Substantially Improved Na-Ion Storage Capability by Nanostructured Organic–Inorganic Polyaniline-TiO₂ Composite Electrodes

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ABSTRACT: Developing sodium (Na)-ion batteries is highly appealing because they offer the potential to be made from raw materials, which hold the promise to be less expensive, less toxic, and at the same time more abundant compared to state-of-the-art lithium (Li)-ion batteries. In this work, the Na-ion storage capability of nanostructured organic–inorganic polyaniline (PANI) titanium dioxide (TiO₂) composite electrodes is studied. Self-organized, carbon-coated, and oxygen-deficient anatase TiO₂-x-C nanotubes (NTs) are fabricated by a facile one-step anodic oxidation process followed by annealing at high temperatures in an argon–acetylene mixture. Subsequent electropolymerization of a thin film of PANI results in the fabrication of highly conductive and well-ordered, nanostructured organic–inorganic polyaniline-TiO₂ composite electrodes. As a result, the PANI-coated TiO₂-x-C NT composite electrodes exhibit higher Na storage capacities, significantly better capacity retention, advanced rate capability, and better Coulombic efficiencies compared to PANI-coated Ti metal and uncoated TiO₂-x-C NTs for all current rates (C-rates) investigated.

KEYWORDS: Na ion, polyaniline, nanotubes, titanium dioxide, batteries

INTRODUCTION

Over the last 30 years, the demand for lithium-ion batteries (LIBs) for powering a variety of applications, from handheld consumer electronics to power-demanding electric vehicles, has been constantly growing.¹ Most LIBs today employ transition-metal oxides, mainly LiCoO₂ or LiFePO₄ as cathode-active materials, which, despite their apparent success, pose severe concerns for future large-scale energy storage. They are toxic, lack sustainability, and are related to a high carbon footprint upon production and subsequent recycling.² In combination with potential shortage in supply and subsequent increase in the price of Li, research on sodium-ion batteries (SIBs) has rapidly gained momentum, as corroborated by a strong increase in the number of publications related to SIBs within the last 5–10 years.³,⁴

Organic electrode materials are interesting candidates for next-generation environmentally benign battery materials, since they are less toxic, less limited, and can easily be recycled compared to commonly employed transition-metal oxides like LiCoO₂ or LiFePO₄. In addition, organic electrode materials are expected to require less energy to be produced and consequently lower the battery-associated carbon footprint.⁵–⁷ Organic p-type polymers that contain moieties, which can be reversibly reduced or oxidized, are particularly promising and are typically employed as cathode materials.⁸–¹⁰ Most p-type polymers though possess limited electronic conductivity and are therefore prone to slow electrode kinetics and subsequent limited rate capabilities. Subsequently high cycling stabilities are challenging to achieve due to deterioration processes of the electrode material itself or of side reactions in combination with the electrolyte.¹¹

Polyaniline (PANI) represents a special case of conjugated polymers that can be doped by acid–base chemistry. In PANI, the transition from an insulator to a metal-like organic conductor occurs through a protonation-induced change in the π-electron system. A protonation via acid–base chemistry allows an internal redox reaction and thereby the transformation from “emeraldine base” with semiconductor properties to the metal-like “emeraldine salt” form of polyaniline.¹² MacDiarmid and his colleagues showed already in 1987 that it is possible to construct a rechargeable LIB employing the
emeraldine base form of PANI as the cathode. Their rechargeable LIB showed already very promising characteristics such as a capacity around 148 mAh g\(^{-1}\) and an energy density of about 340 mWh g\(^{-1}\). More recently, PANI-coated nanostructures have also been investigated for their potential applications in supercapacitors.

The rate capabilities of organic polymers are intimately connected with the electron- and ion-transfer rates to the active redox units that can be reversibly reduced or oxidized. Therefore, issues regarding electrode kinetics may be circumvented by employing substrate nanomaterials in combination with carbon coating. The carbon coating adds the required electronic conductivity to different nanostructures, while at the same time their reduced size significantly decreases the diffusion path for both ions and electrons.

Figure 1. Top-view SEM images (secondary electrons (SEs)) of (a, c) initial TiO\(_2\)-x-C NTs and (b, d) final PANI-coated TiO\(_2\)-x-C NTs.

Figure 2. (a) Schematic illustration of the TiO\(_2\)-x-C NT array and a possible mechanism for the electropolymerization of aniline. (b) Cyclic voltammogram (CV) of the potentiodynamic and (c) chronopotentiogram for the subsequent galvanostatic electropolymerization of aniline on TiO\(_2\)-x-C NTs from 1.2 to 0.0 V vs a normal hydrogen electrode (NHE) at a scan rate of 50 mV s\(^{-1}\) for 10 cycles and at a constant current of 0.1 mA cm\(^{-2}\) for 45 min. (d) Comparison of the CV response and (e) Nyquist plots of the initial TiO\(_2\)-x-C NTs (black) and PANI-coated TiO\(_2\)-x-C NTs (red) in a 0.35 M H\(_2\)SO\(_4\) aqueous electrolyte at open circuit voltage (OCV). Symbols denote the experimental data, and the dashed lines denote the corresponding best fit to the electrochemical equivalent circuit.
Titanium dioxide (TiO₂) forms highly ordered, self-organized TiO₂ nanotubes (NTs) by simple anodic oxidation of the substrate Ti metal using a fluoride-containing electrolyte. This facile, one-step method has been extensively investigated, and its mechanism is well characterized and understood. The aligned pore structure of the TiO₂ NTs supports conduction of electrons and ions in one dimension, while the thin NT walls significantly shorten the solid-state ion diffusion path. Additionally, TiO₂ NTs show a high tolerance toward structural changes. It has been shown that TiO₂ NTs are capable of reversibly accommodating variations in volume that may occur upon sodiation and desodiation cycling when they are capable of reversibly accommodating variations in volume that may occur upon sodiation and desodiation cycling when 

**RESULTS AND DISCUSSION**

Well-aligned TiO₂ nanotube arrays are grown in situ, directly on a Ti metal substrate by anodization using the prescribed method. Top-view scanning electron microscopic (SEM) images of TiO₂−x−C NTs before PANI deposition are shown in Figure 1. The SEM top view displays a homogeneous NT array for TiO₂−x−C NTs with top tube diameters of about 165 nm and top wall thicknesses of about 15 nm (Figure 1c). In this form, the carbon-coated anatase TiO₂−x−C NT offers an ideal template, characterized by its high active surface area, important to foster good adhesion of the PANI-coated layers to the subjacent NT surface with some granular structure on top. The electrodeposition of aniline on self-organized TiO₂ NTs is known to support the phase transition that occurs upon Li-ion intercalation and deintercalation in TiO₂. This enables a significantly better Li-ion battery performance compared to stoichiometric TiO₂, and as a consequence, the charge transfer increases due to lower ohmic drops at the Ti/TiO₂ interface. Furthermore, oxygen deficiency is known to support the phase transition that occurs upon Li-ion intercalation and deintercalation in TiO₂. This enables a slightly sloping line in the Nyquist plot (Figure 2e) with a well-conductive PANI coating in the emeraldine salt form has been formed. The low-frequency branch for pristine TiO₂−x−C NTs is characterized through a slightly sloping line indicating the development of a second time constant, typically observed for nanostructured electrodes, where the diffusion is, in one dimension, bounded by a large porous electrode with capacitive walls. Differently, for the PANI-coated TiO₂−x−C NTs, the low-frequency branch in the Nyquist plot develops in an almost vertical line, indicating a finite space diffusion behavior where a flooded porous layer is present, in our case the freshly formed PANI film, which is terminated by a blocking outer interface of the PANI/electrolyte boundary. This impedance response is expected for electrodes coated by a thin film of conducting polymer like PANI. Levi and Aurbach have thoroughly investigated the electrochemical behavior of thin-film polymer-coated electrodes for LIB applications. By applying the developed finite space model from Levi and Aurbach, with its corresponding electrochemical equivalent circuit and a slightly adopted restricted diffusion element (shown in the Supporting Information Figure S2), the equivalent circuit fits well the measured impedance data (compare the Supporting Information Figure S3 and Table S1). The electronic equivalent circuit consists of two interfaces for the PANI film/TiO₂−x−C NT
interface and the PANI film/solution interface. Since the impedance data is recorded at open circuit voltage (OCV), it is expected that electronic equilibrium occurs across the PANI film/TiO$_{2-x}$-C NT interface while simultaneously ionic equilibrium is established across the PANI film/solution interface. The two interfaces, modeled by $R/C$ ($R_{ct}$ of 4.16 Ω cm$^2$, $C_{dl}$ of 34.35 μF) and $R/CPE$ ($R_{ct}$ of 3.43 Ω cm$^2$, $C_{dl}$ of 0.75 μF) elements, are therefore placed in series to the modified Warburg element for adopted restricted diffusion. One additional $R$ element ($R_d$ of 24.10 Ω cm$^2$) is used, describing the electrolyte resistance that accounts for the impedance response at high frequencies. The deviation-related weighted sum of squares ($X^2/Z$) between the measured impedance response and the equivalent circuit fit for both the initial and final PANI-coated TiO$_{2-x}$-C NTs is low. The deviation-related weighted sum of squares ($X^2/Z$) values are given with $1.13 \times 10^{-3}$ and $0.97 \times 10^{-3}$, respectively, indicating that the equivalent circuit adequately describes the experimentally measured Nyquist plot. One has to point out also that for the initial TiO$_{2-x}$-C NTs without a PANI film present, the restricted diffusion element is not needed to fit the recorded impedance data. Additionally, the assumption of an
The magnification geometry is not altered by the electrodeposition of PANI. The PANI layer provides good coverage of the topmost tube surfaces. The value for the active surface area is obtained by a mathematical model, using the NT geometry analyzed via SEM imaging and additionally verified by the capacitive current contribution in the CV measurement. Values of 230 and 360 cm² were obtained, respectively, which are in reasonable agreement. This infers that the entire NT surface is electrochemically active toward PANI deposition, suggesting the complete coverage of the NT surface by PANI. In summary, SEM top-view and cross-section images in combination with the values obtained for the active surface area and mass increase upon PANI electropolymerization suggest that the outer and inner surfaces of the TiO₂−x-C NTs are coated with a 20–30 nm thin PANI film. The PANI percentage in the composite electrode material is determined by about 31% (compare the experimental part).

X-ray photoelectron spectroscopy (XPS) is a truly important tool allowing a quantitative analysis of the electrode materials and their corresponding redox states. Figure 4a depicts the survey XPS spectra of pristine and PANI-coated TiO₂−x-C NTs. The N 1s signal of the TiO₂−x-C NTs prior to PANI deposition is practically zero, while the Ti 2p, Ti 2s, and the O 1s signals, characteristic for TiO₂, are clearly visible. For the PANI-coated TiO₂−x-C NTs (Figure 4a), the Ti 2s and Ti 2p signals are absent, while a strong peak for the N 1s signal is measured, corroborating the deposition of PANI on the surface of the TiO₂−x-C NTs. High-resolution spectra measured at the Ti 2p, C 1s as well as N 1s regions are shown in Figure 4b–e. The atomic concentrations of the different elements present obtained from the high-resolution spectra are summarized in the Supporting Information Table S2.

The high-resolution C 1s spectra for the pristine TiO₂−x-C NTs (Figure 4e) reveal the presence of carbon deposited at the surface through a TiO₂/C ratio of about 6:1 ratio for pure PANI. In the properly
curve-fitted N 1s XPS core-level spectrum (Figure 4c), the proportion of the quinonoid imine (≡N=), benzenoid amine (−NH−), and positively charged nitrogen atoms (−N′) can be quantitatively segregated.42,43 These peak components have characteristic binding energies of 398.8, 400.5, and 402.3 eV, respectively, and show that around 7 atom % of the nitrogen (N) has been converted into protonated nitrogen species (N+).

Although the low signal intensity prevents a decent, quantitative analysis of the N’ species, from previous studies on the doping level of PANI, doping levels in this order may correspond to PANI with a specific conductivity of around 1−10 S cm−1.42,44 This is on the same order as reported conductivities for TiO2-x-C N Ts of 1−1000 S cm−1,45 supporting the good charge transfer observed in the impedance Nyquist plots after PANI electrodeposition (Figure 2e). The vibrational modes of the PANI film on top of the TiO2-x-C N Ts have been further probed by ex situ Raman (Figure S4) and attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy (Figure S5). All characteristic bond-stretching vibration modes of PANI are observed with these two complementary methods,24,46 further confirming the proper film formation. The most prominent Raman peaks are found at 1172 cm−1 (symmetric C−N stretching vibrations), 1338 cm−1 (C−H bending vibrations), 1376 cm−1 (C=N−H bending vibrations), and 1598 cm−1 (C=C ring stretching vibrations). Prominent infrared signals are measured at 1566 and 1481 cm−1, corresponding to the stretching modes of N = quinoid = N and N−benzene−N, respectively. Additional IR peaks are measured at 1295 cm−1 (C−N stretching in the quinoid unit) and 1236 cm−1 (C=N stretching in the benzenoid unit). The C−H in-plane bending vibrations are observed as a broad signal from 1200 to 950 cm−1 (centered around 1042 cm−1). A detailed evaluation of all of the characteristic vibrational modes measured is summarized in Table S3 in the Supporting Information.

Figure 5a shows the comparison of CV measurements for the PANI-coated Ti metal (dashed green), TiO2-x-C N Ts before PANI deposition (black), and PANI-coated TiO2-x-C N Ts (red) at a scan rate of 10 mV s−1. The CV measurements of TiO2-x-C N Ts do not show any distinct reduction or oxidation peaks that can be correlated toward reversible intercalation of Na ions into TiO2−x-C within the given potential range 2.0−4.0 V (Figure 5a). While TiO2 N Ts have been demonstrated to serve as good model electrodes for studying LIBs,57−59 the exact Na-ion storage mechanism in TiO2 N Ts is still controversially discussed and, up to now, not fully understood.24,30,51 Previous studies revealed that the measured current response upon voltage change is characterized by a simultaneous capacitive and insertion contribution.24 The Na-ion insertion part takes place only well below 2 V (i.e., at ~0.7/0.9 V at a scan rate of 10 mV s−1 compare the Supporting Information Figure S6). The Na-ion insertion at low potentials is known to represent the reversible storage of Na ions in the active material structure. This is followed by reduction of Ti4+ (sodiation) and vice versa by oxidation of Ti3+ (desodiation).52 Therefore, within the given potential range 2.0−4.0 V, TiO2-x-C N Ts can be regarded as an inactive but important support material, offering an aligned, homogeneous pore structure; one-dimensional electronic and ionic conduction; and short solid-state Na-ion diffusion pathways accompanied by a high tolerance regarding structural alterations, and are consequently well qualified as support materials for nanostructured organic−inorganic polyaniline−TiO2 composite electrodes. The current response from the PANI-coated Ti metal (Figure 5a, dashed green line) is substantially smaller compared to the PANI-coated TiO2-x-C N Ts, which results mainly from the lower active surface area. When the current response is multiplied by a factor of 10 (Figure S7), a reductive peak is clearly visible but substantially shifted toward lower potentials (by about 410 mV−2.28 V compared to 2.69 V for PANI-coated TiO2-x−C N Ts). This may be explained by the unfavorable band positions of TiO2.

The polished Ti metal is covered by a thin oxide layer. The lower edge of the conduction and the upper edge of the valence band are situated at about −4 and −7.3 eV vs the vacuum energy level (about −0.5 and +2.8 V vs NHE) for TiO2.53,54 As it is expected that the band edges are pinned by surface states and will not be shifted upon external bias, electron injection into PANI is largely hindered, which is corroborated by the polarization overpotential of about 410 mV, measured in the CV current response.

Figure 5b shows the Nyquist plots for TiO2-x-C N Ts before PANI deposition (black) and PANI-coated TiO2-x-C N Ts (red) at OCP in the battery half-cell using Na-metal foil as the counter electrode and 1 M NaFSI/EC:DMC as the electrolyte system. The Nyquist plots of both electrodes are characterized by a high-frequency semicircle and a low-frequency branch. For the TiO2-x-C N Ts, the low-frequency branch in the Nyquist plot is dominated by a larger imaginary part and immediately develops in an almost vertical line. This characteristic is in accordance with minute currents on the CV at these potentials. For the PANI/TiO2-x−C N Ts, the low-frequency branch initially develops in a slightly sloping line and turns afterward to an almost vertical straight line. This impedance response is again characteristic for thin-film polymer-coated electrodes and can be fitted to the already previously introduced electronic equivalent circuit, depicted in Figure S2 and the comparison between the measured data and the best fit in Figure S3 (Nyquist and Bode plots). The values obtained are given by an Rs of 2.19 Ω cm2 (0.97 Ω), a C_ds of 11.3 μF, an R_1 of 133.58 Ω cm2 (59.06 Ω), a C_d of 3.53 μF, and an R_d of 9.90 Ω cm2 (4.38 Ω, Table S1). The deviation-related weighted sum of squares (X2/Z) between the measured impedance response and the equivalent circuit fit is low with 2.0 × 10−3.

Figure 5c,d shows the galvanostatic sodiation/desodiation cycling (GCPL) measurements of PANI-coated TiO2-x−C N Ts (red) and TiO2-x−C N Ts before PANI deposition (black) at different currents of 16, 80, 160, 800, and 1600 μA. When calculated to the amount of only the PANI material present (0.53 ± 0.15 mg) in the PANI-coated TiO2-x−C N Ts (red), these currents correspond to C-rates of about C/10, C/2, 1C, 5C, and 10C. The charge/discharge measurements of PANI-coated TiO2-x−C N Ts are described by the downward-sloping line featuring three distinct different regions: first, starting from 3.5 V to about 2.6 V, with a slightly downward-sloping trend; second, followed by a rapid decrease in potential from 2.6 V to about 2.2 V; and finally, from 2.2 V onward to 2.0 V again with a more gently downward-sloping trend. The GCPL measurements are congruent with the current-potential response recorded in the CV measurements (Figure 5a). When cycled between 3.5 and 2.0 V, with a current of 16 μA, the PANI-coated TiO2-x−C N Ts exhibit a specific capacity of 22.65 μAh cm−2 in the first and 21.05 μAh cm−2 in the second cycle. Even at 100 times higher constant current of 1600 μA, the PANI-coated TiO2-x−C N Ts still reveal a specific capacity of 6.27
According to the reaction shown in Figure 6, PANI in the electropolymerization is included (or 74 mAh g\(^{-1}\) capacities with only around 0.52 cm\(^{-2}\) constant current of 1600 μA, the specific capacity drops below 1 μAh cm\(^{-2}\). Flat electrodes of the PANI-coated Ti metal in comparison do not exhibit significant specific sodiation capacities with only around 0.52 μAh cm\(^{-2}\) in the first cycle and negligible specific capacities at higher current rates (Figure S8b).

The reaction of Na ions with PANI following initial electropolymerization may be described according to the three-step sequence shown in Figure 6a-c.\(^{13}\)

Figure 6. Schematic illustrations of the mechanism for the reversible reaction of Na ions with PANI (b, c), following the initial electropolymerization of PANI (a).

After electropolymerization in a 0.35 M H\(_2\)SO\(_4\) aqueous solution, the PANI is in the emeraldine salt form (Figure 6a), where the acid protonates the imine nitrogen located within the polymer backbone and thereby induces charge carriers. After the electrode is transferred into the battery half-cell, the NaFISI electrolyte will absorb the protons, transference PANI, to a large extent, from the emeraldine salt into the emeraldine base form (Figure 6b). This transformation is corroborated by an increase in the charge-transfer resistance in the corresponding Nyquist plot at OCV (Figure 5b). Subsequently, upon repeated sodiation and desodiation in the battery electrolyte, the PANI may transform from its emeraldine base form (Figure 6c) and back, respectively. According to the reaction shown in Figure 6, PANI in the emeraldine salt form has a theoretical specific capacity of about 148 mAh g\(^{-1}\) if the PANI weight only is considered and about 97 mAh g\(^{-1}\) when the weight of the HSO\(_4^\text{−}\) anion from the electropolymerization is included (or 74 mAh g\(^{-1}\) when the HSO\(_4^\text{−}\) anion is replaced by the heavier FSI\(^{−}\) anion in the battery electrolyte). A detailed analysis of the specific capacities and corresponding Coulombic efficiencies of our PANI-coated Ti metal, TiO\(_2\)-x-C NTs, and PANI-coated TiO\(_2\)-x-C NTs, as a function of cycle number and applied current, is shown in Figure 7.

Both systems, the TiO\(_2\)-x-C NTs (Figure 7, black) and PANI-coated TiO\(_2\)-x-C NTs (Figure 7, red), undergo an initial capacity decay at a low sodiation current of 16 μA (C/10 rate based on PANI mass loading). The cycling trend for both electrodes is characterized by a more gradual capacity decay obtained for the PANI-coated TiO\(_2\)-x-C NTs compared to the TiO\(_2\)-x-C NTs. The specific capacity for PANI-coated TiO\(_2\)-x-C NTs drops from initially 22.65 μAh cm\(^{-2}\) (96 ± 28 mAh g\(^{-1}\)) in the first cycle to about 15 μAh cm\(^{-2}\) after 10 galvanostatic sodiation/desodiation cycles at a current of 16 μA and tends to stabilize afterward, with 15.25 μAh cm\(^{-2}\) (65 ± 19 mAh g\(^{-1}\)) in the 15th cycle. This initial capacity loss amounts to about 32% of the electrodes’ first sodiation capacity. The specific gravimetric capacity of 65 ± 19 mAh g\(^{-1}\) in the 15th cycle still amounts to about 88% of the theoretical maximum capacity of PANI, including the FSI anion. In comparison to the PANI-coated TiO\(_2\)-x-C NTs, the specific capacity for TiO\(_2\)-x-C NTs drops from initially 9.57 μAh cm\(^{-2}\) in the first cycle to 3.12 μAh cm\(^{-2}\) after 15 galvanostatic sodiation/desodiation cycles at a current of 16 μA, corresponding to a capacity loss of about 67% of the electrodes’ initial capacity. If we further take into account that the absolute capacity decrease for PANI-coated TiO\(_2\)-x-C NTs is 7.4 μAh cm\(^{-2}\) compared to 6.45 μAh cm\(^{-2}\) for the pure TiO\(_2\)-x-C NTs, then only 0.95 μAh cm\(^{-2}\) or 4.2% of the initial capacity decrease is related to the PANI material itself and the rest must be attributed to electrolyte decomposition and/or side reactions. This is consistent with galvanostatic cycling measurements of flat, PANI-coated Ti metal electrodes (Figure 7, green) where the initial capacity decay is on the same order (about 0.4 μAh cm\(^{-2}\)). The corresponding Coulombic efficiency of the galvanostatic sodiation desodiation cycling is shown in Figure 7b. PANI-coated TiO\(_2\)-x-C NTs exhibit higher Coulombic efficiencies compared to PANI-coated Ti metal and uncoated TiO\(_2\)-x-C NTs for all C-rates. In general, the Coulombic efficiencies are almost 100% at elevated C-rates, while at very slow rates (C/10), Coulombic efficiencies below 100% are mainly related to potential electrolyte decomposition and/or side reactions. Nyquist impedance plots and corresponding ex situ ATR–FTIR measurements after the galvanostatic cycling measurements shown in Figure 7 also confirm the excellent PANI film integrity (Figures S5c and S9) on the TiO\(_2\)-x-C NT support.
Although an extensive comparison study of the available literature regarding polymer cathode materials for Na-ion batteries, including specific material and battery-related properties, is beyond the scope of this research article, the performance of PANI-coated TiO$_2$-x-C NTs is comparable to other, recent reports on advanced polymer composite cathode materials. A summary of the most relevant literature, comparing the operation voltages vs specific gravimetric capacities after 100 charge/discharge cycles of different Na-ion organic and organic composite electrodes, is shown in Figure 8.\textsuperscript{55-63} For example, a poly(N-vinylcarbazole) polymer electrode has been reported as a dual-intercalation cathode for Na-ion batteries, which demonstrated specific discharge capacities of about 110 mAh g\textsuperscript{-1} for 100 cycles.\textsuperscript{65} An aluminum-coordinated poly(tetrahydroxybenzoquinone) electrode demonstrated a reversible capacity of 113 mAh g\textsuperscript{-1} and stable cycle performance over 100 cycles.\textsuperscript{56} Graphene-wrapped poly 2,5-dihydroxy-1,4-benzoquinone-3,6-methylene nanocomposites characterized by three-dimensional nanoflower-like structures recently showed stable specific capacities of about 121 mAh g\textsuperscript{-1} after 100 cycles.\textsuperscript{67} Na$_2$FePO$_4$F and Na$_2$V$_2$(PO$_4$)$_3$ encircled by a nanolayer composed of poly(3,4 ethylenedioxythiophene) have been reported with stable cycling performance (over 500 cycles) and specific capacities of 123.1 and 112.4 mAh g\textsuperscript{-1}, respectively.\textsuperscript{58,59} A good review article, summarizing the most recent progress in advanced polymer cathode materials and comparing the performance of different organic polymers as cathode materials for Na-ion batteries, is that by Zhao et al.\textsuperscript{64}

To further investigate potential changes in the NT crystal structure during galvanostatic cycling, ex situ X-ray diffraction (XRD) patterns regarding the pristine and PANI-coated TiO$_2$-x-C NTs are measured before and after the GCPL measurements and are shown in Figure 7. The XRD patterns for both the TiO$_2$-x-C NTs and PANI-coated TiO$_2$-x-C NTs are summarized by intense peaks at $2\theta$ of $\sim$25, 38, 48, 54, and 56$^\circ$ corresponding to (101), (004), (200), (105), and (211) of the anatase structure (Figure 9).\textsuperscript{47,65}

XRD measurements show that after repeated electrochemical sodiation between 3.5 and 2.0 V vs. Li/Li$^+$, no Na-related new phase is detected in the XRD patterns. Therefore, TiO$_2$-x-C NTs maintain their initial anatase structure, which suggests that the sodiation process for PANI-coated TiO$_2$-x-C NTs does not change the crystallographic structure of the subjacent NTs significantly. This further corroborates that Na-ion storage does not happen in the TiO$_2$-x-C NT host structure within the given potential range, since previous studies by our group and others have clearly shown that Na-ion storage in anatase TiO$_2$ is followed by a continuous intensity decrease of the anatase diffraction peaks upon sodiation.\textsuperscript{55,52}

**CONCLUSIONS**

The good cycling performance of PANI-coated TiO$_2$-x-C NTs (Figure 7), together with its well-maintained anatase NT structure after long-term galvanostatic cycling (Figure 9), proves that the carbon-coated anatase TiO$_2$-x-C NT array provides an ideal nanostructured solid template for PANI deposition. The large available surface area of the NT array also appears to be favorable for good adhesion regarding the PANI coating to the supporting substrate, showing little material dissolution upon repeated sodiation/desodiation measurements. In summary, PANI-coated TiO$_2$-x-C NTs exhibit higher Na storage capacities, better capacity retention, superior rate capabilities, and higher Coulombic efficiencies compared to PANI-coated Ti metal and uncoated TiO$_2$-x-C NTs for all C-rates. As for other cathode and/or anode materials, PANI-coated TiO$_2$-x-C NTs require, in the as-prepared state, presodiation (or prelithiation) before it can be used in a full-cell battery.\textsuperscript{66-68} However, its half-cell battery performance will prove to be a good alternative to common cathode materials employed for LIBs if high electron- and ion-transfer rates can be realized, for example, by employing substrate nanomaterials like TiO$_2$-x-C NTs where nanostructures are coated by a thin layer of conductive carbon. PANI on TiO$_2$-x-C NTs may therefore present a cost-effective, abundant, and environmentally benign cathode material for future rechargeable SIBs.
Synthesis of the TiO$_2$−x−C NTs has been performed by a slightly modified procedure reported previously. A summary of the synthesis procedure and a photograph of the amorphous TiO$_2$ NT samples before and anatase TiO$_2$−x−C NTs samples after carbon thermal annealing (Figure S11a,b) can be found in the Supporting Information.

Electropolymerization of PANI onto TiO$_2$−x−C NTs and Ti metal discs has been carried out in an aqueous solution containing 0.4 M aniline (>99.5%, Sigma-Aldrich, used as received) in 0.35 M H$_2$SO$_4$ (Merck, used as received), employing a three-electrode system with TiO$_2$−x−C NTs as the working electrode, a Pt plate as the counter electrode, and a mercury-mercurous sulfate (Hg/Hg$_2$SO$_4$) reference electrode. Electropolymerization of PANI is performed in a two-step process, starting with 10 cycles of potentiodynamic polymerization between 1.2 V vs NHE and 0.0 V vs NHE at 50 mV s$^{-1}$ and followed by a constant current polymerization at 0.1 mA cm$^{-2}$ for 45 min. A photograph of a pristine polished Ti metal disk, Ti metal disk after 10 cycles of potentiodynamic polymerization, and after further constant current polymerization is shown in the Supporting Information, Figure S11c.

For defining the TiO$_2$−x−C NT volume, their morphology has been evaluated by analyzing the SEM images (average tube length: 4.0 ± 0.3 μm; 165 ± 12 nm average pore diameter at the top, and a solid hemisphere at the bottom of each nanotube 225 ± 30 nm; Figure S10). The total volume of the TiO$_2$−x−C NTs is calculated according to the NT morphology, given by a cone-shaped NT configuration. Each NT is closed by a solid hemisphere at the bottom. With this approach, the TiO$_2$−x−C volume has been calculated to approx. 0.445 mm$^3$. The resultant active mass of the TiO$_2$−x−C NTs on the electrode has been calculated by multiplying the TiO$_2$−x−C volume by the density of anatase (3.84 g cm$^{-3}$) to 1708.7 μg. Therefore, the PANI percentage in the composite is about 31%. Battery half-cell measurements were carried out using a commercially available battery cell (ECC-Ref Cell from EL-Cell) in a three-electrode configuration. Details are given in the Supporting Information. The mass specific capacity in Figure 7 is determined by dividing the measured capacity in mAh by the active electrode material mass, and hence the mass of PANI, being 0.53 ± 0.15 mg (the areal capacity has been determined accordingly, by dividing the measured capacity in mAh by the electrodes’ geometrically exposed area of 2.26 cm$^2$).

SEM imaging was performed with a JEOL JSM-7601F field emission electron microscope. Secondary electrons were detected by an in-lens detector to characterize the surface and cross-sectional morphology prior to and also after PANI deposition. An acceleration voltage of 10 kV was chosen. Cross sections were simply prepared by scratching the sample and imaging the fraction of the NTs.

XPS (Thermo MultiLab 2000 spectrometer equipped with a hemispherical energy analyzer) has been utilized to examine the chemical composition of the PANI-coated TiO$_2$−x−C NTs. Additionally, XPS was employed to determine the oxidation states of the individual material components prior to and after PANI electrodeposition. The XPS is measured using a take-off angle of zero with respect to the surface normal. Furthermore, a monochromated Al Kα X-ray source (1486.6 eV) was used. The step size for the high-resolution spectra of the Ti 2p, C 1s, and N 1s regions was 0.02 eV with a dwell time of 0.2 s. The quantitative analysis of the XPS measurements was performed with CasaXPS software (version 2.3.16). A charging correction has been employed for all spectra by shifting the spectra with respect to the location of the Ti(IV) 2p$_{3/2}$ peak of TiO$_2$ at 458.6 eV.

Infrared spectra (diamond ATR, PIKE GaldiATR, Bruker Vertex 70) were measured in the range of 4000–400 cm$^{-1}$ with a resolution of 2 cm$^{-1}$ (32 scans per spectrum). Raman spectra (Bruker BRAVO) were recorded with a resolution of 2 cm$^{-1}$ from 160 to 3200 cm$^{-1}$. The spectrometer suppresses the fluorescence by the patented SSE technology (patent number: US857057B1) and has two temperature-shifted excitation lasers (DuoLaser) with wavelengths of probably 785 and 1064 nm (observed by the manufacturer). IR and Raman spectra were processed in OPUS spectroscopic software.

X-ray powder diffraction (XRD) analysis was performed on a Siemens D5000 X-ray diffractometer, with Cu Kα emission. Diffractograms were measured between 15 and 75° (2θ) and a step size of 0.02° (2θ). The acquisition time for each step was 1 s.
The manuscript was written through contributions of all authors. The authors declare no competing financial interest.

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