performance of titanates, all further electrochemical experiments were carried out using the CMC binder.



Figure 6. Charge/discharge curves after the second and fifth cycles of NTO-5 (**a**) and the $Na_2Ti_3O_7$ reference (**b**) in sodium-ion cells, when PVDF or CMC binder was used for the electrode fabrication. The charging rate of C/20 was used.

Figure 7 presents the charge/discharge curves after the first five cycles for titanates used as electrodes in sodium-ion cells.



Figure 7. Sodium charge/discharge curves after the first five cycles for NTO-2 (a), NTO-5 (b), NTO-30 (c), and $Na_2Ti_3O_7$ (d).

The reference Na₂Ti₃O₇ is capable of intercalating 2 mol of Na⁺ at redox potentials of 0.38/0.20 V, in accordance with previous findings [25]. In comparison with the Na₂Ti₃O₇ reference, the sodium insertion into hydrothermally prepared titanates proceeded in the potential range of 0.1–2.0 V, without the appearance of any voltage plateau. This means that hydrothermally prepared titanates store Na via a mechanism different than that of Na₂Ti₃O₇. The lack of voltage plateaus has also been established for Na2Ti₆O13 when it is discharged to 0 V, and the intercalation reaction follows a solid-state solution mechanism [44]. However, a well-resolved plateau emerges at 0.8 V when $Na_2Ti_6O_{13}$ is discharged to 0.3 V [15]. To check whether the hydrothermally prepared titanates exhibited a voltage plateau upon Na⁺ insertion, Figure S2 (Supplementary Materials) shows the charge/discharge curves of NTO-2 discharged to 0.5 V. As can be seen, the charge/discharge curves displayed only a gradual increase/decrease in the potential range of 2.0–0.5 V, and there were no signs for the development of voltage plateaus. This is further electrochemical evidence that hydrothermally prepared titanates interact with Na⁺ via a different mechanism compared to that of Na₂Ti₆O₁₃ and Na₂Ti₃O₇. The different electrochemical mechanism can be related to the specific nanowires' morphology that ensures 1D electronic pathways for fast charge transport [23]. By providing a high surface-to-volume ratio, the nanowires exposed more Ti ions on the surface, which, in addition to bulk Ti-ions, participated in the electrochemical reactions. This resulted in a variation in the mechanism of electrochemical reactions taking place at nanowires. It is worth mentioning that different local coordination of Ti-ions in nanowires was discussed based on Raman spectroscopy (Figure 3).

Another important parameter is the first irreversible capacity (Table 1). After the first discharge up to 0.1 V, titanates delivered a high capacity, which was not recovered during the subsequent charge to 2.0 V. The Coulombic efficiency for the titanate nanowires reached a value of about 40–45%, which was not dependent on the reaction pressure used upon their synthesis. This shows that a high capacity was lost for the side reactions, which is typical for Na₂Ti₆O₁₃ and Na₂Ti₃O₇ due to the formation of SEI [12]. Due to the low potential limit of

discharge (i.e., 0.1 V), it has been found that a thin layer composed of chemisorbed oxygen, alkyl carbonates, Na_2CO_3 , and NaF covers the surface of $Na_2Ti_3O_7$ [12]. The comparison of the first irreversible capacity between titanates suggested that nanowires participate in the side reactions more intensively than $Na_2Ti_3O_7$. This can be related to the higher surface-to-volume ratio for the nanowires in comparison to that for $Na_2Ti_3O_7$, having a micrometric rod-like morphology. Among hydrothermally derived titanates, the nanowires obtained under a high pressure had a higher irreversible capacity than those obtained at a low pressure (Table 1). This means that the bundled nanowires bonded Na^+ ions more strongly and irreversibly than the isolated ones. Thus, the finding revealed the appearance of reactive sites (i.e., defects) during packing of nanowires under high reaction pressures.

Samples	C/20—First Discharge Capacity, mAh/g	C/20—First Irreversible Capacity, mAh/g	C/2—First Discharge Capacity, mAh/g	C/2—First Irreversible Capacity, mAh/g
NTO-2	406	244	253	112
NTO-5	565	370	258	106
NTO-30	536	324	300	136
Na ₂ Ti ₃ O ₇	380	194	78	51

Table 1. First sodium discharge capacity and irreversible capacity at rates of C/20 and C/2 for NTO-2, NTO-5, and NTO-30.

In addition, the side reactions are rate-dependent. By increasing the rate of charging from C/20 to C/2, the first irreversible capacity decreased by more than two times, but the Coulombic efficiency remained low (i.e., around 60%). Although the specific capacity of hydrothermally obtained titanates at a high rate of charging was still remarkable, the capacity of the Na₂Ti₃O₇ reference became worse under these conditions. Even at a high charging rate, the first irreversible capacity achieved higher values for titanates obtained under a high pressure (i.e., for bundled nanowires). This provides evidence that bundled nanowires exposed additional sites for the irreversible interaction with Na⁺ compared to the isolated nanowires. In general, the higher irreversible sodium capacity for bundled nanowires could shed further light on the fundamental understanding of the performance of dense nanostructure architectures for energy storage [45].

After the first irreversible capacity, the performance of nanowires was significantly improved. Figure 8 compares the cycling stability and rate capability of titanate nanowires and the Na₂Ti₃O₇ reference.



Figure 8. Cycling stability and rate capability for NTO-2 (black lines), NTO-5 (red lines), NTO-30 (green lines), and Na₂Ti₃O₇ (blue lines) in sodium half-cells. The Coulombic efficiency for NTO-2 and NTO-5 is also shown.

Two features can be underlined. Firstly, at a high rate of cell charging, the nanowires delivered a higher capacity than that of Na₂Ti₃O₇, consisting of bigger rod-like particles: 120 mAh/g for NTO-2 vs. 30 mAh/g at a rate of C/2. This demonstrates the advantage of the nanometric morphology for Na-storage in comparison to the micro-metric morphology. Secondly, bundled nanowires (induced by the high reaction pressure) displayed an enhanced capacity at a low charging rate compared to that of isolated nanowires: 120 mAh/g, 137 mAh/g, and 151 mAh/g for NTO-2, NTO-5, and NTO-30, respectively, at a rate of C/2 (Figure 8). By increasing the charging rate, this order was reversed: 63 mAh/g, 48 mAh/g, and 37 mAh/g for NTO-2, NTO-5, and NTO-30, respectively, at a rate of C/5. This suggests a better rate performance for isolated nanowires. It appears that the stacking of nanowires into bundles led to the occurrence of "closed" sites for alkali ions, thus disturbing their performance at a high charging rate. On the contrary, by lowering the charging rate, more and more alkali ions could reach the "closed" sites, thus allowing to achieve a higher capacity for the bundled nanowires than that of the isolated nanowires. In addition, both the cycling stability and the Coulombic efficiency appeared to be independent of the degree of nanowires' bundling. Moreover, the Coulombic efficiency tended to be around 100% at a charging rate higher than C/2. The Na-storage performance of nanowires was comparable with literature data for Na₂Ti₃O₇ with specially optimized interface stability: at a charging rate of C/1, nanowires without any optimization sustained around 115–105 mAh/g, while optimized $Na_2Ti_3O_7$ delivered the capacity of 111.8 mAh/g (after 100 cycles) [46]. The coating of nanowires with carbon has been recognized as an approach for improving the rate capability of titanates due to the enhancement of electronic conductivity: for example, $Li_4Ti_5O_{12}$ nanowires coated with carbon deliver a capacity of 117 mAh g⁻¹ at a rate of C/10 [47].

3.3. Lithium Storage Performance of Sodium Titanate Nanowires

The Li-storage performance of titanate nanowires and Na₂Ti₃O₇ was analyzed in Li half-cells (Figure 9). The reference Na₂Ti₃O₇ intercalated Li⁺ at higher redox potentials than Na⁺: 1.7/1.5 V vs. Li/Li⁺ and 0.38/0.20 V vs. Na⁺ [48]. The titanate nanowires also displayed some plateaus between 1.7 and 1.5 V, but not as well-resolved as in the case of Na₂Ti₃O₇. For the sake of comparison, the intercalation of Li⁺ into Na₂Ti₆O₁₃ is accomplished at a voltage of around 1.35 V [49]. This implies that titanate nanowires store Li⁺ mainly via the intercalation mechanism, which is different to what has been observed for Na⁺ storage. This storage mechanism is stable upon cycling. The most important difference between nanowires and Na₂Ti₃O₇ was seen in the magnitude of the specific capacity: the reversible capacity reached values of 250 mAh/g for the nanowires, while two times lower capacity was obtained for Na₂Ti₃O₇.

As in the case of Na-storage, the Coulombic efficiency after the first cycle was low (i.e., around 40–45%), especially for isolated nanowires (Table 2). This indicates the formation of a surface layer on the nanowires due to their intensive interaction with Li⁺. It appears that isolated nanowires interacted more intensively than the bundled nanowires, which is the opposite trend to that observed for the Na⁺ interaction. By increasing the charging rate from C/20 to C/2, the first irreversible capacity decreased, but to a smaller degree in comparison to that for the Na⁺ interaction. This is a consequence of the capability of nanowires to achieve a larger lithium capacity at a higher charging rate than sodium (Tables 1 and 2). In addition, the stronger irreversible interaction of titanates with Li⁺ than that with Na⁺ implies a different mechanism of storage, which is described in the next paragraph.



Figure 9. Lithium charge/discharge curves after the first five cycles for NTO-2 (**a**), NTO-5 (**b**), NTO-30 (**c**), and $Na_2Ti_3O_7$ (**d**). The number of cycles is indicated.

Table 2. First lithium discharge capacity and irreversible capacity at rates of C/20 and C/2 for NTO-2, NTO-5, and NTO-30.

Samples	C/20—First Discharge Capacity, mAh/g	C/20—First Irreversible Capacity, mAh/g	C/2—First Discharge Capacity, mAh/g	C/2—First Irreversible Capacity, mAh/g
NTO-2	772	497	730	396
NTO-5	988	629	735	388
NTO-30	820	482	616	292
Na ₂ Ti ₃ O ₇	244	122	153	71

The titanate nanowires demonstrated a remarkable performance in lithium half-cells (Figure 10). As can be seen, the nanowires outperformed Na₂Ti₃O₇ with respect to the magnitude of the specific capacity and the rate capability. At a charging rate of C/2, NTO-2 delivered a reversible capacity of 230 mAh/g, while the reversible capacity for Na₂Ti₃O₇ was only 73 mAh/g. The difference became more significant at a faster charging rate: at a rate of 10C, the reversible capacity of NTO-2 was 140 mAh/g, vs. 30 mAh/g for Na₂Ti₃O₇. As in the case of the Na⁺, the Li⁺ storage was also dependent on the reaction pressure used upon the titanate synthesis. The titanates obtained under the low pressure (i.e., at 2 bar) delivered a low capacity at slow charging rates (i.e., 230 mAh/g for NTO-2 vs. 240 mAh/g for NTO-30 at a rate of C/2), but they offered a higher capacity at a faster charging rate (i.e., 140 mAh/g for NTO-2 vs. 105 mAh/g for NTO-30 at a rate of 10C). This revealed an excellent rate capability for the titanates with isolated nanowires. Taking into account that the comparison of the Li-storage properties of sodium titanates is more complicated than that for sodium, we provide a rough evaluation of the performance of hydrothermally synthesized titanates in comparison with the available data in the literature. The previously

reported titanates with the best performance are Na_{1.5}H_{0.5}Ti₃O₇, having nanoparticles (with a 5 ± 0.5 nm) in clusters mixed and with extended thin nano-sheets [50]. These Na_{1.5}H_{0.5}Ti₃O₇ titanates deliver a capacity of 260 and 160 mAh/g at a current load of 50 and 750 mA/g, while the titanate nanowires prepared by us were characterized by 230 and 165 mAh/g at 114 and 1140 mA/g, respectively. In addition, Na₂Ti₆O₁₃ optimized with self-doping and carbon coating is characterized by a specific capacity of 180.5 mAh/g after 500 cycles at 5C [51]. These data demonstrate once again a remarkable performance of isolated nanowires in Li-storage.



Figure 10. Cycling stability and rate capability for NTO-2 (black lines), NTO-5 (red lines), NTO-30 (green lines), and Na₂Ti₃O₇ (blue lines) in lithium half-cells. The Coulombic efficiency for NTO-2 and NTO-5 is also shown.

3.4. Mechanism of Lithium and Sodium Storage into Sodium Titanate Nanowires

To understand the good performance of isolated nanowires, we performed CV experiments and ex situ XRD and TEM analyses. Figure 11 (as well as Figure S3, Supplementary Materials) compares the CV curves of NTO-2 in Li and Na half-cells. At a low scan rate, the electrochemical interaction of NTO-2 with Li⁺ proceeded at a redox peak of 1.75/1.60 V vs. Li/Li⁺, while the interaction of NTO-2 with Na⁺ was accomplished in a broad potential range, with a barely resolved redox peak at 1.16/1.03 V vs. Na/Na⁺. This is consistent with the galvanostatic observations. By increasing the scan rate from 0.1 mV/s to 20 mV/s, the CV profile of NTO-2 in both Li- and Na-ion cells became smoother, without distinct redox peaks. This indicates that the CV profiles resembled those of capacitive reactions rather than those of intercalation reactions. To evaluate the contributions of the capacitive and the intercalation reactions, the dependence of the current (i) on the scan rate (v) was quantified following the equation: $i(V) = k_1 v + k_2 v^{1/2}$ [52]. As can be seen, the storage of Na⁺ in NTO-2 was mainly the result of the capacitive reactions, even at low scan rates, while both intercalation and capacitive reactions governed the Li⁺ storage (Figure 11). This can be associated with the nanowire's morphology: the high surface-to-volume ratio favored the surface redox reactions with Li⁺ and Na⁺ (i.e., capacitive-like reactions), while cylindricallike channels provided favorable paths for diffusion of smaller Li⁺ ions compared to the bigger Na⁺ ions (i.e., Faradaic reactions). The hybrid mechanism of Li-storage gives rise to the remarkable performance of nanowires as anodes in lithium half-cells.



Figure 11. CV curves at a 0.1 mV/s scan rate for NTO-2 in sodium and lithium half-cells (**top**). The contribution of capacitive and diffusive (i.e., intercalation) reactions to the storage of Na and Li by NTO-2 (**bottom**).

To rationalize the structural stability of titanates during cycling, Figure 12 shows the ex situ XRD patterns. The subject of study was NTO-2 cycled in lithium and sodium cells, as shown in Figures 8 and 10. After 120 cycles, the cell was switched off at 2.5 V and the electrode was analyzed. The indexing of the cycled electrodes revealed that, in sodium cells, the titanate nanowires sustained their composition, while in lithium cells there was a crystallization of new lithium phases with compositions of $Li_{0.54}Ti_{2.86}O_6$ and $Li_{0.5}TiO_2$. However, considering the low quality of the XRD patterns, it was difficult to form a straightforward conclusion. Hence, the electrodes were further analyzed by means of TEM (Figure 13).



Figure 12. Ex situ XRD patterns of NTO-2 cycled in sodium (b) and lithium (c) ion cells. The pristine phase NTO-2 is also shown (a).



Figure 13. Bright-field TEM images of NTO-2 cycled in lithium (**a**) and sodium (**b**) ion cells. HR-TEM images of NTO-2 cycled in Li-ion cells (**c**) and Na-ion cells (**d**). The white box indicates the calculated HR-TEM images.

The TEM images indicate a preservation of the morphology of hydrothermally derived titanates after the cycling in both lithium and sodium cells: isolated nanowires were clearly resolved (Figures 5 and 13). When NTO-2 was cycled in sodium cells, the HR-TEM analysis allowed to distinguish Na₂Ti₆O₁3 and Na₂Ti₃O₇ phases. However, the indexation of Na₂Ti₃O₇ was not unambiguous since the distance of the (101) plane for Na₂Ti₃O₇ coincided with that of the (400) plane of Na_{2.04}Ti₄O₉. Thus, combining XRD and TEM analyses, it appeared that there was no significant transformation in the phase composition during cycling of titanates in sodium ion cells. It is of importance that the retention of phase composition agrees with the capacitive mechanism of Na-storage by titanates. In lithium cells, the two phases, Li_{0.54}Ti_{2.86}O₆ and Li_{0.5}TiO₂, which were observed by XRD, were clearly detected by HR-TEM. In addition, the HR-TEM showed the occurrence of a phase a with mixed lithium-sodium composition, Na_{2-x}Li_xTi₆O₁₃: the insertion of Li into $Na_2Li_xTi_6O_{13}$ led to a decrease in the dimension of the (-201) plane from 0.63 to 0.60 nm. Based on ex situ XRD and TEM analyses, the storage of Li by sodium titanates took place via the formation of the mixed lithium-sodium phase Na_{2-x}Li_xTi₆O₁₃, which was decomposed to distinct lithium phases, Li_{0.54}Ti_{2.86}O₆ and Li_{0.5}TiO₂. As a result of this

decomposition, the lithium electrolyte was enriched with Na⁺ ions. Considering that the nanowires' morphology enabled the intercalation of smaller Li⁺ ions only (Figure 11), it is reasonable to expect that these Na⁺ ions could contribute to the capacitive reactions, in addition to Li⁺ ions. This is another source of enhancing the capacity of titanates when they are cycled in lithium-ion batteries. Therefore, the titanate nanowires appear to be suitable candidates for electrodes in hybrid Li,Na-ion batteries.

4. Conclusions

Hydrothermal synthesis using a reaction pressure from 2 to 30 bar yielded sodium titanates with a nanowire-like morphology. At a low pressure, isolated nanowires with a length of 0.5–0.70 μ m and an average diameter of 0.05 μ m were formed, while at a high pressure, there was a tendency for nanowires to bundle. In sodium titanates, the local coordination of Ti atoms (in terms of Ti–O bond length and Na-surrounding) slightly depended on the reaction pressure used in the synthesis procedure. After annealing the titanates at 350 °C in Ar atmosphere, the local Ti coordination underwent further changes. The annealed nanowires were highly defective, and they easily crystallized into Na₂Ti₆O₁₃ and Na₂Ti₃O₇ phases under an electron beam.

The electrochemical performance of sodium titanates critically depends on the type of binder used during the electrode fabrication: the best performance (in terms of the magnitude of capacity and cycling stability) was obtained when carboxymethyl cellulose (CMC) binder was used. The nanowires stored lithium via a hybrid capacitive-diffusive mechanism between 0.1 and 2.5 V, thus enabling to reach a high specific capacity. The Li⁺ diffusion into sodium titanates took place by the formation of the mixed lithium–sodium phase Na_{2-x}Li_xTi₆O₁₃, which was decomposed to distinct lithium phases, Li_{0.54}Ti_{2.86}O₆ and Li_{0.5}TiO₂. In contrast to Li, sodium titanates stored sodium predominantly by capacitive reactions, as a result of which the phase composition was retained. Sodium titanates displayed a good cycling stability and an exceptional rate capability. The isolated nanowires outperformed the bundled nanowires. In Li-ion cells, the isolated nanowires delivered a capacity of 230 mAh/g and 140 mAh/g at a rate of C/2 and 10C, while in Na-ion cells, the capacities were 120 and 40 mAh/g, respectively.

Due to the high specific capacity and excellent rate capability, isolated nanowires of sodium titanates can serve as effective negative electrodes in hybrid Li,Na-ion batteries. Furthermore, isolated nanowires can be prepared by a simple and reproducible hydrothermal method, followed by annealing at 350 °C. This method, without any further optimization, is sufficient to obtain isolated titanate nanowires with improved electrochemical properties.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/batteries9050271/s1, Figure S1: SEM image of Na₂Ti₃O₇ prepared by the solid-state reaction; Figure S2: Charge/discharge curves after 1st discharge, 2nd, 10th, and 20th cycles of NTO-2 in sodium-ion cells, cycled between 0.5 and 2.0 V at a rate of C/20; Figure S3: CV curves at 0.5, 1, 5, and 10 mV/s scan rates for NTO-2 in sodium (left) and lithium half-cells (right).

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