Pipe-Wire TiO$_2$–Sn@Carbon Nanofibers Paper Anodes for Lithium and Sodium Ion Batteries

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Supporting Information

ABSTRACT: Metallic tin has been considered as one of the most promising anode materials both for lithium (LIBs) and sodium ion battery (NIBs) because of its high theoretical capacity and an appropriate low discharge potential. However, Sn anodes suffer from a rapid capacity fading during cycling due to pulverization induced by severe volume changes. Here we innovatively synthesized pipe-wire TiO$_2$–Sn@carbon nanofibers (TiO$_2$–Sn@CNFs) via electrospinning and atomic layer deposition to suppress pulverization-induced capacity decay. In pipe-wire TiO$_2$–Sn@CNFs paper, nano-Sn is uniformly dispersed in carbon nanofibers, which not only act as a buffer material to prevent pulverization, but also serve as a conductive matrix. In addition, TiO$_2$ pipe as the protection shell outside of Sn@carbon nanofibers can restrain the volume variation to prevent Sn from aggregation and pulverization during cycling, thus increasing the Coulombic efficiency. The pipe-wire TiO$_2$–Sn@CNFs show excellent electrochemical performance as anodes for both LIBs and NIBs. It exhibits a high and stable capacity of 643 mA h/g at 200 mA/g after 1100 cycles in LIBs and 413 mA h/g at 100 mA/g after 400 cycles in NIBs. These results would shed light on the practical application of Sn-based materials as a high capacity electrode with good cycling stability for next-generation LIBs and NIBs.

KEYWORDS: Pipe-wire structure, TiO$_2$–Sn@carbon nanofibers, binder-free flexible anode, electrospinning, lithium and sodium ion batteries

However, the aggregation of Sn nanoparticles (NPs) still limits the cycle stability. Extensive effort has been conducted to mitigate this challenge. For example, a nanostructured Sn/C composite provides a high capacity of 500 mA h/g for more than 100 cycles where the carbon matrix acts as a buffer to accommodate the volume change and prevent Sn particle aggregation. We demonstrated that nano-Sn dispersed evenly in a carbon matrix could retain a high capacity of 710 mA h/g in 130th cycle. However, the high surface of nano-Sn/C composites also increases the irreversible capacity, reducing the initial Coulombic efficiency. A rigid shell over nano-Sn/C composite can significantly enhance both Coulombic efficiency and cycling stability. It has been reported that TiO$_2$ coating on active materials can significantly enhance the cycling stability and Coulombic efficiency for sulfur and other high capacity electrode materials.

Herein, pipe-wire TiO$_2$–Sn@CNFs were successfully synthesized via electrospinning and atomic layer deposition (ALD), where the nano-Sn was uniformly dispersed in carbon.
nanoﬁbers to buffer the stress/strain and maintain 3D conductive matrix. Depositing thin TiO₂ film on the Sn@carbon nanoﬁbers (Sn@CNFs) surface using ALD techniques can reduce its surface to electrolyte, thus enhancing the Coulombic efﬁciency. In addition, the TiO₂ pipe can also reduce the Sn aggregation and restrain volume variation to prevent Sn from pulverization during cycling. Thus, pipe-wire TiO₂−Sn@CNFs show excellent electrochemical performance as an anode material both in LIBs and NIBs.

The synthesis process of pipe-wire TiO₂−Sn@CNFs is schematically shown in Figure 1a. First, Sn@CNFs was synthesized by electrospinning. The nanoﬁbers showed a narrow diameter distribution and lengths up to several millimeters (Figure 1b). The Sn@CNFs was then coated by a thin layer of TiO₂ via ALD, producing core−shell TiO₂−Sn@CNFs (Figure 1c). The following calcination of these core−shell nanoﬁbers at 400 °C for 1 h in air led to the partial oxidation and constriction of carbon nanoﬁbers, forming pipe-wire TiO₂−Sn@CNFs with an average diameter of around 160−220 nm (Figure 1d). In addition, the ﬂexibility of pipe-wire TiO₂−Sn@CNFs paper was tested by bending experiment (Figure 1e−g). The paper can still keep intact and ﬂexible even with a 180° bend, showing excellent ﬂexibility.

The 1D pipe-wire structure and uniform morphology can be conﬁrmed by transmission electron microscopy images (Figure 2a), where TiO₂ pipe about 15 nm thick is coated on the Sn@CNFs, leaving some space to relieve the volume expansion. From the high resolution TEM image (Figure 2b), the (200) crystal facet of metallic Sn with space of 0.29 nm can be seen. Sn nanoparticle is dispersed evenly in the carbon matrix. The faint polycrystalline rings in the selected area electron diffraction (SAED) pattern (inset in Figure 2b) further conﬁrm the presence of crystalline Sn. Energy-dispersive spectroscopy (EDS) elemental mapping images (Figure 2c−f) well match results shown in the Figure 2a, demonstrating that TiO₂ are uniformly distributed along the axial direction of Sn@CNFs. Metallic tin are evenly embedded in the carbon, and a tunnel can be easily observed. Pipe-wire TiO₂−Sn@CNFs with different TiO₂ layer thicknesses (5, 15, and 25 nm) are shown in Figure S1. Compared to intact and uniform morphology of pipe-wire TiO₂−Sn@CNFs with 15 nm TiO₂ layer, a TiO₂ layer of 5 nm thickness split and crack after annealing, while a TiO₂ layer of 25 nm thickness fractures and forms TiO₂ particles, attributed to high stress and an excess of TiO₂.

X-ray diffraction (XRD) pattern is measured and shown in Figure 3a. All peaks can be indexed to metallic Sn (tetragonal phase, JCPDS Card No. 04-0673) and TiO₂ (anatase phase, JCPDS Card No. 21-1272). Graphite peaks are completely absent, suggesting the carbon exists in amorphous due to the low calcination temperature. The components in pipe-wire TiO₂−Sn@CNFs were conﬁrmed by the EDS analysis (Figure S2). The Cu peaks are from the copper net, which is used in EDS characterization. To quantify the amount of components in the composites, thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) analysis of pipe-wire TiO₂−Sn@CNFs were carried out in air (Figure 3b). A mass loss of about 2.68% observed below 150 °C on the TGA curve.
may correspond to the loss of free water, physically adsorbed water. The weight addition from 150 to 450 °C could be attributed to the oxidation of metallic tin to tin dioxide.\textsuperscript{8} The composites show an obvious weight loss of 16.24% between

Figure 3. (a) XRD pattern of pipe-wire TiO$_2$–Sn@CNFs and (b) TGA (black line) and DTG (blue line) curves of pipe-wire TiO$_2$–Sn@CNFs in air at a rate of 10 °C/min.

Figure 4. (a) Survey XPS spectra of pipe-wire TiO$_2$–Sn@CNFs. (b–d) High-resolution XPS spectra of C, Sn 3d, and Ti 2p, respectively.

Figure 5. Cyclic voltammetry curves of pipe-wire TiO$_2$–Sn@CNFs in (a) LIBs and (b) NIBs at a scan rate of 0.2 mV/s. Galvanostatic charge/discharge profiles of pipe-wire TiO$_2$–Sn@CNFs in (c) LIBs and (d) NIBs at a current density of 100 mA/g.
cells by directly using pipe-wire TiO\textsubscript{2} CNFs, which agrees well with the XRD results. The electrochemical performance was evaluated in coin-type cells by directly using pipe-wire TiO\textsubscript{2}−Sn@CNFs paper as a working electrode and Li or Na metal as the counter-electrode.

450 and 620 °C, which is ascribed to the oxidation process of carbon. The final product with a retention rate of 92.1% is a mixture of SnO\textsubscript{2} and TiO\textsubscript{2}. According to the transformation of metallic tin to SnO\textsubscript{2} with a weight change of 127%, the weight ratio of metallic tin in composites can be estimated to be 40.8%.

To determine the chemical composition of pipe-wire TiO\textsubscript{2}−Sn@CNFs and to identify the chemical status of the C element in the samples, X-ray photoelectron spectroscopy (XPS) measurements were carried out using an ESCALAB 250 in the region of 0−1351.2 eV (Figure 4). Figure 4a exhibits the XPS survey spectra of pipe-wire TiO\textsubscript{2}−Sn@CNFs and peaks of Sn 3d, Ti 2p, O 1s, and C 1s can be clearly observed. Figure 4b shows a high-resolution C 1s XPS spectra of pipe-wire TiO\textsubscript{2}−Sn@CNFs. Three peaks which correspond to carbon atoms in different functional groups appear clearly. The main peak centered at 284.8 eV corresponds to extensively delocalized sp\textsubscript{2} hybridized carbon atoms, and independent peaks with binding energies of 286.2, and 288.9 eV can be assigned to carbon hybridized sp\textsubscript{2} and sp\textsubscript{3} hybridized carbon atoms, respectively. The high-resolution Sn 3d XPS spectra of pipe-wire TiO\textsubscript{2}−Sn@CNFs exhibit two peaks at 486.6 and 495.1 eV, corresponding to Sn 3d\textsubscript{5/2} and Sn 3d\textsubscript{3/2} spin orbit peaks of metallic tin (Figure 4c). As for the high-resolution Ti 2p (Figure 4d), two peaks at 464.5 and 458.8 eV are attributed to Ti 2p\textsubscript{1/2} and Ti 2p\textsubscript{3/2}, respectively. The XPS results further confirm the coexistence of metallic tin and TiO\textsubscript{2} in pipe-wire TiO\textsubscript{2}−Sn@CNFs, which agrees well with the XRD results.

The electrochemical performance was evaluated in coin-type cells by directly using pipe-wire TiO\textsubscript{2}−Sn@CNFs paper as a working electrode and Li or Na metal as the counter-electrode. The binders, conductive additives, and Cu current collector are all free, which can reduce the electrode weight, thus increasing the energy/power densities of the cell. Figure 5a shows cyclic voltammograms (CVs) of pipe-wire TiO\textsubscript{2}−Sn@CNFs electrode in the first, second, and 10th scans at a scan rate of 0.2 mV/s between 0.01 and 3 V versus Li/Li\textsuperscript{+}. The first cathodic scan shows a reversible peak at 1.52 V and a wide irreversible current peak in the range of 0.6−0.9 V. The peak at 1.52 V is due to the Li intercalation, which is in accordance with that reported for anatase TiO\textsubscript{2}.\textsuperscript{31} The irreversible peak in 0.9−0.6 V corresponds to the decomposition of electrolyte to form solid-electrolyte interface (SEI) films, resulting in irreversible capacity loss.\textsuperscript{30} The further cathodic scan of Sn anodes presents three reversible peaks at 0.27, 0.48, and 0.62 V, which are related to the lithium reactions between Sn and Li (Figure 5a). In the anodic scan, anodic peaks at 0.41, 0.72, 0.81, and 0.86 V are attributed to the delithiation of Li\textsubscript{2}Sn (Figure 5a). These delithiation potentials are in good agreement with the calculated potential plateaus by Ceder’s group if overpotential is considered due to slow Li diffusion in Sn during the CV scan.\textsuperscript{31} The sharp peak at 2.17 V is attributed to Li-ion extraction from anatase TiO\textsubscript{2}. The two-phase reaction occurs during electrochemical Li\textsuperscript{+} insertion/extraction according to the following reaction:

\[ \text{TiO}_2 + x\text{Li}^+ + xe^- = \text{Li}_x\text{TiO}_2 \]

Small deviations in the peak positions are noticed in the subsequent cycles, which can be contributed to the structural rearrangement in the TiO\textsubscript{2} crystal lattice. Similar to cyclic voltammograms of pipe-wire TiO\textsubscript{2}−Sn@CNFs in LIBs, wide peaks in the range of 0.7−1.0 V are observed in the first anode scan of pipe-wire TiO\textsubscript{2}−Sn@CNFs in NIBs, which are also attributed to the desodiation of partially amorphous Na\textsubscript{3}Sn (Figure 5b).\textsuperscript{32} In the first cathodic scan, a wide irreversible current peak from 0.1 to 0.8 V versus Na/Na\textsuperscript{+} corresponds to the formation of SEI film and NaN\textsubscript{3}. The peaks located at 0.2 and 0.55 V in the subsequent cathodic scans are assigned to the sodiation process.\textsuperscript{33} Different from TiO\textsubscript{2}−Sn@CNFs in LIBs, no sodiation/desodiation peaks of TiO\textsubscript{2} at high potential were observed, demonstrating that TiO\textsubscript{2} is inactive for Na ions.\textsuperscript{34}
wire TiO$_2$–Sn@CNFs for LIBs are 1644 and 1099 mA h/g, corresponding to a Coulombic efficiency (CE) of 66.8%. The high CE can be attributed to embedment of Sn NPs in CNFs, which greatly avoids detrimental reactions between Sn nanoparticles and electrolyte. The high capacity can be derived from the synergistic effect of nanoscale Sn grain, pipe-wire structure, and close interaction of pipe-wire TiO$_2$ nanoparticles and electrolyte. The high capacity can be derived from the formation of SEI films. The ion extraction voltages for Na are lower than that for Li, implying that Sn is more suitable as anodes for NIBs. The charge capacity of pipe-wire TiO$_2$–Sn@CNFs anodes in NIBs is 610 mA h/g, which is smaller than that (1099 mA h/g) in LIBs. The lower capacity of pipe-wire TiO$_2$–Sn@CNFs anodes in NIBs than LIBs is mainly due to poor electrochemical sodiation/desodiation kinetics. In addition, Sn has a different theoretical capacity in NIBs and LIBs because of its different alloy composition with Na and Li.

The cycling performance of pipe-wire TiO$_2$–Sn@CNFs electrodes in LIBs is measured at the current density of 100 mA/g. As illustrated in Figure 6a, pipe-wire TiO$_2$–Sn@CNFs electrodes show a stable cycling performance beyond initial several cycles. The capacity fading in the first several cycles may be derived from the formation of SEI film and partial irreversible insertion of Li$^+$ into carbon nanofibers. After 200 cycles, the electrode can still deliver a discharge capacity of 831 mA h/g. A prolonged cycle life of pure CNFs, Sn@CNFs, core–shell TiO$_2$–Sn@CNFs, and pipe-wire TiO$_2$–Sn@CNFs at 200 mA/g in Li ion battery are depicted in Figure 6b. After 1100 cycles, pipe-wire TiO$_2$–Sn@CNFs electrodes can still retain 643 mA h/g in capacity, superior to core–shell TiO$_2$–Sn@CNFs (544 mA h/g after 44 cycles), Sn@CNFs (484 mA h/g after 370 cycles), and pure CNFs (142 mA h/g after 500 cycles), highlighting pipe-wire structure of TiO$_2$–Sn@CNFs contributing to long cycle life and high specific capacity. The slightly increasing in capacity of pipe-wire TiO$_2$–Sn@CNFs from 200 to 350 cycles could be attributed to the elevating temperature and an activation process. The pipe-wire TiO$_2$–Sn@CNFs show the best electrochemical performance in Sn/C composites reported previously. Also, it should be pointed out that a high Coulombic efficiency of >99% is achieved after several cycles, indicating high reversibility of pipe-wire TiO$_2$–Sn@CNFs.

The cycle stability of pipe-wire TiO$_2$–Sn@CNFs in NIBs was also evaluated by galvanostatically discharging and charging at 100 mA/g for 400 cycles (Figure 6c). The reversible capacities are 490 and 413 mA h/g at the end of 10 and 400 cycles, respectively, with about a 15.7% capacity decrease over 400 cycles. Meanwhile, capacities of core–shell TiO$_2$–Sn@CNFs, Sn@CNFs and pure CNFs are 285 (after 100 cycles), 255 (after 50 cycles), and 142 mA h/g (after 200 cycles), much lower than that of pipe-wire TiO$_2$–Sn@CNFs. Remarkably, the Coulombic efficiency approaches 100% (>99.9%), implying that superior cycle stability of pipe-wire TiO$_2$–Sn@CNFs electrode for reverse Na$^+$ storage was highly repeatable. Compared to core–shell TiO$_2$–Sn@CNFs and Sn@CNFs, pipe-wire TiO$_2$–Sn@CNFs electrodes show more stable cycle life in NIBs than LIBs, ascribed to the formation of amorphous Na$_x$Sn phase during charge/discharge. Therefore, Sn nanoparticles experience well-proportioned volume expansion in NIBs, while Li$_x$Sn nanocrystals undergo unidirectional volume variation in LIBs, causing faster capacity decay.

To further confirm the importance of TiO$_2$ pipe, pipe-wire TiO$_2$–Sn@CNFs with 5, 15, and 25 nm TiO$_2$ pipe were galvanostatically tested at 200 mA/g in LIBs. As shown in Figure 6d, three electrodes display a similar trend. Meanwhile, pipe-wire TiO$_2$–Sn@CNFs electrodes with a 15 nm TiO$_2$ pipe obtain a higher capacity than those with 5 and 25 nm TiO$_2$ pipe, which could be attributed to uniform and stable TiO$_2$ pipe with 15 nm thickness in accordance with the XRD pattern of TiO$_2$–Sn@CNFs.

Figure 6e depicts the rate capability and cycling performance of the as-synthesized pipe-wire TiO$_2$–Sn@CNFs in LIBs. At a low current density of 100 mA/g, pipe-wire TiO$_2$–Sn@CNFs delivers a reversible capacity as high as 1020 mA h/g. As the current rate increased gradually to 200, 400, 600, 800, and 1000 mA/g, the corresponding reversible capacities reach 780, 570, 430, 360, and 280 mA h/g, respectively. The capacity recovers to 1010 mA h/g after the current density is reduced to 100 mA/g and maintains 950 mA h/g after 100 cycles.

The detailed reaction kinetics of pipe-wire TiO$_2$–Sn@CNFs in LIBs and NIBs were investigated before and after 200 cycles using electrochemical impedance spectroscopy (EIS) in the frequency range of 100 kHz to 0.01 Hz at 10 mV amplitude (Figure 6f). The equivalent circuit model of the studied system is inset in Figure 6f. The impedance spectra are composed of one depressed semicircle at high frequencies corresponding to the interfacial resistance including charge transfer and SEI resistance, and a straight sloping line at an approximate 45° angle to the real axis related to the Li$^+$-diffusion process within...
the bulk of the electrode material. As shown in Figure 6f, interfacial resistance $R_i + R_s$ only slightly increases after 200 cycles both in LIBs and NIBs, indicating superior cycling stability. $R_i$ represents the resistance of solid-electrolyte interphase, while $R_s$ represents the resistance of charge transfer. The fast ion-transfer kinetics of pipe-wire TiO$_2$–Sn@CNFs electrodes benefit from Sn nanograins homogeneously distributed in conductive carbon nanofibers, which could facilitate Li$^+$ and Na$^+$ diffusion. In addition, pipe-wire TiO$_2$–Sn@CNFs anodes experience larger interface impedance in LIBs than NIBs, which could be attributed to either higher SEI film resistance or larger charge-transfer resistance, and is also an evidence that Sn is more suitable for NIBs.

The morphology changes of pipe-wire TiO$_2$–Sn@CNFs after 200 discharge/charge cycles at 100 mA/g in LIBs were investigated (Figure 7a–c). In comparison to the morphology of the fresh pipe-wire TiO$_2$–Sn@CNFs anode in Figure 1d, no obvious morphology change was observed after 200 cycles, indicating that pipe-wire structure of TiO$_2$–Sn@CNFs can effectively cope with the mechanical strain that is induced by the Li$^+$ intercalation/extraction, resulting in stable cycling performance. It can be clearly seen from Figure 7b that Sn@CNFs after 200 cycles become thicker compared to the fresh one (Figure 1b), while the overwhelming majority of TiO$_2$ pipe keep intact. Particles on the surface of TiO$_2$ pipe may originate from salt precipitation from residual electrolyte (Figure 7a, b). Meanwhile, Sn nanoparticles still keep evenly dispersed in CNFs without evident aggregation, revealing that CNFs can act as a good buffer material to prevent Sn aggregation (Figure 7c). Although the volume of Sn varies owing to mechanical stress with cycling, the pipe-wire structure provides sufficient room, and the TiO$_2$ pipe restricts the volume expansion, both of which contribute to excellent cycle life.

In summary, we have innovatively designed and fabricated a pipe-wire structure for high-capacity and electrochemically stable TiO$_2$–Sn@CNFs electrodes. The structure takes advantage of the high capacity of Sn, excellent electrochemical stability of TiO$_2$ and high electrical conductivity of carbon nanofibers together. The pipe-wire arrangement consists of Sn nanoparticles embedded in CNFs matrix completely protected by a thin, conformal, and self-supporting TiO$_2$ pipe. The rationally designed vacant space between TiO$_2$ pipe and Sn@CNFs allows for the expansion of Sn without deforming TiO$_2$ pipe or disrupting SEI on the surface. The pipe-wire TiO$_2$–Sn@CNFs anodes exhibit a high reversible capacity and stable cycling performance of 643 mA h/g at 200 mA/g after 1100 cycles in LIBs and 413 mA h/g at 100 mA/g after 400 cycles in NIBs. These results would shed light on the practical application of Sn@CNFs-based materials as a high-capacity electrode with good cycling stability for next-generation LIBs and NIBs.

[ASSOCIATED CONTENT]

2 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b01152.

Details of experimental methods, characterizations, electrochemistry, and additional figures (Figures S1–S2) (PDF)

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Notes
The authors declare no competing financial interest.

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