Li⁺ Pre-Insertion Leads to Formation of Solid Electrolyte Interface on TiO₂ Nanotubes That Enables High-Performance Anodes for Sodium Ion Batteries

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Recently, sodium ion batteries (SIBs) have been widely investigated as one of the most promising candidates for replacing lithium ion batteries (LIBs). For SIBs or LIBs, designing a stable and uniform solid electrolyte interphase (SEI) at the electrode–electrolyte interface is the key factor to provide high capacity, long-term cycling, and high-rate performance. In this paper, it is described how a remarkably enhanced SEI layer can be obtained on TiO₂ nanotube (TiO₂ NTs) arrays that allows for a strongly improved performance of sodium battery systems. Key is that a Li⁺ pre-insertion in TiO₂ NTs can condition the SEI for Na⁺ replacement. SIBs constructed with Li-pre-inserted NTs deliver an exceptional Na⁺ cycling stability (e.g., 99.9 ± 0.1% capacity retention during 250 cycles at a current rate of 50 mA g⁻¹) and an excellent rate capability (e.g., 132 mA h g⁻¹ at a current rate of 1 A g⁻¹). The key factor in this outstanding performance is that Li-pre-insertion into TiO₂ NTs leads not only to an enhanced electronic conductivity in the tubes, but also expands the anatase lattice for facilitated subsequent Na⁺ cycling.

Since the first practical application of lithium ion batteries (LIBs) in 1991,[1] these type of batteries have become of global significance in renewable applications. While the market was first dominated by portable electronics, the attention for development now is moving toward large-scale applications, such as electric vehicles and smart grids.[2,3] However, with this drastically increasing demand for Li, the material is increasingly costly; the price of lithium carbonate has increased by 97% from 2016 to 2018.[4] Therefore, developing alternative large scale battery systems using abundant resources is highly desired.[5,6] As a result, sodium ion batteries (SIBs) have received great attention in science and technology, as an alternative to LIB. Recently, research increasingly demonstrated the feasibility of the concept using an element with no shortage of supply: sodium is the 6th abundant substance on earth. As sodium ions and lithium ions show a similar chemistry, it is expected that reaction mechanisms and cell design from LIB can be adapted to SIB, resulting in predictable and tunable outcomes. However, the design of suitable components of an SIB system is significantly more difficult, as the Na⁺ ion has a significantly larger radius (1.02 Å) than the Li⁺ ion (0.76 Å). For example, graphite that is commonly used as an anode material in LIB systems does not allow Na⁺ intercalation into its interlayer spacing.[7,8] In addition, vinylene carbonate, the most common additive for forming stable solid electrolyte interphases (SEIs) on the LIB-anode, cannot be applied in the SIB system, as it causes electrolyte decompositions.[9,31] In other words, optimized LIB components (such as the anode, cathode, electrolyte, separator, and design) often cannot be directly transferred to the SIB system.

In recent years, extensive research on negative and positive electrode materials for SIBs has been carried out; especially addressing the large size and sluggish kinetics of Na⁺. For cathode materials, layered NaMnO₄ (M = Co, Cr, Mn, V, etc.) and phosphate-based NaMPO₄ (M = V, Fe, Co, Ni, Mn, etc.) materials are the focus of interest. In the case of anode materials, various non-graphitic carbon materials (Sn/C, Sb/C)[10–14] and non-carbon materials, including sodium-intercalated (sodium titanates)[15,16] and sodium-free (Sb₂O₃, W₂S₃, SnSb)[17–19] compounds have been widely investigated, displaying increasingly high-rate capabilities and long-term cycling stability. In particular, among various anode candidates, the nontoxic, stable, and inexpensive TiO₂, which is a viable anode material in LIB systems, is receiving increased attention in SIB systems.[20–24] In spite of the irreversible first discharge–charge cycle (low initial coulombic efficiency) and the initially low conductivity, particularly, the anatase form of TiO₂ is becoming increasingly interesting due to a competitive cycle stability and a high-rate capability. To overcome the drawback of a sluggish Na⁺ kinetics, studies using nonmetal doping such as S, P, and N into TiO₂ were carried out and showed some promising results.[25–27]
Nonetheless, most of the SIB research up to now focused on the search of suitable electrode materials. A key factor is to establish a system with the ability to form a functional SEI layer, which is the mechanistic heart of any intercalation battery.[28,29] Since the introduction of SEI layer model by Peled in 1979,[30] the importance of the formation of stable and uniform SEI layer during charge/discharge cycles has drawn great attention in the battery community. An SEI layer acts as an electronically insulating ion-conducting layer on an electrode, that is, it allows selectivity for the passage of only desired cations (e.g., Li⁺, Na⁺) from the electrolyte. SEI layers often consist of alkali carbonate (A₂CO₃) and alkyl carbonate (ROCO₂A) (A = Li⁺ or Na⁺), which are insoluble in the electrolyte and are formed by the reaction between carbonate-based electrolytes and the ionic species (Li⁺ or Na⁺) on the surface of the anode. In the case of an unstable or inhomogeneous SEI layer, from cycle to cycle, the SEI thickness can be steadily altered through repeated dissolution and reforming[11–33]—this leads to significant electrolyte decomposition and an irregular Li⁺ diffusion length. These effects are undesired as they strongly deteriorate the performance of the battery. Tools to tailor the SEI in SIBs are the use of additives such as fluoroethylene carbonate[34–36] or adjusting the cutoff voltage.[37,38] However, a decreased cutoff value does not allow to take full advantage of the capacity provided by the Na⁺ red-ox reaction at low voltages.

Another way to shape the SEI layer is by pre-lithiation. This is a well investigated method for LIB systems—it improves the coulombic efficiency by lowering open circuit voltage and preventing electrolyte decomposition.[39–41] Most recently, Li et al. examined the use of the pre-lithiation technique on a hard carbon (HC) anode for the SIB system.[42] However, the authors found that a pre-formed Li-based SEI layer hinders Na⁺ intercalation for HC and thus pre-lithiation is detrimental to the battery performance. While the HC electrode used for SIB without lithiation had a capacity of 100 mAh g⁻¹, the pre-lithiated SIB showed a lower specific capacity of only 50 mAh g⁻¹.

In the present study, we explore the potential of pre-lithiation on anatase TiO₂ nanotubes used as anodes in SIBs. We find that lithiated nanotubes (Li-TiO₂ NTs) can yield a remarkably high reversible capacity, cycling stability, and outstanding high-rate performance in the SIB system. These strong performance improvements are attributed to an expansion of the anatase lattice in Li-TiO₂ NTs as compared with unlithiated TiO₂ NTs. Additionally, a significantly enhanced conductivity of the nanotube electrode is induced by the pre-lithiation.

The overall process for the fabrication of the Li-TiO₂ NTs is illustrated in Figure 1a (more details are provided in Experimental Section). To insert Li⁺ into anatase TiO₂ NTs, cyclic voltammetry was used in the voltage range between 3.0 and 0.75 V in propylene carbonate containing 1 m LiClO₄ (Figure S1, Supporting Information). In a first step, different types of TiO₂ NTs were produced: amorphous TiO₂ NTs (am-TiO₂ NTs), anatase TiO₂ NTs (A-TNT), Li⁺ inserted anatase TiO₂ NTs (Li-TiO₂ NTs), and Li⁺ inserted/de-inserted anatase TiO₂ NTs (Li-TiO₂ NTs-De). Amorphous tubes are directly obtained after growing the tubes by self-organizing anodization (see Experimental Section for details). These nanotubes can be annealed in air at 450 °C to form anatase crystalline tubes. For lithiation, only the cathodic reaction from 3.0 to 0.75 V was carried out, for intercalated/de-intercalated tubes, one cycle of cathodic and anodic reaction was carried out. Optical images of these samples are shown in the inset of Figure 1g: from left, A-TNT, Li-TiO₂ NTs, and Li-TiO₂ NTs-De. These electrodes were then tested as anode materials in the SIB system. The TEM (left side) and high-resolution TEM (HRTEM) (right side) images show following samples: A-TNT (Figure 1b), Li-TiO₂ NTs (Figure 1c), 50 times cycled A-TNT in the SIB system (Figure 1d), and 50 times cycled Li-TiO₂ NTs in the SIB system (Figure 1e). Very clear differences in their SEI layer are observed. Only a very thin SEI layer (=2 nm) is formed on the surface of the TiO₂ NTs by lithiation (Figure 1c). This thin layer is expected to be Li₂CO₃ which is a typical product of LIB system, confirmed by X-ray photoelectron spectroscopy (XPS) results below. Furthermore, for the lithiated samples, the anatase (101) lattice spacing is expanded from 3.60 to 3.70 Å (Figure 1b,c). Most important differences between A-TNT and Li-TiO₂ NTs became obvious after extended charging–discharging of the samples. Figure 1d shows the data for 50 times cycled samples. Clearly, a relatively thick (30–50 nm) and rough SEI layer is formed on the A-TNTs, and the lattice spacing is hardly expanded by Na⁺ cycling (3.60–3.62 Å after 50 cycles of Na⁺ charging–discharging). On the contrary, a smooth and thin (=10 nm) SEI layer is observed on the Li-TiO₂ NTs after 50 cycles. In particular, the expanded lattice spacing, created by lithiation, still remains after the Na⁺ insertion–extraction cycles (Figure 1e). That is, the original increase and an even slight additional enlargement from 3.60 to 3.73 Å (3.6%) caused by lithiation (and sodiation) is observed after 50 times Na⁺ cycling.

The Na⁺ charge–discharge behavior on A-TNT, Li-TiO₂ NTs, and Li-TiO₂ NTs-De was then characterized by cyclic voltammograms (CVs) (Figure 1f). As previously reported by others for titania nanocrystals and nanofibers,[43,44] sodium insertion provides during the first scan a cathodic peak at 0.8 V that corresponds to the SEI formation. The subsequent cathodic peak between 0.01 and 0.4 V is likely related to electrolyte decomposition. This peak is then suppressed in the following cycles by the lithiation in the first cycle. This effect is highly beneficial to the cyclability also in SIBs in charge–discharge tests as shown later. Remarkably, when CVs for Na⁺ intercalation/de-intercalation are taken for the pre-lithiated sample (Figure 1f), distinct redox peaks are observed at 1.10 V (Na⁺/Na) for the cathodic reaction and 1.88 V (Na⁺/Na) for the anodic reaction, while these peaks are absent for other samples. While the cathodic peak shows a very slight shift from cycle 1 to cycle 3 (to the then constant value of 1.2 V), the anodic peak stays instantaneously at 1.88 V (Figure S2a, Supporting Information). Important is that in all these cycles, we obtain still well-defined peaks corresponding to distinct insertion/extraction reactions. The slight shift in the redox peaks is likely related to the structural rearrangements occurring in the lattice of Li-TiO₂ NTs during extended cycling. Additionally, Figure S2b, Supporting Information shows the fundamental process not to be dependent on the tube length. Another crucial point is that there is no more substantial change in the peak positions after the 3rd cycle, showing the high reversibility of the insertion/extraction reactions. The voltage profiles at 50 mA g⁻¹ in Figure S3, Supporting Information exhibit voltage plateaus at ≈1.20 V for sodium insertion and ≈1.69 V for sodium extraction after
50 cycles, which is consistent with CVs. Moreover, the Li-TiO$_2$ NTs show overall a higher capacity than any reference sample (inset of Figure 1f). These results illustrate that characteristic of the Na$^+$ insertion–extraction reaction for Li-TiO$_2$ NTs is a battery-like behavior,$^{[45,46]}$ as defined Na$^+$ intercalation/de-intercalation peaks occur. Up to now, these pronounced redox peaks have not been reported for any anatase TiO$_2$ SIB system.$^{[20–24,44–47]}$ Please note that the other samples in Figure 1f show a typical supercapacitor-like behavior. From above, we propose that for Li-TiO$_2$ NTs, Na$^+$ can in our case be inserted into the enlarged lattice of the lithiated anatase. This is further supported by the investigation of Li-TiO$_2$ NTs-De that were delithiated prior to testing in the SIB system. For these Li-TiO$_2$ NTs-De, a cathodic peak was observed at 0.78 V (Na$^+$/Na), that is, at a slightly lower value than for A-TNT (0.8 V) in the 1st cycle. This is probably caused by some Li$^+$ residue (see Figure S7, Supporting Information). But on the whole, the Li-TiO$_2$ NTs-De show similar characteristics to A-TNT, without characteristic insertion peaks and with only slightly higher current values for the redox reactions.

In order to test for long-term cyclability, further investigations were done with galvanostatic cycling conducted at a rate of 50 mA g$^{-1}$ (Figure 1g). In the experiments, A-TNT and Li-TiO$_2$ NTs-De show a rapid capacity drop over 50 cycles, followed by a further steady decrease up to the test end after 200th cycle. In stark contrast, the Li-TiO$_2$ NTs, during initial cycling, show even an increase in capacity and demonstrate an outstanding cyclability with a stable high capacity ($\approx$ 220 mAh g$^{-1}$) over 250 cycles. It is evident that in the initiation phase, the capacity of Li-TiO$_2$ NTs is lower than that of A-TNT between 1st and 20th cycling, but then starts to increase after the 20th cycle. The reason for this is likely that as initially

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**Figure 1.** a) Schematic illustration of the synthesis of Li$^+$ pre-inserted SEI layer. TEM and HRTEM images of: b) A-TNT, c) Li-TiO$_2$ NTs, d) 50 cycled A-TNT, and e) 50 cycled Li-TiO$_2$ NTs. f) CVs curves of A-TNT, Li-TiO$_2$ NTs, and Li-TiO$_2$ NTs-De electrodes in the range of 0.01–2.5 V (versus Na$^+$/Na) at a scan rate of 0.5 mV s$^{-1}$; inset shows CV data of 5th cycle. g) Cycling performance at a current density of 50 mA g$^{-1}$; inset shows optical images of A-TNT, Li-TiO$_2$ NTs, and Li-TiO$_2$ NTs-De (from left).
Li$^+$ is occupying the sites for ion insertion, only few sites are available for Na$^+$ insertion. Therefore, until Li$^+$ is sufficiently depleted from the insertion sites, the capacity is below maximum.$^{[42]}$ In order to trace the change of the lithium amount in the initial cycles, we measured XPS and time-of-flight secondary ion mass spectrometry (ToF-SIMS) data shown in Figure S4, Supporting Information. The XPS data reveal that Li$^+$ content decreases after initial lithiation with every sodium intercalation step, while the sodium ion amount increases with every cycle. These results are in accordance with ToF-SIMS depth profiles (Figure S4b, Supporting Information). These results confirm that the pre-inserted Li$^+$ can exit the TiO$_2$ NTs during sodium ion cycling, leading to the formation of a conductivity enhanced SEI layer consisting of mixed Li$^+$ and Na$^+$ compounds (e.g., involving Li$_2$CO$_3$ and Na$_2$CO$_3$).

Between the 20th and 50th cycles, the capacity increases due to the increasingly better Na$^+$ penetration (enlarged lattice). Lastly, after the 50th cycle, a very stable cyclability is obtained after a stable SEI layer is established that also prevents electrolyte decomposition. The Li-TiO$_2$ NTs-De show a slightly higher capacity and cycling stability than A-TNT (but with essentially the same characteristics as A-TNTs). As mentioned, the slight differences can be attributed to Li$^+$ residues that were not completely extracted during anodic cycling.

The X-ray diffraction (XRD) data in Figure 2a show that A-TNT, Li-TiO$_2$ NTs, and Li-TiO$_2$ NTs-De consist mainly of anatase (ICSD No.73-1764). As shown in the inset of Figure 2a, the (101) peak of anatase (A-TNT) is shifted to a lower value by lithiation, in good agreement with the results of lattice-resolved HRTEM images. Moreover, the peak associated with (101) plane...
of Li$_0.5$TiO$_2$ is also detected at 23.9° for Li-TiO$_2$ NTs. Figure 2b shows the XRD patterns for the above samples after 50 cycles of Na$^+$ insertion–extraction. For the analysis, samples were disassembled in the discharged (sodiated) state and then washed by water. For all samples, the intensity of anatase (101) peak is reduced, indicating a decrease in crystallinity for all types of TNTs, in agreement with results reported by Wu et al. and Cha et al.$^{[47,48]}$ It is worth noting that 50 times cycled Li-TiO$_2$ NTs show the strongest shift of the (101) peak to lower 2θ angles among the three TNTs (inset of Figure 2b), even more than for the original Li-TiO$_2$ NTs (Figure S5a, Supporting Information). This shows that further lattice rearrangement has occurred by Na$^+$ insertion. These phenomena are even more apparent for the (200) anatase peak (Figure S5c,d, Supporting Information).

In order to investigate the process of Na$^+$ insertion/extraction in Li-TiO$_2$ lattice more in detail, we carried out—in parallel with a CV curve—XRD measurements at characteristic points (Figure S6, Supporting Information). Based on the CV, the samples were taken out from the cell during the cathodic sweep (at 1.3 V, 0.7 V, and 0.01 V) and in the anodic direction (at 1.7, 2.1, and 2.5 V), and then analyzed with XRD. Evidently, a clear (101) peak shift corresponding to Na$^+$ insertion is observed between 1.3 and 0.7 V during the cathodic sweep, and a reverse (101) peak shift corresponding to Na$^+$ extraction is observed between 1.7 and 2.5 V during anodic sweep.

The surface chemistry of the TNTs was studied by XPS. After lithiation and delithiation (Figure S8, Supporting Information) and after one cycle of Na$^+$ insertion–extraction at a current rate of 25 mA g$^{-1}$, and after washing with propylene carbonate solution (see Experimental Section). Figure 2c,d shows Li 1s and Na 1s region of the XPS spectrum for Li-TiO$_2$ NTs. As shown in Figure 2c, the Li 1s peak consists of two contributions. The peak at 54.7 eV is attributed to Li$_2$CO$_3$ and the peak at 54.2 eV is ascribed to ROCO$_2$Li (the Li 1s spectrum of pre-lithiated A-TNT is shown in Figure S7, Supporting Information). Furthermore, for Na, a peak was found at 1071.8 eV in the spectrum of Figure 2d, which can be attributed to Na$_2$CO$_3$. This suggests that Li$_2$CO$_3$ and Na$_2$CO$_3$ co-exist in the SEI layer on the surface of the Li-TiO$_2$ NTs. The existence of Li$^+$ and Na$^+$ was confirmed by TOF-SIMS analysis after 1 cycle in SIB system (Figure S9, Supporting Information).

From XPS in Figure 2e,f, for the non-lithiated or delithiated sample, the Na peak is of a different nature than in the lithiated sample (Figure 2d)—the position at 1070.4 eV can be ascribed to NaClO$_4$ that is present in the electrolyte. We also show sample (Figure 2d)—the position at 1070.4 eV can be ascribed to ROCO$_2$Li (the Li 1s spectrum of pre-lithiated A-TNT, Li-TiO$_2$ NTs, and Li-TiO$_2$ NTs-De show an outstanding capacity recovery ability after high-rate cycling, while more than 50% of capacity decay (from 70 mAh g$^{-1}$ to 35 mAh g$^{-1}$) is observed with A-TNT and A-TNT-De a value of 17 000 kΩ. These results indicate that the Li$^+$ pre-insertion aids in forming a high-rate conductive SEI layer on the surface of TiO$_2$ NT during Na$^+$ charge/discharge cycles—this is expected to contribute to an excellent high-rate capability. Moreover, 50 times cycled Li-TiO$_2$ NTs show much better RSEI properties than corresponding A-TNT and A-TNT-In-De (Figure S11b, Supporting Information)—see also additional discussion in Figure S12, Supporting Information.

In order to investigate the effect of the lithiation pre-treatment on the conductivity of tubes, solid state two-point conductivity measurements were carried out through the tube layers. Figure 3c shows that for the Li-TiO$_2$ NTs a highly enhanced conductivity (212 kΩ) is observed after 50 cycles in the SIB system. For comparison, the A-TNT yields 240 000 kΩ and Li-TiO$_2$ NTs-De a value of 17 000 kΩ. These results indicate that the Li$^+$ pre-insertion aids in forming a highly conductive SEI layer on the surface of TiO$_2$ NTs during Na$^+$ charge/discharge cycles—this is expected to contribute to an excellent high-rate capability. Moreover, 50 times cycled Li-TiO$_2$ NTs show a higher conductivity than 50 cycled A-TNT (see Figure 3d). These results are in line with the galvanostatic cycling tests, that is, the residue of Li$^+$ that could not be de-inserted from the TNTs during anodic cycles can contribute to the formation of a somewhat more stable and conductive SEI layer.

Figure 3e displays the rate performance of the electrodes. Li-TiO$_2$ NTs show an exceptionally high-rate performance displaying highly reversible capacities of around 210, 193, 169, and 142 mAh g$^{-1}$ at applied current rates of 100 mA g$^{-1}$, 200 mA g$^{-1}$, 500 mA g$^{-1}$, and 1 A g$^{-1}$, respectively. Interestingly, Li-TiO$_2$ NTs and Li-TiO$_2$ NTs-De show an outstanding capacity recovery ability after high-rate cycling, while more than 50% of capacity decay (from 70 mAh g$^{-1}$ to 35 mAh g$^{-1}$) is observed with A-TNT after high-rate cycling. Therefore, these results support the conclusion that Li$^+$ contributes to the formation of a stable SEI layer on the TiO$_2$ NTs surface, preventing the decomposition of the electrolyte leading also to an outstanding cycling stability. In order to examine the high-rate capability of Li-TiO$_2$ NTs, another long-term cycling test was carried out with a current rate of 1 A g$^{-1}$ (Figure 3f). The Li-TiO$_2$ NTs retains a capacity of 132 mAh g$^{-1}$ after 250 cycles, corresponding to a capacity retention of 99%—this is a key prerequisite for a practical application as an SIB anode. In comparison with previously reported TiO$_2$ electrodes (Table S2, Supporting Information), this is an outstanding sodium ion anode characteristics based on an entirely novel concept.

In order to study the effect of Li$^+$ pre-insertion and Na$^+$ cycling on the TiO$_2$ NTs on the morphological stability of the tube structures, SEM images were taken after 50 times cycling A-TNT, Li-TiO$_2$ NTs, and Li-TiO$_2$ NTs-De. Figure 4a,e shows the typical top surface and cross-sectional SEM images of TNTs fabricated in 3 vol% of H$_2$O containing ethylene-glycol-based 0.15 M of NH$_4$F electrolyte. In the inset of Figure 4a, a typical initiation layer is formed on the top surface, and TiO$_2$
NTs layer has a thickness of \( \approx 1.5 \) µm. The TiO\(_2\) NTs have an outer diameter of \( \approx 120 \) nm and an inner diameter of \( \approx 80 \) nm (Figure S13, Supporting Information). For SEM images taken after cycling, the Li-TiO\(_2\) NTs show outstanding mechanical properties. Santoro et al. demonstrated that aggregation as well as swelling of TiO\(_2\) nanoparticles (NP) can occur during cycling in SIB systems, leading to the decrease of battery capacity.\(^5\) Our study using nanotubes shows a clearly superior mechanical stability after pre-lithiation. In Figure 4b,d, many cracks are observed from top surface for the 50-cycled A-TNT and Li-TiO\(_2\) NTs-De, suggesting that classic TNTs also encounter mechanical problems similar to TiO\(_2\) NP, that is, degradation caused by stress or swelling of the tube walls during Na\(^+\) insertion–extraction. These cracks are also observed from cross-sectional image in Figure 4f. On the other hand, Li-TiO\(_2\) NTs do not show these effects. As shown in Figure 4c,g, no cracks or fissures are observed with Li-TiO\(_2\) NTs, indicating that a stable SEI layer aids to prevent or strongly suppress stress-induced deterioration during cycling. This exceptional mechanical stability of Li-TiO\(_2\) NTs was also maintained after 150 cycles (Figure S14, Supporting Information). We also confirmed that the expanded lattice spacing of 3.73 Å created by lithiation still remains after 150 times Na\(^+\) cycling (Figure S15, Supporting Information). It is noteworthy that smooth and thin (\( \approx 13 \) nm) SEI layer is observed on the Li-TiO\(_2\) NTs after 150 cycles.

Another fact worth mentioning is the wettability of tubes. As shown in the insets of Figure 4a–d, contact angles of 25.0°, 13.0°, 58.0°, and 12.5° were obtained for A-TNT, 50 cycled A-TNT, 50 cycled Li-TiO\(_2\) NTs, and 50 cycled Li-TiO\(_2\) NTs-De, respectively, indicating that lithiation makes the tubes more hydrophobic than bare anatase tubes. This is of a further benefit as the adsorption or adhesion of H\(_2\)O on the electrode surface is harmful to the operation of a SIB cell.

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**Figure 3.** Nyquist plots of the Li-TiO\(_2\) NTs according to cycle number a) 1st, 5th, 20th, 50th; b) 50th, 200th, 250th, 300th. c,d) Conductivity measurements of 50 cycled A-TNT, Li-TiO\(_2\) NTs, and Li-TiO\(_2\) NTs-De. e) Rate performance of A-TNT, Li-TiO\(_2\) NTs, and Li-TiO\(_2\) NTs-De at various current densities. f) Cycling performance of Li-TiO\(_2\) NTs at a current density of 1 A g\(^{-1}\).
In summary, we have demonstrated for the first time strong and robust enhancement of electrochemical properties of titania nanotubes as an anode material in a SIB system by pre-lithiation of the nanotube layer and the formation of a defined SEI layer. Li\textsuperscript+ pre-insertion results in: i) lattice expansion of anatase well apparent in the XRD (101) and (200) planes, ii) a significant conductivity increase, and iii) formation of a stable and uniform SEI layer. When evaluated in a SIB system, Li\textsuperscript+ pre-inserted sample delivers a reversible capacity of 250 mAh g\textsuperscript{−1} and 99% capacity retention at 50 mA g\textsuperscript{−1} after 250 cycles, and retains a reversible capacity of 132 mA h g\textsuperscript{−1} at 1A g\textsuperscript{−1}. Please note that these gravimetric data (Table 1) are based on a reliable mass-balance procedure\textsuperscript{[52,53]} described in the Supporting Information. Noteworthy is that a very small amount of Li source was used for the formation of an enhanced SEI layer as compared to the significant consumption of Li (for cathode material and electrolyte) in traditional LIB systems. Moreover, conceptually, the pre-lithiation treatment described above also provides a promising approach to ameliorate issues with SEI layers on other metal oxide materials.

### Experimental Section

**Materials Synthesis:** Ti foils (Advent Materials, 0.125 mm thick and 99.6% purity) were cut into 1.6 cm × 1.6 cm samples and cleaned using the same procedure as in ref. [52]. Electrochemical anodization was conducted in a two-electrode O-ring cell (8 mm in diameter) at room temperature. A Pt foil and Ti foil act as counter and the working electrode, respectively. The TiO\textsubscript{2} NTs (1.5, 3.0, and 6.0 µm-thick) were formed by anodizing cleaned Ti foils in ethylene-glycol-based electrolyte containing 0.15 M NH\textsubscript{4}F and 3 vol% H\textsubscript{2}O at 60 V for 3, 6, and 12 min.

| Anodization time [min] | Length [µm] | Weight (after annealing) [µg] |
|------------------------|-------------|-----------------------------|
| 3                      | 1.5         | 100                         |
| 6                      | 3.0         | 200                         |
| 12                     | 6.0         | 400                         |

Table 1. Weight table of TiO\textsubscript{2} nanotube membranes according to different lengths: 1.5 µm, 3.0 µm, and 6.0 µm.

![Figure 4. Top SEM images of a) A-TNT, b) 50 cycled A-TNT, c) 50 cycled Li-TiO\textsubscript{2} NTs, and d) 50 cycled Li-TiO\textsubscript{2} NTs-De; insets show contact angle images. Cross-sectional SEM images of e) A-TNT, f) 50 cycled A-TNT, and g) 50 cycled Li-TiO\textsubscript{2} NTs.](image-url)
The insertion and extraction of Li\(^+\) were carried out by cyclic voltammetry using PCGU 1A-OEM (ips-jaisle) at a scan rate of 1.0 mV s\(^{-1}\) in an Ar filled glove box (with water/oxygen content lower than 0.5 ppm). The electrolyte consists of 1 M LiClO\(_4\) in propylene carbonate. After Li\(^+\) insertion (or extraction), the nanotube layers were rinsed with ethanol and dried in a N\(_2\) stream and then immediately transferred to the glove box.

**Materials Characterization:** Field-emission scanning electron microscope (FE-SEM Hitachi S4800) was used to characterize the morphology of the samples. Transmission electron microscope (TEM, Philips CM30) was employed to characterize the morphology of the sample and to determine lattice spacing of TiO\(_2\). In order to determine crystallographic structure of the samples (1.5 \(\mu\)m-thick), X-ray diffraction analysis (XRD, X'pert Philips MPD with a Panalytical X'celerator detector) was performed using graphite-monochromized Cu K\(_\alpha\) radiation (\(\lambda = 1.54056\) Å). Additional acquisition parameters were: step size 0.03° and scan rate 0.09° min\(^{-1}\). The chemical composition of the TiO\(_2\) samples was analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5600 US). The A-TNT, Li-TiO\(_2\) NTs, and Li-TiO\(_2\) NTs-De electrodes (1.5 \(\mu\)m thick) were charged and discharged (Na\(^+\) insertion-extraction) at a current rate of 25 mA g\(^{-1}\) with beaker type cell in a glove box and then rinsed with propylene carbonate in air. Finally, the samples were dried in a nitrogen stream before XPS measurements. To investigate the presence of Li, Na species in the depth of the nanotubular structures, time of flight secondary ion mass spectrometry (ToF-SIMS) negative depth profiles were recorded on ToF-SIMS V (Ion-Tof) instrument in dual beam mode. A pulsed 25 keV Bi\(^+\) liquid-metal ion beam bunched down to <0.8 ns was used for spectra generation and a 1 keV Cs\(^+\) ion beam for sputter-removal, on a 100 \(\times\) 100 \(\mu\)m area in the center of a 500 \(\times\) 500 \(\mu\)m sputter crater. Signals were identified according to their isotopic pattern as well as exact mass, and Poisson correction was employed. Spectra are calibrated to CH\(_2\) as internal standard.

**Electrochemical Measurements:** The electrochemical performances of the A-TNT, Li-TiO\(_2\) NTs, and Li-TiO\(_2\) NTs-De electrodes (6.0 \(\mu\)m-thick) were measured with Swagelok cells. Na metal (99.9% trace metals basis, Sigma Aldrich) was used as counter electrode, 1 M NaClO\(_4\) (98.0%, Sigma Aldrich) in a mixture of ethylene carbonate (anhydrous, 99.0%, Sigma Aldrich) and propylene carbonate (anhydrous, 99.7%, Sigma Aldrich) (1:1 by volume) were used as electrolyte, and glass fiber (GF/F, Whatman) was used as separator. The working electrodes were used as is without active and binder material (binder free) and all the cells were assembled in an Ar filled glove box. Cyclic voltammetry and EIS tests for Na\(^+\) insertion-extraction were carried out with two-electrode system (Na metal as counter and reference electrode, and TiO\(_2\) NTs as working electrode). For the CV, a scan rate of 0.5 mV s\(^{-1}\) was used for Na\(^+\) insertion/extraction in Ar filled glove box with beaker type cell. The galvanostatic discharge/charge tests were carried out between 2.5 and 0.01 V versus Na\(^+\)/Na on a CT-4008 (NEWARE) in room temperature, and cells were pre-cycled at a current rate of 25 mA g\(^{-1}\). EIS measurements for the different samples were performed at open circuit potential in a frequency range of 5 mHz to 10\(^5\) Hz and with a peak-to-peak amplitude of the AC signal of 10 mV using a Zahner IM6 (Zahner Elektrik, Kronach, Germany).

**Conductivity Measurements:** Solid state two-point conductivity measurements were conducted using a semiconductor characterization system (Keithley 4200-SCS) with adapted scanning electron microscope (SEM, TESCAN LYRA3 XMU). The ramping rate of 5 mV s\(^{-1}\) was used for conductivity measurements between –2 V and 2 V and then resistivity values were obtained from I-V curves. The TNT samples have a thickness of 1.5 \(\mu\)m.

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**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

anodization, pre-lithiation, sodium ion batteries, solid electrolyte interphases, TiO\(_2\) nanotubes

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