Exfoliation of Layered Na-Ion Anode Material Na$_2$Ti$_3$O$_7$ for Enhanced Capacity and Cyclability

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ABSTRACT: We report the exfoliation of layered Na$_2$Ti$_3$O$_7$, a promising anode material for Na-ion batteries, and restacking using HNO$_3$ and NaOH to form H-[Ti$_3$O$_7$] and Na$_x$-[Ti$_3$O$_7$] compositions, respectively. The materials were characterized by a range of techniques (SEM, TEM, solid-state NMR, XRD, PDF). Although the formation of aggregated nanoparticles is favored under acidic restacking conditions, the use of basic conditions can lead to control over the adherence between the exfoliated layers. Pair distribution function (PDF) analysis confirms that the local TiO$_6$ connectivity of the pristine material is maintained. The lowest sodium-containing phase Na(1)-[Ti$_3$O$_7$], which is the stable product upon Na$^+$ leaching after consecutive washing steps, displays the best performance among the compositions studied, affording a stable reversible capacity of about 200 mAh·g$^{-1}$ for 20 cycles at a C/20 rate. Washing removes the excess of “free/reactive” Na$^+$, which otherwise forms inactive Na$_2$CO$_3$ in the insufficiently washed compositions.

INTRODUCTION

The discovery of atomically thick graphene has recently aroused great interest in the properties and phenomena exhibited by two-dimensional (2D) materials, which in general can be considered as the exfoliation products of layered structures to form either single or few layers. The exfoliation of layered structures to individual or few nanosheets can be advantageous for applications requiring high surface activity, such as catalysis, electrochemistry, and photoelectrochemistry.$^{1,2}$

In the extended family of layered inorganic structures, including metal oxides, metal chalcogenides (for example, reduced TiS$_2$, MoS$_2$, and WS$_2$), LiCoO$_2$ and others,$^{1,2}$ interlayer counterions are often required to preserve/maintain the electroneutrality. This is advantageous for ion-exchange properties, but makes their exfoliation to generate individual layers more challenging than for graphite$^{3,4}$ because of the strong Coulombic forces that hold them together.$^1$

In general, Na-ion batteries are considered as a lower-cost alternative to their Li-ion counterparts, which operate in a similar manner. This is in part due to the high natural abundance of sodium, along with the option to use aluminum current collectors on the anode side, instead of the more expensive copper used for Li-ion batteries. One of the key challenges for implementation of the Na-ion technology is related to discovering new anode materials since graphite, the anode of choice for Li-ion batteries, does not show electrochemical activity in Na-ion batteries.$^5,6$ Hard (nongraphiteable) carbon can however reversibly intercalate Na$^+$ ions via a combined mechanism of Na$^+$ insertion between the nearly parallel layers and into nanopores, but much of this storage takes place close to the sodium-plating voltage, raising potential safety concerns.$^7,8$ Other potential anode materials are also being explored,$^9,10$ among them, a variety of titanium-based structures, but these show low specific capacity in part due to the limited Na storage sites within the host structures.$^9$
Titanium-based structures are often preferred for various anode applications due to their lack of toxicity and relatively low cost compared to other transition metals, such as cobalt or manganese, and the redox activity of titanium being in the appropriate voltage window.\textsuperscript{12}

Layered Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} is a well-known potential anode material for Na-ion batteries demonstrating good electrochemical properties at a low intercalation potential of around 0.3 V vs Na\textsuperscript{+}/Na\textsuperscript{−}\textsuperscript{13,14}. It is built up of corrugated (Ti\textsubscript{3}O\textsubscript{7})\textsubscript{2−} layers (formed by series of corner-sharing trioctahedral ribbons) and Na\textsuperscript{+} ions sitting in the interlayer space. The low intercalation potential of Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} is advantageous when coupled with a high-voltage cathode in a full cell to achieve a higher energy density. For example, Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} nanotubes have recently been tested as anode materials in full-cell batteries using the high-voltage cathode material VOPO\textsubscript{4} (V = 3.75 V vs Na\textsuperscript{+}/Na\textsuperscript{−}), demonstrating promising electrochemical performance.\textsuperscript{15}

It is generally believed that reduction of Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} occurs via the reversible intercalation of two additional Na\textsuperscript{+} ions in the structure, forming Na\textsubscript{4}Ti\textsubscript{3}O\textsubscript{7}\textsuperscript{13,14} with 2/3 of the Ti(IV) ions being reduced to Ti(III).\textsuperscript{13} Several studies have attempted to enhance the electrochemical capacity of this material by generating sodium vacancies within the crystal structure\textsuperscript{16} and by fabrication of carefully controlled nanostructures. Recent advances in the field showing promising performance include bottom-up (BU) techniques for growing Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} based structures, such as growth of nanotube arrays,\textsuperscript{17} formation of a 3D spider-web architecture assembled by nanotubes,\textsuperscript{18} and growth on carbon-coated hollow spheres.\textsuperscript{19} Promising results have also been reported when techniques favoring reduced particle size are used; these include crystalline rods prepared by ion exchange using alkyl ammonium ions in aqueous solutions of amines (MA: methylamine and PA: propylamine). Each reaction was performed solvothermally at 120 °C for 48 h in an autoclave, with the concentrations used as reported previously.\textsuperscript{15}\textsuperscript{2} The resulting colloidal suspensions were centrifuged at 6000 rpm for 5 min and the precipitates were washed and centrifuged a further three times, until neutral pH. The MA-Ti\textsubscript{3}O\textsubscript{7} and PA-Ti\textsubscript{3}O\textsubscript{7} samples were then dried in an oven at 60 °C prior to further characterization. The final titanate product of amine swelling (PA-Ti\textsubscript{3}O\textsubscript{7}) was then dispersed in water (0.1 g in 50 mL H\textsubscript{2}O), followed by sonication in order to exfoliate to titanate layers/nanosheets. The nonexfoliated material was collected as the precipitate of centrifugation at 6000 rpm for 5 min. The supernatant suspension, containing the dispersed exfoliated nanosheets, was then restacked by mixing with HNO\textsubscript{3} or NaOH aqueous solutions, in 1:1 ratio by volume. After being left overnight to settle, the precipitates were easily separated by centrifugation (3000 rpm for 3 min). In the case of restacking by NaOH, the washing procedure of the precipitate was carefully controlled, resulting in different amounts of inserted Na in the exfoliated/restacked samples. All the samples were dried, initially in air at 60 °C and finally at 100 °C in a vacuum oven.

**Powder X-ray Diffraction (PXRD).** PXRD measurements were performed in a reflection mode (Analytical Empyreey diffractometer, with Cu K\textsubscript{α} radiation (λ = 1.5406 Å)).

**Electron Microscopy.** Transmission Electron Microscopy (TEM) images were recorded at magnification between 40 000× and 800 000× in a JEM-3011 electron microscope operated at 300 kV, with objective lens characteristics Cs = 0.6 mm and Cc = 1.2 mm. With a LaB\textsubscript{6} emitter these produced an interpretable resolution limit of 0.17 nm and an absolute information limit of 0.14 nm. Scanning Electron Microscopy (SEM) images were recorded with a Hitachi S-5500 in lens field emission electron microscope.

**Pair Distribution Function (PDF) Analysis.** Data from the samples, packed into kapton capillaries, were collected at the I15 beamline at Diamond Light Source, Didcot, U.K. An X-ray beam of energy of 76 keV (λ = 0.1631 Å) was used in conjunction with an amorphous silicon area detector (PerkinElmer). The sample geometry and the sample-to-detector distance were determined using a CeO\textsubscript{2} standard. The data were converted to intensity vs Q using the software Data Analysis WorkbeNch (DAWN).\textsuperscript{24} Standard corrections (background subtraction, Compton scattering, detector effects) were applied, and the data were Fourier transformed to obtain G(r) using the software PDFGetX2 using a Qmin of 24 Å\textsuperscript{-1}.\textsuperscript{24} Reﬁnements against known TiO\textsubscript{2} phases were performed in PDFGuiz.\textsuperscript{25} Reﬁnements against single-layer models were performed in the Difﬁpy-CMI complex modeling framework.\textsuperscript{27} The starting model was simulated from supercells of the Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} structure, where all atoms except for a single-layer in the middle of the unit cell were removed. The structure function was simulated from the Debye scattering equation,\textsuperscript{28} which was then Fourier transformed over a range of 1–24 Å\textsuperscript{-1}. The model was reﬁned using a least-squares approach; unit cell parameters, a, b, c, and β, an isotropic thermal parameter, U\textsubscript{iso}, for each atomic species and a scale factor were allowed to refine.

**Solid-State NMR.** All solid-state \textsuperscript{1}H and \textsuperscript{23}Na NMR spectra were acquired on a 16.4 T Bruker Avance III spectrometer using a 1.3 mm HX probe head. A rotor-synchronized Hahn-echo (for \textsuperscript{1}H) and a single-pulse sequence (for \textsuperscript{23}Na) were used to acquire magic-angle spinning (MAS) spectra with spinning frequencies of 55–60 kHz, recycle delays of 5 and 40 s (for \textsuperscript{1}H and \textsuperscript{23}Na, respectively), and radiofrequency (rf) field strengths of 125 and 140 kHz, respectively. \textsuperscript{1}H and \textsuperscript{23}Na shifts were externally referenced to solid adamantane at
1.87 ppm and solid NaCl at 7.21 ppm, respectively. Simulations of \textsuperscript{23}Na MAS NMR spectra were performed with SIMPSON.\textsuperscript{29} 

**First-Principles Calculations.** Density Functional Theory (DFT) computations were performed using CASTEP with on-the-fly generated pseudopotentials.\textsuperscript{30−32} For the electron–electron exchange and correlation interactions, the functional of Perdew, Burke, and Ernzerhof (PBE)\textsuperscript{33−36} was employed. Nonspin-polarized calculations were performed for the geometry optimization of the bulk Na$_2$Ti$_3$O$_7$ system. The k-points mesh used was $3 \times 3 \times 3$ with cutoff energy of 700 eV. 

**Compositional Analysis.** For C/H/N analysis, an Exeter analytical CE440 analyzer was used. Typically, 1−2 mgs of sample were combusted at 950 °C in oxygen. For the inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis, a Thermo scientific iCAP 7400 OES instrument was used. Samples were digested at 80 °C for 4 h in 2 mL aqua regia. They were then made up to 50 mL using Millipore 18 M water. The ICP was calibrated using 10 and 1 ppm standard samples. 

**Electrochemical Measurements.** Electrochemical testing was carried out in CR2032 coin cells vs sodium metal, in galvanostatic mode. The electrolyte used was 1 M NaPF$_6$ in propylene carbonate (PC, > 99% Aldrich) and glass fiber (Whatman GF B 55) was used as a separator. The working electrode was prepared by mixing 70% active materials with 30% carbon Super C-65 (Timcal) and 10% binder (PVdF-HFP copolymer) in NMP in a mortar and pestle. The mixed slurries were cast on copper foil using a doctor blade. A cell containing only carbon was also prepared for comparison reasons in a similar way, but the electrode slurry consisted of 70% carbon Super C-65 (Timcal) and 30% binder to ensure adequate adhesion to the copper foil and between particles. The laminates were vacuum-dried at 100 °C for 12 h prior to punching and pressing the electrodes, followed by further drying at 100 °C under vacuum for 12 h. The cells were assembled in a glovebox under argon atmosphere (O$_2$ < 0.1 ppm and H$_2$O < 0.1 ppm). The typical electrode loading was 20−25 mg. 

**RESULTS AND DISCUSSION**

Pristine Na$_2$Ti$_3$O$_7$ was made by solid-state synthesis, as reported previously,\textsuperscript{13} and was characterized by PXRD (Supporting Information SI, Figure S1 and Table S1, also included in Figure 1B in red) and \textsuperscript{23}Na NMR (SI, Figure S2 and Table S2). SEM shows that the pristine material comprises...
well-shaped nanorods of approximately 2.5 μm length and 0.1 μm thickness (Figure 2A).

The Na₂Ti₃O₇ exfoliation protocol used in this study is a modified version of previous reports for liquid exfoliation of titanates, niobates and titanoniobate nanosheets and is illustrated in Figure 1A. It consists of the three successive processes of swelling, exfoliation, and restacking. Na₂Ti₃O₇ was initially ion-exchanged to its protonated H₂Ti₃O₇ form. Complete ion exchange was achieved in agreement with the literature, as confirmed by ²³Na NMR (SI Figure S2) and ¹H NMR (SI Figure S3).

Although the interlayer distance (d) in the proton analogue H₂Ti₃O₇ (d = 7.87 Å) is smaller than that in pristine Na₂Ti₃O₇ (d = 8.46 Å), the former is more reactive toward acid–base reactions and the layers may consequently be swollen by incorporation of protonated organic bases. This was done by ion exchange in two steps involving aqueous solutions of amines of increasing size (MA: methylamine, PA: propylamine) forming first MA-Ti₃O₇ and then PA-Ti₃O₇. Chemical analysis (SI Table S3, C:N ratio) confirmed the alkyl ammonium ions were intercalated as whole ions and did not decompose under the reaction conditions. The ion exchange was complete for the first amine exchange step, while the final product after intercalation of PA (PA₁₋₂·½Na₂Ti₃O₇) was slightly amine deficient. ¹H NMR of these materials (SI Figure S3) confirm the presence and the stability of the alkyl ammonium ions; in the case of the PA-Ti₃O₇, a residual amount of protons remain in the structure bound to the Ti₃O₇⁻ host. The yield of the exfoliation protocol strongly depends on the amount of sufficiently swollen titanate; the nonexfoliated content is removed at a later stage. The amine-driven swelling of the titanate framework results in general broadening of the reflections in the XRD patterns. The progressive shift of the 001 reflection position to lower angle indicates the increase of the interlayer spacing (d) upon intercalation of the alkyl ammonium ions (d = 10.13 and 13.55 Å for H₂Ti₃O₇-MA and H₂Ti₃O₇-PA, respectively). Upon enlargement of the interlayer distance along the a-axis, all the (hk0) reflections of Na₂Ti₃O₇ are expected to remain intact, with the 020 reflection at approximately 2θ (Cu Kα) = 48° being the most intense. The (001) and (020) planes of pristine Na₂Ti₃O₇ are displayed in Figure 1F.

In order to exfoliate the titanate layers/nanosheets, the amine-swollen titanate product (PA-Ti₃O₇) was dispersed in water and then sonicated. After centrifugation to remove the precipitate containing nonexfoliated material, the supernatant containing the dispersed nanosheets was collected. The difference between the TEM of the exfoliated and the pristine material is striking. While the latter shows clearly defined flakes and particles (SI Figure S4), typical TEM images of the exfoliated (and dried) material (Figure 1C) are indicative of individual and multiple layers which have coalesced and collapsed as the solvent is removed, coming together in an extremely disordered arrangement with greatly reduced flake thickness. Arrays of layers can be seen in the high-contrast regions at the edges of the specimen (Figure 1D), but their arrangement is mostly irregular. In the regions where they form some sort of ordering, as for example at the very bottom of Figure 1D, no more than six layers with regular spacing are found. In these areas, the spacing between layers is in the order of 8–9 Å, similar to the regular layer spacing observed for the pristine material, indicating the structural similarity upon removal of the solvent. The exfoliated suspension was then restacked by NaOH; a representative SEM picture is displayed in Figure 1E showing layers stacked in a rather disordered fashion.

In order to control and understand the restacking process, a careful investigation of the effect of different restacking conditions was made, with two series of experiments being performed. In the first method, HNO₃ (either 1 or 2 M) was added to the nanosheet suspension, with the obtained white
Table 1. ICP/OES Results, PXRD Indicating the Major Crystalline Product Identified after Heating to 800 °C and Composition Na(x)-[Ti3O7] Determined from the Composition of the Crystalline Phase

<table>
<thead>
<tr>
<th>Restacking and Washing Conditions</th>
<th>ICP (Na:Ti)</th>
<th>PXRD Phase at 800 °C</th>
<th>Na(x)-[Ti3O7]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large excess of NaOH (aq)</td>
<td>1.89</td>
<td>Na2TiO3</td>
<td>Na(6)-[Ti3O7]</td>
</tr>
<tr>
<td>Mild washing conditions (x1)</td>
<td>0.56</td>
<td>Na2Ti3O7</td>
<td>Na(2)-[Ti3O7]</td>
</tr>
<tr>
<td>Washed thoroughly (x3), pH = 7</td>
<td>0.29</td>
<td>Na2Ti3O13</td>
<td>Na(1)-[Ti3O7]</td>
</tr>
</tbody>
</table>

Table 2. Samples Prepared in This Manuscript and Details of Synthesis Conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Comment</th>
<th>Synthesis Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na2Ti3O7</td>
<td>pristine titanate</td>
<td>made by solid state synthesis at 800 °C/40 h</td>
</tr>
<tr>
<td>H2Ti3O7</td>
<td>protonated titanate</td>
<td>prepared by ion exchange of Na2Ti3O7 in HCl (aq) solution</td>
</tr>
<tr>
<td>MA-Ti3O7</td>
<td>swollen H2Ti3O7 by MA+ (MA+:CH3NH3+)</td>
<td>prepared by ion exchange of MA-Ti3O7 by propylamine (PA) aqueous solution</td>
</tr>
<tr>
<td>PA-Ti3O7</td>
<td>swollen H2Ti3O7 by PA+ (PA+:CH3CH2CH2NH3+)</td>
<td>prepared by ion exchange of MA-Ti3O7 by propylamine (PA) aqueous solution</td>
</tr>
<tr>
<td>Na(6)-[Ti3O7]</td>
<td>exfoliated/restacked sample, with Na:Ti ratio = 6:3</td>
<td>as made exfoliated/restacked compositions (all dried at 100 °C in vacuum oven)</td>
</tr>
<tr>
<td>Na(2)-[Ti3O7]</td>
<td>exfoliated/restacked sample, with Na:Ti ratio = 2:3</td>
<td>exfoliated and restacked with large excess of NaOH (aq), followed by washing under mild conditions</td>
</tr>
<tr>
<td>Na(1)-[Ti3O7]</td>
<td>exfoliated/restacked sample, with Na:Ti ratio = 1:3</td>
<td>exfoliated and restacked with large excess of NaOH (aq), followed by thorough washing</td>
</tr>
<tr>
<td>Na(x)-[Ti3O7]</td>
<td>post-treatment conditions for exfoliated/restacked compositions Na(x)-[Ti3O7]</td>
<td></td>
</tr>
<tr>
<td>Na2TiO3</td>
<td>model compound, with Na:Ti ratio = 1:3</td>
<td>solid state synthesis at 800 °C/40 h</td>
</tr>
<tr>
<td>NaTiO3</td>
<td>model compound, with Na:Ti ratio = 6:3</td>
<td>solid state synthesis at 800 °C/40 h</td>
</tr>
</tbody>
</table>

Precipitate separated by centrifugation. For the second method, a large excess of NaOH (aq) was added to the nanosheet solution, followed by washing under different conditions. The morphology of the products was determined by SEM (Figure 2A). The nanorods observed for pristine (Na2Ti3O7, Figure 2A) are still observed, but their shape is mostly irregular. The formation of stacked nanosheets was found to be strongly dependent on the washing procedure, with reduced order observed as the samples are further washed (Figure 2D–F). The composition of the nanosheets restacked by NaOH was first determined by ICP/OES (Table 1). The composition was also determined indirectly by converting the poorly crystalline Na(x)-[Ti3O7] phases at high temperatures into more well-defined crystalline phases; the Na:Ti ratio of the resulting phases as determined by PXRD (SI Figures S6–S8) and confirmed by solid-state NMR (SI Figure S10) provides a second estimate of Na content (assuming all the titanate material has been converted to crystalline material). The resulting compositions were expressed via the simplified formula Na(x)-[Ti3O7], so as to focus only on the Na(x) content (Table 1). The Na(x) content in the Na(x)-[Ti3O7] exfoliated/restacked specimens was found to be approximately Na(6), Na(2), and Na(1) based on the PXRD analysis. Slightly lower Na contents were systematically determined by ICP/OES, which may be due to the techniques reported low sensitivity for Na, due to weak emission of alkali metal ions in general and interference issues for Na. However, it may also reflect the presence of (amorphous) Na-deficient phases not seen by PXRD. The information obtained regarding the Na(x) content...
of the Na(x)-[Ti3O7] compositions demonstrate that washing induces leaching of Na⁺ accommodated in the titanate exfoliated layers. Hence, control over washing can determine both the composition and the stacking order of the Na containing nanosheets. For easy reference, all of the exfoliated/restacked samples, and samples prepared with subsequent heat treatments and washings are listed in Table 2, along with the synthesized model compounds.

The PXRD patterns of all exfoliated/restacked Na(x)-[Ti3O7] compositions are plotted together in Figure 3A and compared with those of crystalline NaOH·H₂O and Na₂CO₃ references, to exclude the presence of excess NaOH, as well as H₂O and CO₂ adsorption from the atmosphere. All the Na(x)-[Ti3O7] samples display very broad reflections, demonstrating their inherent disordered nature and absence of the 001 reflection at low angles, indicating that there is no significant ordered stacking of the layers. The PXRD pattern of the low-sodium phase Na(1)-[Ti3O7] only displays the 020 reflection at about 48° 2θ, which appears to be indicative of the structural coherence of the TiO₆ octahedral layered framework upon swelling (Figure 1B). This characteristic reflection is also observed in the patterns of the higher sodium containing phases Na(2)-[Ti3O7] and Na(6)[Ti3O7], along with increasing amount of crystalline Na₂CO₃.

PDF Analysis. In order to probe the local connectivity of the exfoliated materials, pair distribution functions (PDFs) were extracted from total scattering data for Na(1)-[Ti3O7], Na(2)-[Ti3O7], and the pristine Na₂Ti₃O₇ material (as shown by the dashed lines in Figure 3B), indicating that the immediate connectivity of the TiO₆ framework remains the same as the parent material.

Furthermore, the peak positions in the experimental data for Na(1)-[Ti3O7] are a poor match to all TiO₂ polymorphs (SI Figure S12), and the residual factors obtained from least-squares refinements of TiO₂ polymorph structures against the experimental data for Na(1)-[Ti3O7] are very high (SI Table S4). This confirms that the basic exfoliation/restacking conditions have not converted the material into other TiO₂ polymorphs, as was observed in acid conditions.

To further probe the extent to which the [Ti3O7] layers remain intact in the exfoliated material, a model of a single [Ti3O7] layer, approximately 50 × 50 Å² in size was constructed (SI Figure S13(A)). Only the contributions from Ti and O are considered in the model; no Na atoms were placed in the model because the ²³Na NMR data indicate that a range of sodium environments exist (see below) and so are unlikely to

![Figure 3. (A) PXRD patterns of all exfoliated/restacked Na(x)-[Ti3O7] compositions, including NaOH·H₂O and Na₂CO₃ reference compounds. (B) Pair Distribution Function (PDF) analysis data for pristine Na₂Ti₃O₇, Na(1), and Na(2) compositions and comparison with the PDF simulated for a single layer. Dashed lines highlight the position of low-r peaks. (C) ²³Na MAS NMR spectra acquired at 16.4 T for pristine Na₂Ti₃O₇, (highlighting the two different Na coordination environments in the structure) all exfoliated/restacked Na(x)-[Ti3O7] compositions, NaOH and Na₂CO₃ references.](image-url)
contribute well-defined peaks to the PDF. Peak positions in the one-layer model show a good match to the experimental data, including the intense peak at 9.8 Å, which results from Ti–Ti interactions within the titanate layer. When this model was refined against experimental data for Na(1), a reasonable fit was obtained (SI Figure S13(A), $R_w = 0.39$), indicating that the structure of the exfoliated/restacked material is similar to that of a single layer of the Na$_2$Ti$_3$O$_7$ parent phase.

The fit remains imperfect; peaks in the residual of the refinement ($G(r)_{\text{model}} - G(r)_{\text{experimental}}$) remain, indicating that some aspects of the structure are not captured by the current model and, therefore, the exfoliated/restacked materials’ structure shows some differences to Na$_2$Ti$_3$O$_7$-like Ti$_3$O$_7$ layers. There are several possible sources for these differences including: (a) additional broad contributions from the disordered sodium which are not accounted for in this model; (b) the presence of some interlayer correlations, which although likely to be disordered, may lead to some changes in intensity; (c) additional structural complexity induced by defects in the exfoliated material; and (d) a possible range of sheet sizes and connectivities. The fit to experimental data can be slightly improved by using a fragment with smaller dimensions, where some connectivity between the corner-sharing octahedra has been broken. Of the models tried (see SI Section S4), a fragment with extended connectivity along the $b$-axis, but only a single set of corner sharing octahedra shows the best fit to the data (SI Figure S13(B), $R_w = 0.35$). This implies that some breakdown/modification of the layers may have taken place during the exfoliation/restacking, either from sheet termination, or from defective areas within layers. However, the calculated PDF for a single unit of six edge-sharing TiO$_6$ octahedra, the basic building block of the Ti$_3$O$_7$ layers, shows no peaks beyond approximately 10 Å (SI Figure S13(D)). As intertare correlatons are observed well beyond this distance in the experimental PDF, this confirms that the sheets have not been broken down into very small units of the starting material. More detailed structural characterization will be the subject of another paper.

The principal difference between the two PDFs of the two restacked compositions is the intensity of the first peak, which is likely related to the presence of a low scattering component Na$_2$CO$_3$ in Na(2)-[Ti$_3$O$_7$] (as evidenced from XRD and NMR measurements) and/or difference in the amount of oxygen vacancies present.

NMR Analysis. The $^{23}$Na NMR spectra of the three exfoliated/restacked ($Na(x)$-[Ti$_3$O$_7$]) compositions are shown in Figure 3C and compared with pristine Na$_2$Ti$_3$O$_7$ and NaOH and Na$_2$CO$_3$ references. The $^{23}$Na NMR spectrum of Na$_2$Ti$_3$O$_7$ consists of two signals in agreement with previously reported data and the Density Functional Theory (DFT) calculations performed in this work (SI Figure S2). These are assigned to the different Na coordination environments in the Na$_2$Ti$_3$O$_7$ layered structure, the Na1 site at lower chemical shift (at around $-10$ ppm, 9-fold coordinated, coordination number (CN) = 9) with a significant second order quadrupolar broadening effect and the Na2 site (at approximately +3 ppm, 7-fold coordinated, CN = 7). While the spectrum of the high sodium containing Na(6)-[Ti$_3$O$_7$] phase is a good match with that of the reference Na$_2$CO$_3$ spectrum, in agreement with PXRD for high carbonate content, the low sodiated Na(1)-[Ti$_3$O$_7$] phase only shows a single resonance with a shift at about $-10$ ppm. Although not displaying the characteristic second order quadrupolar broadening, this resonance was labeled Na’ to reflect the similarity in shift position to that of the Na1 site (CN = 9) in the pristine material. We do not necessarily assign this resonance to the same crystallographic site, but merely suggest that it has a similar CN. It is anticipated that there is some variation in the Na–O bond lengths in the disordered titanate network resulting in a distribution of slightly different chemical shifts and broader $^{23}$Na NMR resonances compared to the pristine material. The intermediate sodium containing Na(2)-[Ti$_3$O$_7$] phase has a spectrum that appears to correspond to a mixture of Na$_2$CO$_3$ and Na1’, displaying the most intense shift for Na$_2$CO$_3$ at +5.5 ppm and an asymmetric resonance at lower frequency (around $-9$ ppm), due to the presence of overlapping carbonate and Na1’ signals.

All exfoliated/restacked compositions, display one $^1$H NMR resonance with a shift at around +6 ppm (SI Figure S14). This resonance could not be assigned to NaOH, and this signal is assigned to protons incorporated into the titanate network. H$_2$Ti$_3$O$_7$ gives rise to $^1$H NMR shifts above +10 ppm (SI Figure S3) and thus the proton signal is likely due to H$_2$O/ H$_2$O$^+$ molecules/ions that are incorporated into the structure (along with residual amine groups); the slightly displaced shift of +4.8 ppm is assigned to free water molecules. Spatial constraints associated with the order of nanosheet stacking (Figure 2D–F), which is enhanced with increasing the Na(x) content, could dictate the amount of water intercalated into the titanate network.

The absence of excess NaOH in the Na(6)-[Ti$_3$O$_7$] and Na(2)-[Ti$_3$O$_7$] phases is explained by the observation of Na$_2$CO$_3$ formed by reacting with H$_2$O and CO$_2$ from the atmosphere; with Na$_2$CO$_3$ presumably crystallizing on the surface upon drying. A proposed mechanism is demonstrated in SI Figure S15, which involves the formation of a Na$_2$[Ti$_3$O$_7$]$\rightarrow$ metastable phase (for $x \geq 2$), which transforms to the more stable Na(1)-[Ti$_3$O$_7$] phase and liberates the excess Na$^+$. The excess Na$_2$CO$_3$ can cleanly be removed on washing, leaving Na(1)-[Ti$_3$O$_7$] as the final stable phase. The Na atoms in Na(1)-[Ti$_3$O$_7$] are accommodated in a high coordination site, additional coordination environments likely coming from bound water. (TGA and $^1$H NMR indicate that this material contains approximately 2 H$_2$O per [Ti$_3$O$_7$] unit, SI Figure S16). The titanate framework in the as-made Na(1)-[Ti$_3$O$_7$] composition is preserved as shown from the PDF analysis. In order to maintain charge neutrality in this phase, oxygen vacancies may be present or more likely, the Na ions are coordinated by both water and H$_2$O$^+$ ions, the charge compensating protons being lost as water on heating. A transition to crystalline Na$_2$Ti$_3$O$_{13}$ (Na$_2$Ti$_3$O$_{13}$) is expected to occur once sintered at temperatures above 600 °C and is observed in this study as well when heated at 800 °C (SI Figures S8 and S10 for Na(1)-[Ti$_3$O$_7$]) consistent to the cation ratio present in the exfoliated phase.

Electrochemistry. The exfoliated/restacked H(x)-[Ti$_3$O$_7$] and Na(x)-[Ti$_3$O$_7$] compositions were evaluated as anode materials for Na-ion batteries in the 0.005–2.5 V range, at a C/20 rate (corresponding to the addition of 2 Na$^+$ in 20 h). Preliminary data were also collected at C/10 and 1C for some of the compositions. The protocol initially adopted for pristine Na$_2$Ti$_3$O$_7$ with 30% carbon as a conductive additive was used for all samples to ensure consistency with the literature, and hand-grinding as opposed to mechanical milling was used to mix the reagents was used to avoid any structural rearrangement within the electrode materials. The cycling behavior of the cell containing only carbon was also investigated for...
The cycling data over 20 cycles of both H(a) and H(r)-[Ti₃O₇] compositions are shown in Figure 4A, where closed and open symbols correspond to discharge and charge steps, respectively. The first discharge capacity is notably high for both materials (≥1000 mAh·g⁻¹), indicating that a large amount of Na⁺ atoms are consumed irreversibly by forming the solid-electrolyte interphase (SEI) layer.

Although crystallizing as different TiO₂ polymorphs, both specimens demonstrate similar electrochemical performance after the initial 10 cycles, both reaching about 150 mAh·g⁻¹ after 20 cycles, at C/20 rate. During the initial 10 cycles, the capacity values diverge with slightly higher values for H(r)-[Ti₃O₇] than H(a)-[Ti₃O₇] during discharge, and converge during charge steps. The capacity values for H(r)-[Ti₃O₇], with particle size distribution between 3 and 10 nm (Figure 2C and SI Figure S5), are significantly improved when compared to commercial rutile TiO₂ (Sigma-Aldrich #224227, particle size < 5 μm) measured at the same conditions for this study (Figure 4B). This demonstrates that nanostructuring TiO₂ has a significant effect on the electrochemical properties and it is the first report of nanorutile being tested as a material for a Na-ion anode to the best of the authors’ knowledge.⁵⁸⁻⁶⁰ Among the several TiO₂ polymorphs, the bronze-type TiO₂(B) has the most open crystal structure, followed by anatase, rutile, and brookite in decreasing order, and is able to accommodate 1 Li⁺ per Ti giving a capacity of 335 mAh·g⁻¹ for Li ion batteries in both bulk and nanostructured forms;⁶¹ much lower capacity values are observed for sodium ion batteries due to the larger size of the Na⁺ ions.⁶² Nanosized TiO₂ typically shows poor cycling performance in Na-ion batteries; this is attributed to the formation of unstable SEI and side-reactions while cycling.⁶³⁻⁶⁵

Figure 4. Cycling data over 20 cycles for (A) H(a) and H(r)-[Ti₃O₇] compositions; (B) comparison of H(r)-[Ti₃O₇] with commercial TiO₂ rutile; (C) all Na(x)-[Ti₃O₇] compositions and comparison with pristine Na₂Ti₃O₇; (D) Na(1)-[Ti₃O₇] and comparison with Na₂Ti₆O₁₃, which is the model compound with the same Na:Ti ratio. In all cases, the closed and open symbols correspond to discharge and charge steps, respectively.

The cycling data over 20 cycles of Na(x)-[Ti₃O₇] compositions are shown in Figure 4C. The capacity increases with reduced Na(x) content, with Na(1)-[Ti₃O₇] displaying the best performance and attaining the highest stable capacity of about 200 mAh·g⁻¹ over 20 cycles. Despite the high first discharge irreversible capacity, similar to that obtained by other nanostructuring methods,¹⁷⁻²¹ all the exfoliated/restacked Na(x)-[Ti₃O₇] compositions demonstrate improved cycling performance compared to pristine Na₂Ti₃O₇, which was measured under the same conditions and suffers from poor capacity retention;⁵¹ this is a common problem for many potential materials used as anodes in Na-ion batteries.¹⁰,⁵² We note however that we have not attempted to optimize the electrode formulation. Further studies would be required to understand the effect that the first cycle losses have on long-term cyclability and in full cells.

The reduced capacity values observed for the Na(2)-[Ti₃O₇] and Na(6)-[Ti₃O₇] compositions compared to Na(1)-[Ti₃O₇] are ascribed to the increasing Na₂CO₃ content. However, the presence of Na₂CO₃ in these phases is not detrimental to the properties when compared to pristine and/or the model crystalline compounds, with the same Na:Ti ratio (Figure 4D for Na(1) and SI Figure S17(A, B) for Na(6) and Na(2) respectively). This suggests that Na₂CO₃ is inactive, and the improved capacity is related to the available space for Na intercalation and the amount of the active Na(1)-[Ti₃O₇] component.
Reduction of all the Ti(IV) content would be expected to occur via the intercalation of three sodium atoms and formation of Na5Ti3O7 (C_{theoretical} = 267 mAh.g\(^{-1}\)) during cycling. In bulk Na2Ti3O7, two sodium atoms are reversibly intercalated in the structure with concomitant reduction of 2/3 of the Ti(IV) to Ti(III) in Na4Ti3O7 (C_{theoretical} = 177 mAh.g\(^{-1}\)).\(^{13}\) The diverse values in the literature for pristine Na2Ti3O7 depend largely on the formulation of the electrode, the additives and the choice of electrolyte, which has not as yet been standardized.\(^{52}\) Further optimization studies would be required to evaluate the effect of electrode formulation and processing to the capacity values measured for Na(1)-[Ti3O7]. At this point, it should be noted that preliminary studies on intermediate compositions between the Na(2)-[Ti3O7] and Na(1)-[Ti3O7] end members, such as Na(ca.1.7), (SI Figures S9 and S10 for Na(ca.1.7)-[Ti3O7]) display higher capacities for initial cycles (e.g., about 240 mAh.g\(^{-1}\) after 10 cycles) but these values are not stable and decrease to about 200 mAh.g\(^{-1}\) after 20 cycles (SI Figure S17(C)).

The galvanostatic curves of all exfoliated/restacked Na(x)-[Ti3O7] compositions during the first cycle are shown in Figure 5A and compared with those of parent Na2Ti3O7 and carbon cells. All the cells exhibit irreversible plateaus at about 0.6–1.0 V vs Na'/Na and at lower voltages (0.1–0.2 V) during the first discharge. These are not observed during the first charge or in subsequent cycles, demonstrated here for the second cycle (Figure 5B) and the 20th cycle (Figure 5C). The differential capacity analysis dQ/dV plots are shown in SI Figure S18. These irreversible plateaus are believed to be due to reaction of Na' with the carbon additive and to the SEI formation from electrolyte decomposition.\(^{13,22,51}\)

It should be noted that the existence of Na2CO3 in the Na(2)-[Ti3O7] and Na(6)-[Ti3O7] compositions may have an additional effect on the nature of the SEI forming during operation, due to its solubility in the electrolytes commonly used for sodium-ion batteries.\(^{51}\) Moreover, the water molecules, whose existence was evidenced by \(^{1}H\) NMR (SI Figure S14), likely participate to the processes occurring at the first discharge step. These intercalated water molecules were only removed upon further drying/treatment at 400 °C (SI Figure S16), which is likely to have an effect to the nanosheet stacking. The capacity values of Na(x)-[Ti3O7]-400 compositions were reduced by about 100 mAh.g\(^{-1}\) during the first discharge step compared to as-made samples, while there was no significant difference for the subsequent cycles (SI Figure S19). Although the incorporation of water molecules would be expected to influence the electrochemical performance while cycling by continuously reacting with the electrolyte, this was not observed for these samples under the conditions tested. It is however anticipated that the existence of intercalated water molecules might affect further high rate capability studies.

After the formation of SEI during the first discharge step, the electrochemical processes for the pristine Na2Ti3O7 occur at distinct active sites in the bulk favoring a two-phase reaction, accompanied by flat voltage plateaus at around 0.2 and 0.4 V vs Na'/Na during discharge (sodiation) and charge (desodiation) steps, respectively.\(^{15}\) (Figure 5B, C for the 2nd and 20th cycles, respectively, dQ/dV plots in SI Figure S18). The additional
small plateau at about 0.1 V vs Na+/Na, observed for pristine and all exfoliated/restacked compositions, is believed to be related with the carbon additive (SI Figure S18(D)). On the contrary, all the cells containing the exfoliated/restacked Na(x)·[Ti3O7] compositions display sloping discharge/charge potential profiles (shown separately for Na(1) in Figure SD) compared to the pristine material, with a very broad plateau at average voltage about 0.6 V vs Na+/Na, most intense for Na(1)·[Ti3O7] composition (also observed at dQ/dV plots, SI Figure S18). This plateau is likely to be related to the existence of the Na intercalation sites (as evidenced by 23Na NMR, Figure 3C) and is not observed for the H-[Ti3O7] compositions (SI Figure S20). In general, sloping potential profiles are indicative of single-phase behavior, where the intercalation/deintercalation processes occur at nonequivalent sites with different energies, in part due to the disorder of these systems and the large exposed surfaces of reduced particle-size materials.33,34 The overall surface area of the exfoliated/restacked materials in this study, is expected to be higher than for the pristine crystalline Na2Ti3O7 (BET = 1.3 m²·g⁻¹); reliable BET measurements would require synthesis on a larger scale. In the general case of nanosized materials, the intercalation/deintercalation processes are accompanied by shortened diffusion/transport distances, which is often advantageous for the overall specific capacity. For the restacked Na(x)·[Ti3O7] nanosheets, the existence of Na intercalation sites is likely related to the observed improved capacity retention. Although higher rate data were not collected for Na(1)·[Ti3O7], preliminary data for Na(2)·[Ti3O7] indicate that the capacity of about 120 mAh·g⁻¹ remains stable when cycled at C/20 and 1C for 40 cycles (SI Figure S20(F)). Clearly, there is further scope for optimization and high rate studies.

CONCLUSIONS

In summary, we report the exfoliation and subsequent restacking of Na2Ti3O7 using HNO3 and NaOH to form H-[Ti3O7] and Na(x)·[Ti3O7] compositions, respectively; these were tested as potential Na-ion anode materials. The formation of aggregated TiO2 (rutile and anatase) nanoparticles is favored upon drying of the H-[Ti3O7] compositions, resulting in high capacity materials, but which suffer from poor capacity retention. In the case of the Na(x)·[Ti3O7] compositions, the overall connectivity of the titane framework was retained. Control over the composition can be achieved by washing, which induces gradual Na leaching from the titane network resulting in reduced degrees of adherence between the exfoliated layers. The final composition is Na(1)·[Ti3O7], washing removing the excess of “free/reactive” Na⁺, which otherwise forms inactive Na2CO3 in the insufficiency washed compositions. All the exfoliated/restacked Na(x)·[Ti3O7] compositions show significantly improved capacity retention compared to the pristine Na2Ti3O7 and/or the crystalline compounds with the same Na:Ti ratio. This is likely related to enhanced kinetics due to nanosize effects and the formation of a more open titane framework. The optimal electrochemical performance among the series of exfoliated/restacked Na(x)·[Ti3O7] compositions studied is demonstrated for the Na(1)·[Ti3O7] phase, where Na atoms likely occupy a range of slightly different Na intercalation sites, Na(1)·[Ti3O7] displaying a stable capacity of about 200 mAh·g⁻¹ after 20 cycles at C/20 rate. In situ and/or postcycling studies would be required to conclude whether the intercalation of additional sodium atoms compared to pristine Na2Ti3O7 is dominating over surface factors.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b03753.

Additional data related to this publication are available at the Cambridge data repository: https://doi.org/10.17863/CAM.18615. Further details about the characterization of materials (pristine, intermediates and products) by chemical and NMR measurements, PDF, XRD, and TGA analysis, DFT calculations and TEM images, as well as supplementary electrochemical data and analysis, including Tables S1–S4 and Figures S1–S20 (PDF).

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