Robust SnO$_{2-x}$ Nanoparticle-Impregnated Carbon Nanofibers with Outstanding Electrochemical Performance for Advanced Sodium-Ion Batteries

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Abstract: The sluggish sodium reaction kinetics, unstable Sn/Na$_2$O interface, and large volume expansion are major obstacles that impede practical applications of SnO$_2$-based electrodes for sodium-ion batteries (SIBs). Herein, we report the crafting of homogeneously confined oxygen-vacancy-containing SnO$_{2-x}$/C composites that address the issues noted above for advanced SIBs. Notably, SnO$_{2-x}$/C composites can be readily exploited as the working electrode, without need for binders and conductive additives. In contrast to past work, SnO$_{2-x}$/C composites-based SIBs show remarkable electrochemical performance, offering high reversible capacity, ultralong cyclic stability, and excellent rate capability. A discharge capacity of 565 mAh g$^{-1}$ at 1 A g$^{-1}$ is retained after 2000 cycles.

The past few decades have witnessed substantial advances in the utilization of low-cost, renewable energy sources to meet the global demand. Sodium-ion batteries (SIBs) have developed rapidly as they have attractive attributes, such as decent energy density, excellent sustainability, and abundant, low-cost sodium resources.$^{[1,2]}$ The electrode materials with high discharge capacity, outstanding rate capability, and long cycle life are the key to high performance SIBs.$^{[3,4]}$ Recently, SnO$_2$ has garnered much attention because of its high abundance, large theoretical capacity and nontoxicity. However, the large volume expansion and low intrinsic conductivity greatly plague its practical applications.$^{[5,6]}$ The reactions between SnO$_2$ and Na can be described as follows [Eqs. (1)–(3)]:

\[ \text{SnO}_2 + 2\text{Na}^+ + 2\text{e}^- \rightarrow \text{Sn} + \text{Na}_2\text{O} \quad (1) \]
\[ \text{SnO} + 2\text{Na}^+ + 2\text{e}^- \rightarrow \text{Sn} + \text{Na}_2\text{O} \quad (2) \]
\[ \text{Sn} + \text{xNa}^+ + \text{x}e^- \rightarrow \text{SnNa}_x (0 < x \leq 3.75) \quad (3) \]

The SnO$_2$ conversion [i.e., Eq. (1) and (2)] offers a theoretical capacity of 710 mAh g$^{-1}$. However, such irreversible conversion usually leads to a fast capacity fading after the initial cycle.$^{[7,8]}$ In contrast, Sn can be reversibly alloyed [i.e., Eq. (3)] with up to 3.75 mol of Na$^+$, resulting in a theoretical capacity of 665 mAh g$^{-1}$, while accompanying by a large volume expansion of over 400% and the aggregation of metallic Sn upon cycling. The latter in turn causes the mechanical failure and the formation of unstable solid electrolyte interface (SEI) film. It is also notable that the low conductivity of SnO$_2$ leads to poor reaction kinetics and rate capability.$^{[9]}$

The enhanced electrochemical performance can usually be achieved by nanosizing SnO$_2$ and binding with the conductive matrix.$^{[10–12]}$ However, despite these strategies that can effectively suppress the volume expansion and accelerate the ionic and electronic transportation to some extent, they cannot retain the long-term stability and rate capability. This is because the nanostructured SnO$_2$ would inevitably tend to crack, detach from the conductive matrix and diminish the electronic contact during electrochemical reactions.$^{[13,14]}$ The use of defects, such as oxygen vacancies, has been proved to effectively dominate the electronic structure of semiconductor oxides for a wide range of applications, such as to improve the cyclability and rate capability for batteries.$^{[15,16]}$

In this context, we report a robust strategy for crafting oxygen-vacancy-containing SnO$_{2-x}$ nanoparticle-encapsulated carbon nanofibers with outstanding electrochemical performance for advanced SIBs. Intriguingly, flexible and free-standing “mats” composed of SnO$_{2-x}$/C composites can be directly employed as electrodes in SIBs, eliminating the addition of binders and conductive additives, thus not only markedly increasing energy density but also showing great potential for flexible energy storage devices.$^{[17,18]}$ The SnO$_{2-x}$/C composite-based SIBs display an array of out-

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standing electrochemical performance, including high reversible capacity, ultralong cyclic stability, and excellent rate capability. The discharge capacities of SIBs of 634 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\), 602 mAh g\(^{-1}\) at 0.2 A g\(^{-1}\), 565 mAh g\(^{-1}\) at 1 A g\(^{-1}\) and 447 mAh g\(^{-1}\) at 2 A g\(^{-1}\) were found to retain after 300, 800, 2000, and 2500 cycles, respectively. This effective strategy opens up new possible routes for addressing the fundamental challenges of fabricating high-performance SnO\(_2\)-based SIBs.

Figure 1 illustrates the route to the SnO\(_2\)/C electrode based on a flowable sulfur template and electrospinning technique (see Supporting Information for detailed experimental description). It is important to note that oxygen vacancies were found to emerge on the surface of SnO\(_2\) nanocrystals (i.e., changing from SnO\(_2\) to SnO\(_{2-x}\); Figures S1, S2 and S3 in the Supporting Information) as revealed by the XRD and XPS studies discussed below. Figure 1b shows that the freestanding SnO\(_{2-x}\)/C electrode was composed of highly uniform nanofibers with an average diameter of approximately 500 nm. A close-up of Figure S4 reveals that there are many macroporous holes along the SnO\(_2\)/C nanofibers (Figure 1c). Such relatively large holes allow for the easy penetration of electrolyte and fast transportation of Na\(^+\) ions. Moreover, no obvious SnO\(_{2-x}\) nanoparticles were observed on the surface of nanofibers, indicating the full encapsulation of SnO\(_{2-x}\) nanoparticles within carbon nanofibers. Transmission electron microscopy (TEM) study was performed to examine the inner structure of SnO\(_{2-x}\)/C nanofibers. Figure 1d,e clearly demonstrate that SnO\(_{2-x}\) nanoparticles were highly dispersed within carbon nanofibers with appropriate void space, which is beneficial for alleviating the volume expansion and pulverization. Moreover, the one-dimensional carbon matrix also imparts the fast electronic transfer, thereby improving the electrochemical properties.\(^{[19,20]}\) High-resolution TEM image reveals that SnO\(_{2-x}\) nanoparticles possess good crystallinity, and a lattice spacing of 0.33 nm can be ascribed to the (110) plane (inset in Figure 1e). The corresponding energy dispersive X-ray spectroscopy (EDS) analysis (Figure S6) also demonstrates the uniform elemental distribution of C, N, Sn, and O in SnO\(_{2-x}\)/C composites. The as-fabricated flake-type SIB was assembled to power commercial LEDs (Figure S7). It is notable that these red LEDs can be readily lit, even when the SIB was bent to 90\(^\circ\), 180\(^\circ\) or twisted, signifying the great potential for flexible devices.

Figure 2a shows the X-ray diffraction (XRD) patterns for SnO\(_2-x\)/C and SnO\(_2\). The major diffraction peaks of both samples can be indexed as rutile-phase SnO\(_2\). Interestingly, further scrutiny of (110), (101), and (200) peak positions reveals the shift to a lower angle associated with the formation of oxygen vacancies.\(^{[16,21]}\) Thermogravimetric analysis (TGA) shows that the mass content of SnO\(_{2-x}\) nanoparticles in SnO\(_{2-x}\)/C composites is approximately 54% (Figure S8). X-ray photoelectron spectroscopy (XPS) measurements were carried out to reveal the redox states of Sn, O, and N elements. Two peaks located at the binding energies of 495.5 and 487 eV can be assigned to Sn 3d\(_{3/2}\) and Sn 3d\(_{5/2}\) for SnO\(_2\), respectively (Figure 2b). Notably, a blue-shift of approximately 0.3 eV in the SnO\(_{2-x}\)/C electrode relative to that of SnO\(_2\) noted above was seen. Together with the XRD study, this observation signifies the formation of oxygen vacancies.\(^{[16,19,22]}\) In sharp contrast to the SnO\(_2\) sample, the full XPS spectrum of the SnO\(_{2-x}\)/C electrode clearly demonstrates the presence of N element (Figure S10a). The deconvolution of N signals yields three main peaks distributed at 398.2, 400.1, and 400.9 eV, which can be ascribed to pyridinic-,
pyrrolic-, and quaternary-N, respectively (Figure 2c), and thus may improve the electronic conductivity of the SnO$_2$/C electrode.[23–25]

Figure 3a shows the cycling performance of SnO$_2$/C and SnO$_2$ electrodes at 0.1 A g$^{-1}$. The discharge capacity of the first two cycles were 1185 and 654 mAh g$^{-1}$ for SnO$_2$/C, and 1277 and 565 mAh g$^{-1}$ for SnO$_2$, corresponding to the initial capacity retention (ICR) of 55.2% and 44%, respectively. As the cycling continued, the capacity of pristine SnO$_2$ gradually decayed and reached 60 mAh g$^{-1}$ after the 195th cycle. In stark contrast, the SnO$_2$/C electrode displays an outstanding stability with a discharge capacity of 634 mAh g$^{-1}$ after 300 cycles. Figure 3b compares the rate capability of SnO$_2$/C and SnO$_2$ electrodes at the current densities of 0.1, 0.5, 1, 2, and 5 A g$^{-1}$. Clearly, SnO$_2$/C displays the better high rate performance with higher specific capacity, varying from 646 to 608, 548, 440, and 340 mAh g$^{-1}$ at 0.1, 0.5, 1, 2, and 5 A g$^{-1}$, respectively. Remarkably, when the current rate turned back to 0.1 A g$^{-1}$ after 50 cycles, the reversible capacity can recover 630 mAh g$^{-1}$. The capacity retention is 52.6% for SnO$_2$/C, which is more than 5-fold higher than that for pristine SnO$_2$ (i.e., 9.3%) when the discharge rate increases from 0.1 to 5 A g$^{-1}$. Galvanostatic charge/discharge curves of SnO$_2$/C at different current densities are depicted in Figure S11, where all profiles show the distinct features, suggesting the similar reaction processes.

Cyclic voltammetry (CV) measurements were conducted to scrutinize the Na$^+$ storage behavior of SnO$_2$/C and SnO$_2$. Figure 3c,d display the first three CV profiles of SnO$_2$/C and SnO$_2$ electrodes at a scan rate of 0.1 mVs$^{-1}$, respectively. Compared with SnO$_2$/C electrode, a broad peak in the range of 0.75–1.3 V of SnO$_2$ electrode in the initial discharge process was observed, which can be attributed to the conversion reactions of SnO$_2$→SnO→Sn [Eq. (1) and (2)], as well as the irreversible formation of the SEI film caused by the electrolyte decomposition on the surface of active materials. Moreover, the peak located in the range of 0.01–0.6 V for both SnO$_2$ and SnO$_2$/C electrodes can be ascribed to the reversible alloying reaction of Sn→Na$_x$Sn [Eq. (3)]. On the basis of the comparison of charging/discharging analysis of SnO$_2$/C and SnO$_2$ electrodes shown in Figure S12, it is clear that the SEI formation is more stable and the irreversible loss is much less for the SnO$_2$/C electrode. In the following anodic scan, the obvious peaks at 0.5, 1.05, and 1.25 V of SnO$_2$/C electrode can be ascribed to the dealloying of Na$_x$Sn to Sn, the oxidation of Sn to SnO, and the further oxidation of SnO to SnO$_2$, respectively. In sharp contrast, only a peak at 0.45 V and a weak peak at 0.65 V can be observed for the SnO$_2$ electrode, indicating the highly reversible Na$^+$ reaction kinetic of SnO$_2$/C electrode. Moreover, the CV curves of SnO$_2$/C and SnO$_2$ electrodes at various scan rates from 0.1 to 0.7 mVs$^{-1}$ are also shown in Figure S13a and S13b, respectively. It can be seen that the pristine SnO$_2$ sample exhibits an obvious polarization with the increasing scan rate (marked with an arrow, Figure S13b), while the SnO$_2$/C electrode continue displaying the similar reaction kinetic even at higher working current (Figure S13a), demonstrating an outstanding rate capability.

Figure 3e shows the long-term cycling test for SnO$_2$/C, SnO$_2$ and pure porous carbon nanofibers (PCNFs) electrodes at 1 A g$^{-1}$ with the initial discharge capacities of 1080, 742, and 211 mAh g$^{-1}$ (corresponding to the ICES of 53.5, 35.5, and 56%), respectively. A discharge capacity of 565 mAh g$^{-1}$ was retained for the SnO$_2$/C electrode after 2000 cycles, which contrasts sharply to only 57 mAh g$^{-1}$ after 800 cycles for the pristine SnO$_2$ electrode. Moreover, importantly, the SnO$_2$/C electrode also achieved and maintained 602 and 447 mAh g$^{-1}$ after 800 and 2500 cycles with the Coulombic efficiencies of 97.6% and 106% at the current densities of 0.2 and 2 A g$^{-1}$, respectively (Figure S14), which may be attributed to the synergy of the unique nanostructure and the gradual activation of active materials. It is worth noting that these are the best high-rate and high-cycle-stability results of SIBs compared to those reported in literature (Table S1). Figure 4a summarizes the XRD patterns of SnO$_2$/C electrode at various voltages after the 20th cycle. Clearly, there exist three main characteristic peaks, that is, 110, 101, and 211 at 20 of 26.6°, 33.9°, and 51.8°, respectively, for the fresh electrode. As the discharge (i.e., sodiation) process advances, the peak intensities corresponding to SnO$_2$/C composite decrease,
accompanied by the emergence of new peaks at 20 of 50.7° and 43.8° ascribed to SnO and Sn phases, signifying the progressive conversion of SnO₂ (i.e., SnO₂ → SnO → Sn). Quite intriguingly, all the peaks belonging to SnO₂, SnO and Sn tend to disappear when discharged to 0.01 V, and the peaks at 20 of 29.4°, 47.5° and 48.6° may be attributed to Na₃Sn alloy phases, manifesting the full alloying reaction between Sn and Na⁺. Conversely, as the desodiation process continues, the peaks of Na₃Sn alloyed phase gradually disappear, associated with the recovery of Sn, SnO, and SnO₂ phases.

On the basis of all the results described above, we conceived the reaction mechanisms of SnO₂ and SnO₂/C electrode during the charge/discharge process as illustrated in Figure 4b,c. Typically, for the SnO₂ electrode, the generated metallic Sn nanoparticles and amorphous NaO tend to separate and self-aggregate[26] (second panel in Figure 4b). Moreover, the next alloying reaction [Eq. (3)] further promotes the separation of NaO from the Na/Sn/NaO interface due to the volumetric strain (third panel in Figure 4b), thus hindering the conversion of Sn → SnO₂. Furthermore, Sn nanoparticles tend to aggregate, pulverization, and finally form cracks during the cycling process (Figure S19), which is primarily caused by the large volumetric stress and eventually leads to severe capacity fading in the following cycles. In stark contrast, in the present study, the rationally designed SnO₂/C electrodes resolved these issues and greatly improved the energy storage performance. First, the convenient yet robust homogeneous confinement of SnO₂ nanoparticles within microporous carbon nanofibers not only greatly prevents the separation and aggregation of Sn and NaO phases (second to fourth panels in Figure 4c) that occur in pristine SnO₂ electrode case discussed above, but also effectively suppresses the large volume variation during the charge/discharge process (Figure 4c). Second, the one-dimensional porous carbon matrix of SnO₂/C electrode provides the effective pathway for facilitating the charge transfer and ionic insertion, and moreover functions as artificial barrier to form stable SEI film[27] (fifth panel in Figure 4c), as clearly evident in the insets of Figure S17b, S17d and S17f. Third, the presence of oxygen vacancies within SnO₂ nanoparticles imparts the lowering of the reaction energy barrier and the enhancement of the intrinsic electronic conductivity.

In summary, we developed a viable strategy by crafting oxygen-vacancy-containing SnO₂/C nanoparticle-impregnated carbon nanofibers (i.e., SnO₂/C composites) as electrodes for advanced SIBs with outstanding electrochemical performance (i.e., high reversible capacity, long cyclic stability, and excellent rate capability). Such intriguing nanoparticle-encapsulated one-dimensional conductive nanofiber architectures not only retain the intrinsic advantages of nanosizing SnO₂/C, but also offer benefits, such as effectively restraining the volume variation and enhancing the SnO₂ conversion kinetics [Eqs. (1) and (2)]. Consequently, the SnO₂/C composite exhibits remarkable reversibility of the Sn—SnO₂ conversion and high specific capacity with excellent cyclic stability. As such, the strategy developed herein may open up opportunities to produce other metal-oxide-nanoparticle-containing carbon fibers as electrodes for high-performance energy-storage systems including sodium-/lithium-ion batteries.

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Conflict of interest

The authors declare no conflict of interest.

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