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This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record.

To be cited as: ChemElectroChem 10.1002/celc.201901999

Link to VoR: https://doi.org/10.1002/celc.201901999
Plasma-enabled ternary SnO$_2$@Sn/nitrogen-doped graphene aerogel anode for sodium-ion batteries

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Abstract: SnO$_2$-based sodium-ion batteries usually suffer from rapid capacity fading during the sodiation/desodiation caused by aggregation and cracking of Sn and irreversible formation of Na$_2$O. To this respect, we design a ternary SnO$_2$@Sn core-shell structure decorated on nitrogen-doped graphene aerogel (SnO$_2$@Sn/NGA) which is fabricated by a microwave plasma-based process. The converted Na$_2$O can prevent agglomeration of Sn, thus stabilizing the structure during the cycles. Close contact between Na$_2$O and Sn ensures Na$^+$ ion diffusion to the Sn core and reversible conversion Sn $\leftrightarrow$ SnO$_2$. Moreover, the deoxygenation effect of the plasma on NGA improves its degree of graphitization and electrical conductivity, which substantially improves the electrode rate performance. As a result, the SnO$_2$@Sn/NGA anode delivers a high initial discharge capacity of 448.5 mAh g$^{-1}$ at 100 mA g$^{-1}$. Importantly, this unique nanohybrid electrode design can be extended to advanced anode materials for both lithium- and sodium-ion batteries.

Introduction

Development of the new environment-friendly energy storage technologies is particularly important because of the fast fossil energy consumption and related environmental issues. Among them, sodium-ion batteries (SIBs) have attracted an ever increasing attention owing to abundant resources, low cost, and environmental friendliness. [1-3] To overcome the difficult insertion and extraction of Na$^+$ ion in electrodes caused by the large radius (0.102 nm) [4-6], numerous efforts have been devoted to developing new electrode materials. [7-9]

Tin (Sn) is recognized as a promising anode for SIBs for its high theoretical capacity of 847 mAh g$^{-1}$. However, fast agglomeration and large volume expansion (520%) during the sodiation lead to particle pulverization/exfoliation, impeding Na$^+$ ion diffusion, and rapid capacity fading. [10-12] Alternatively, despite a little lower capacity (667 mAh g$^{-1}$), SnO$_2$ can be easily reduced to nanoscale. The storage of Na$^+$ in SnO$_2$ is executed by the conversion of SnO$_2$ [Eq. (1)] followed by the alloying of Sn and Na$^+$ [Eq. (2)]. Na$_2$O formed by the conversion reaction can prevent agglomeration and accommodate the associated volume expansion. [13-19] However, the formation of Na$_2$O consumes Na$^+$ ions in the electrolyte thus leading to the large irreversible capacity loss and low initial coulombic efficiency (CE). [20]

\begin{align}
\text{SnO}_2 + 4\text{Na}^+ + 4\text{e}^- & \leftrightarrow \text{Sn} + 2\text{Na}_2\text{O} \quad (1) \\
\text{Sn} + x\text{Na}^+ + xe^- & \leftrightarrow \text{Na}_x\text{Sn} \quad (2)
\end{align}

Recent efforts have demonstrated that the combination of SnO$_2$ and Sn could partially solve the problems described above. Mediation of the dual factors of Na$_2$O in SnO$_2$/Sn composites, i.e., preventing agglomeration of Sn particles and irreversible capacity loss, would deliver better electrochemical performances than either single-component Sn or SnO$_2$. For example, in a Sn/SnO$_2$/C composite anode, the introduction of Sn improved the SnO atomic ratio, leading to high initial reversible capacity, whereas the Na$_2$O could effectively prevent the aggregation of the Sn nanoparticles. [15] In a (SnO$_2$-Sn)@few-layered graphene composite anode of SIBs, the Na$_2$O prevented agglomeration and relieved the volume expansion of Sn during the sodiation process. [14] Another potential function of Na$_2$O is to make the conversion reaction Eq. (1) reversible, which is possible under the close contact between Na$_2$O and Sn and the presence of excessive Sn, thereby increasing the CE and reversible capacity. This idea has been demonstrated for both Li$_2$O in lithium-ion batteries (LIBs) and Na$_2$O in SIBs. [18, 21]

Here, we design a customized SnO$_2$@Sn core-shell structure, which might have several advantages: 1) Na$_2$O converted from the SnO$_2$ shell can prevent the aggregation of the inner Sn core, thus stabilizing the structure; 2) a thin SnO$_2$ shell leads to thicker Na$_2$O layer and solid electrolyte interface (SEI), thus reducing the irreversible energy loss; 3) close contact between Na$_2$O and Sn and the presence of excessive Sn (impure Na$_2$O) drives the conversion reaction Eq. (1) partially reversible, thereby increasing the CE and reversible capacity. The SnO$_2$@Sn core-shell structure decorated on nitrogen-doped graphene aerogel (SnO$_2$@Sn/NGA) anode of SIBs was converted from hydrothermally synthesized SnO$_2$/NGA composite in a microwave plasma-enabled process. The SnO$_2$ was partially reduced to Sn by the plasma, then the SnO$_2$@Sn core-shell structure was formed by phase segregation. Moreover, the
microwave plasma reduced the content of the oxygen containing functional groups in graphene oxide and improved the degree of graphitization and electrical conductivity. As a result, the SnO$_2@$Sn/NGA SIB anode exhibits the improved CE of 46%, a reversible capacity up to 415.8 mAh g$^{-1}$ at a current density of 0.1 A g$^{-1}$, capacity retention of 81.8% after 200 cycles at a current density of 1 A g$^{-1}$, as well as the superior rate performance.

Results and Discussion

Scheme 1 illustrates the synthesis of SnO$_2$/GA, SnO$_2$/NGA, and SnO$_2@$Sn/NGA composites. Briefly, SnO$_2$/GA was synthesized using a hydrothermal method.$^{[25-27]}$ Nitrogen dopant was introduced by adding ammonia to the reactants of the hydrothermal reaction.$^{[28-29]}$ The resulting SnO$_2$/NGA was subject to the microwave plasma, in which free electrons partially reduced the SnO$_2$ to SnO$_2@$Sn structure.$^{[30-31]}$ A control sample was obtained by thermal annealing the SnO$_2$/NGA with temperature (650 °C), atmosphere (Ar 40 sccm, H$_2$ 10 sccm), and time (20 min) same as the plasma process.

![Scheme 1. Schematics of the synthesis procedures for SnO$_2$/GA, SnO$_2$/NGA, and SnO$_2@$Sn/NGA composites.](image)

Porous and loose spongy features of the SnO$_2$/NGA can be observed under SEM, which could effectively promote ion transport (Figure 1a). Fine SnO$_2$ nanoparticles are dispersed in the porous NGA. After the microwave plasma treatment, larger spherical particles appear on the graphene surface (Figure 1b). Particle size distribution ranging from 30 to 200 nm is illustrated in the inset in Figure 1b. The control sample, SnO$_2$/NGA annealed at 650 °C, exhibits no significantly different morphology from the SnO$_2$/NGA (Figure S1a in the Supporting Information). This finding indicates that the microwave plasma is crucial to the formation of the SnO$_2@$Sn core-shell structure. Moreover, the N content of 3.17 wt. % in the SnO$_2@$Sn/NGA can be estimated from the energy-dispersive X-ray spectrometry (EDS) results (Table S1 in the Supporting Information). TEM image shows SnO$_2$ nanoparticles evenly and densely distributed on a graphene sheet (Figure 1c), while the particles tend to agglomerate after the microwave plasma treatment (Figure 1d). The core-shell structure of SnO$_2@$Sn was confirmed by HRTEM. Figure 1e shows an SnO$_2@$Sn nanoparticle with a diameter of 35 nm anchored on the surface of graphene, exhibiting a core-shell structure. The outer layer, 5 nm in thickness, shows a well-defined lattice fringe of 0.33 nm, corresponding to (110) plane of SnO$_2$. The core presents an inter-plane spacing of 0.27 nm, corresponding to (101) plane of Sn. The element mappings of tin, nitrogen, and oxygen are also provided in Figure S2 in the Supporting Information. TGA analysis reveals that the mass loadings of active materials are approximately 66 and 71 wt. % for SnO$_2@$Sn/NGA and SnO$_2$/NGA, respectively (Figure 1f). With these results, it can be assumed that the fine SnO$_2$ particles were partially reduced first by the plasma, then a phase segregation followed by coalescence of the Sn wrapped by the residual SnO$_2$ to minimize surface/interface free energy. A similar phenomenon was reported in an N–C@SnO$_2$/Sn3D-GNs composite, where the SnO$_2$ was reduced by carbon at the N–C/SnO$_2$ interface in a carbothermal reaction, but the Sn moved to the innermost core.$^{[16]}$
The crystal structures of SnO\textsubscript{2}@Sn/NGA, SnO\textsubscript{2}/NGA, and SnO\textsubscript{2}/GA have been characterized by XRD, as shown in Figure 2a. The SnO\textsubscript{2}/GA and the SnO\textsubscript{2}/NGA show similar features with 4 diffraction peaks at 2\theta = 26.6, 33.9, 51.8, and 65.9\degree, corresponding to the (110), (011), (211), and (301) peaks of tetragonal rutile-like SnO\textsubscript{2} respectively (PDF No.41-1445). For the SnO\textsubscript{2}@Sn/NGA, the diffraction peaks of SnO\textsubscript{2} remains unchanged, while sharp peaks appear at 2\theta = 30.6, 32.0, 43.9, 44.9, 55.3, 62.5, 64.5, and 79.5\degree, corresponding to (200), (101), (200), (211), (301), (112), (321), and (312) peaks of metallic Sn (PDF No. 04-0673). Calculated from the Bragg equation, the interplane spacing of (110) plane of SnO\textsubscript{2} and (101) plane of Sn are 0.334 and 0.276 nm, respectively, which are consistent with the HRTEM observation. In contrast, the control sample, SnO\textsubscript{2}/NGA annealed at 650 °C, has diffraction peaks of SnO in addition to those of Sn and SnO\textsubscript{2} (Figure S1b). Again, it indicates that simple thermal annealing used alone is unable to form the SnO\textsubscript{2}@Sn core-shell structure.

The successful N doping and the improved degree of graphitization of graphene by the microwave plasma were investigated by Raman spectroscopy, as shown in Figure 2b. For reduced graphene oxide (RGO), the peak centered at 1339 cm\textsuperscript{-1} corresponds to the D-band which is related to disordered carbon, edges, and other defects, while the peak centered at 1572 cm\textsuperscript{-1} corresponds to the G-band representing ordered sp\textsuperscript{2} carbon.\textsuperscript{[32-34]} The absence of the 2D-band at approximately 2700 cm\textsuperscript{-1} indicates the highly disordered structure of RGO.\textsuperscript{[35]} After N doping, the D-band and G-band are upshifted from 1339 to 1341 cm\textsuperscript{-1} and from 1572 to 1574 cm\textsuperscript{-1}, respectively. This may be due to distortion of graphene basal plane caused by different C-C and C-N bond lengths. Moreover, the NG shows a higher peak intensity ratio I\textsubscript{D}/I\textsubscript{G} = 1.23 than that of the RGO (1.16), suggesting a more disordered structure in the NG owing to the introduction of N heteroatoms in graphene lattice.\textsuperscript{[26, 36]} After the microwave plasma treatment, the improved degree of graphitization and restored defective structure are reflected by the appearance of the 2D peak at 2700 cm\textsuperscript{-1} as well as the sharpening and increase of the G-band (I\textsubscript{D}/I\textsubscript{G} = 0.85).

As shown in Figure 3d, the C 1s peak of SnO\textsubscript{2}/NGA comprises the four binding states, namely C-C (284.6 eV), C-N (285.2 eV), C-O-C (epoxy groups, 286.2 eV), and O-C=O (carboxyl, 288.7 eV) can be discerned.\textsuperscript{[30, 40-41]} In the case of SnO\textsubscript{2}@Sn/NGA, (Figure 3e) only C-C (284.6 eV), C-N (285.2 eV), and C-O-C (epoxy groups, 286.2 eV) can be discerned. The areal percentage of the O 1s peak is reduced from 36.2\% for the SnO\textsubscript{2}/NGA to 21.3\% for the SnO\textsubscript{2}@Sn/NGA. Obviously, the microwave plasma improved the quality of NGA by removing some of the oxygen, while the nitrogen-containing functional groups remained (Figure S3). Overall, the microwave plasma converts the defective graphene to the better-quality one, partially reduces SnO\textsubscript{2} to Sn, while it is less effective in N doping. The induced changes in the structural features could favor electrochemical performances, as will be discussed in the following.

The electrochemical reactions on the as-prepared SnO\textsubscript{2}/NGA and SnO\textsubscript{2}@Sn/NGA electrodes are studied by the cyclic...
voltammetry (CV) in a voltage window of 0.01 – 3.0 V with a scan rate of 1 mV s\(^{-1}\) for four cycles, as shown in Figure 4a-b. In the first cathodic scan, the SnO\(_2\)/NGA shows a strong peak around 0.6 – 1.0 V, representing the irreversible formation of the solid electrolyte interface (SEI) and Na\(_2\)O [Eq. (1)].\(^{14,42}\) However, for the SnO\(_2\)/Sn/NGA, only a weak and broad hump around 1.2 V can be observed and disappears in the subsequent scans, which is also due to the formation of SEI but less content of SnO in the electrode. The peak located at 0.01 – 0.6 V for both electrodes can be ascribed to the alloying reaction Sn \(\rightarrow\) Na\(_x\)Sn [Eq. (2)].\(^{42}\) In the following anodic scan, the SnO\(_2\)/Sn/NGA shows dealloying peaks around 0.65 and 0.75 V, and a partially reversible oxidation peak of Sn to SnO\(_2\) at 1.25 V.\(^{14,44}\) The differences between the peak potential and the potential at the half peak [\(\Delta E = E_{1/2}\)] are approximately 0.56 mV for both dealloying peaks, which are indications of good reversibility. In sharp contrast, only a large oxidation peak at 1.25 V can be observed for the SnO\(_2\)/NGA, indicating a slow desodiation process. The notable overlap of the CV laps of the SnO\(_2\)/Sn/NGA after the 2nd cycle reveals good reaction reversibility and structural stability. In fact, the CV curves are stable in the next 10 cycles, shown in Figure S4b. Nevertheless, the CV curves of the SnO\(_2\)/NGA vary largely during the first 4 cycles and gradually become stable in the next 10 cycles (Figure S4a). These results indicate the repeated formation and fracture of the SEI, leading to the large irreversible energy loss and low initial CE. Increasing the scan rate from 2 to 10 mV s\(^{-1}\), the SnO\(_2\)/NGA electrode exhibits an obvious polarization with the increasing scan rate (marked with an arrow, Figure S4c), while the SnO\(_2\)/Sn/NGA electrode displays almost constant peak positions (Figure S4d), indicating a fast reaction kinetics, even at high current and outstanding rate capability for the SnO\(_2\)/Sn structure.

Figure 4. CV curves of (a) SnO\(_2\)/Sn/NGA and (b) SnO\(_2\)/NGA electrodes for the first 4 cycles. (c) Charge-discharge curves of SnO\(_2\)/Sn/NGA at a current density of 100 mA g\(^{-1}\) from the 2nd to the 60th cycle. Charge-discharge curves for the 1st cycle are displayed in the inset. (d) Cycling performance of SnO\(_2\)/GA, SnO\(_2\)/NGA, and SnO\(_2\)/Sn/NGA at a current density of 100 mA g\(^{-1}\).

Figure 4c shows charge-discharge curves of the SnO\(_2\)/Sn/NGA electrode at a current density of 100 mA g\(^{-1}\). A high discharge capacity of 975.6 mAh g\(^{-1}\) and a charge capacity of 446 mAh g\(^{-1}\) in the initial cycle in the potential window of 0.01-3.0 V vs. Na\(^+\)/Na is recorded, corresponding to a CE of 46%. The specific capacity is determined based on the mass of the total active substance, i.e. SnO\(_2\)/Sn. In the second cycle, this electrode discharges a capacity of 453.2 mAh g\(^{-1}\). After 60 charge-discharge cycles, 402.4 mAh g\(^{-1}\) are retained, with a capacity retention of 88.6% (with respect to the 2nd cycle, Figure 4c, d). In contrast, the SnO\(_2\)/NGA and SnO\(_2\)/GA electrodes have the initial CEs of 33% and 36%, respectively; and have the capacity retention of 85.5% and 80.3%, respectively, after 60 cycles (with respect to the 2nd cycle, Figure S5 and Figure 4d). Obviously, the highest specific capacity of SnO\(_2\)/Sn/NGA among the three electrodes stems from the presence of metallic Sn, and the lowest amount of the oxides. The core-shell structure can enhance the reverse conversion reaction [Eq. (1)], increasing CE, which is consistent with the CV results. Ex-situ XRD were also conducted on the electrodes after the CV cycles. The XRD patterns reveal emergence of metallic Sn for the SnO\(_2\)/NGA electrode after cycling, indicating electrochemical irreversibility, while the reversible SnO\(_2\)/Sn/NGA electrode preserves its XRD pattern well (Figure S6). Additionally, the side reaction of oxygen containing functional groups in RGO with Na\(^+\) causes degradation in the capacity as well.\(^{45-46}\) Less oxygen containing functional groups in SnO\(_2\)/Sn/NGA, can improve the reversible specific capacity, as well as the stable cyclic performance.\(^{14}\)

Figure 5. (a) Rate capability of SnO\(_2\)/Sn/NGA, SnO\(_2\)/NGA, and SnO\(_2\)/GA anodes tested at current densities from 100 to 2000 mA g\(^{-1}\). (b) Nyquist plots of electrochemical impedance spectra (EIS) of SnO\(_2\)/Sn/NGA and SnO\(_2\)/NGA. (c) Cycling performance of SnO\(_2\)/Sn/NGA at current densities of 600, 1000, and 2000 mA g\(^{-1}\). (d) LED lights ignited by SnO\(_2\)/Sn/NGA cells.

Figure 5a compares the rate performances of SnO\(_2\)/Sn/NGA, SnO\(_2\)/NGA and SnO\(_2\)/GA. The SnO\(_2\)/Sn/NGA delivered the discharge capacity is 448.5 mAh g\(^{-1}\) at 100 mA g\(^{-1}\), approximately 35.7% of which was retained (160 mAh g\(^{-1}\)) when the current density was progressively increased to 2000 mA g\(^{-1}\). After the deep charge-discharge cycles, a reversible capacity can still reach 415.8 mAh g\(^{-1}\) at 100 mA g\(^{-1}\). As a control, only 87.2 mAh g\(^{-1}\) (~25%) was retained at 2000 mA g\(^{-1}\) for the SnO\(_2\)/NGA, while almost no discharge capacity remained at 2000 mA g\(^{-1}\) for the SnO\(_2\)/GA anode.
The excellent rate performance of the SnO$_2$@Sn/NGA is mainly attributed to improved electron and ion transport. First, the microwave plasma processed NGA has better degree of graphitization, thus the higher electrical conductivity. Second, the Na$_2$O converted from SnO$_2$ prevent agglomeration of Sn particles. As solid-state diffusion often represents the rate-limiting step in the sodiation processes, the small particle size is essential to ensure the fast alloying kinetics. Third, thin Na$_2$O layer can also promote the Na$^+$ ion diffusion since it can act as a solid state electrolyte with high ionic diffusivity ($2.04 \times 10^{-6}$ cm$^2$ s$^{-1}$). A diffusion pathway of Na$^+$ ion through Na$_2$O to Sn must exist because of the close contact between Na$_2$O and Sn as revealed by the CV tests. Given the excellent rate performance, the SnO$_2$@Sn/NGA composite could be potentially applied in pseudocapacitor applications.

To further evaluate the electron/ion transport in the electrodes, electrochemical impedance spectra (EIS) measurements were carried out after 200 discharge/charge turns (Nyquist plots shown in Figure 5b). All of the curves have similar intercepts on the Z$_0$ axis, which represents the electrolyte resistance ($R_0$). The depressed semicircles in the high frequency zone are attributed to the resistance arising from SEI ($R$) and charge transfer impedance ($R_{ct}$). The slope in the low frequency zone is related to the diffusion capability of Na$^+$ through electrode material. To extract the EIS parameters, an equivalent circuit was used to simulate the experiment data (see Figure S7A in the Supporting Information). Results are listed in Table 1. The SnO$_2$@Sn/NGA electrode shows the smallest semicircles and the lowest charge transfer impedance ($R_{ct} = 21.8$ $\Omega$) among the three electrodes. The presence of Na$_2$O [Eq. (1)] hinders the subsequent alloying reaction [Eq. (2)] and contributes to the $R_{ct}$. Accordingly, the shrinkage of the semicircle stems from the decreased content of SnO$_2$ in electrode, reflecting faster charge transfer kinetics in the SnO$_2$@Sn/NGA than in other electrodes. Furthermore, fewer oxygen containing functional groups and the improved quality of the anode material also boosts the charge transfer and lead to smaller $R_{ct}$. Moreover, the diffusion coefficients of Na$^+$ ($D_{Na^+}$) in the electrodes can be obtained by linear fitting between the real component (Z') of the impedance and angular frequency $\omega^{1/2}$ (see Supporting Information for the detail). The fitted ionic diffusion coefficient ($1.03 \times 10^{-11}$ cm$^2$ s$^{-1}$) of the SnO$_2$@Sn/NGA is one order of magnitude higher than that of the SnO$_2$/NGA. The faster ionic diffusion in the SnO$_2$@Sn/NGA can be attributed to the limited coarsening of Sn particles and promoted Na$^+$ ion diffusion through the Na$_2$O.

Long-term cyclability of the SnO$_2$@Sn/NGA electrode was evaluated at high current densities of 600, 1000, and 2000 mA g$^{-1}$, 254.1, 197.3, and 116.8 mAh g$^{-1}$ were retained after 200 cycles, respectively, as shown in Figure 5c. In contrast, only 63.7 mAh g$^{-1}$ was retained for the SnO$_2$/NGA electrode after 200 charge-discharge cycles at 2000 mA g$^{-1}$, while no capacity can be discharged for the SnO$_2$/GA at such a high current (Figure S8). The as-fabricated SIB coin cells can light commercial LEDs (Figure 5d). The excellent long-term cycling performance is closely related to the structural stability of the ternary SnO$_2$@Sn/NGA electrode, as elucidated by post-mortem observation. As shown in Figures 6a-d, the SnO$_2$@Sn/NGA electrode remains integral without cracks. Close inspection reveals individual particles with clear boundaries and particle size ~ 100 nm, which is similar to the fresh electrode. By contrast, active materials peeled off from the SnO$_2$/NGA electrode, with the current collector being exposed (Figure 6e).

Cracks and merged particles (~ 200 nm) can be observed in the SEM images of the SnO$_2$/NGA (Figures 6f-h). The comparison clearly demonstrates the stabilizing effect of the SnO$_2$@Sn structure. The rate performance of our SnO$_2$@Sn/NGA anode is among the top rank of recently reported tin oxide based SIB anodes, as compared in Table 2.

![Figure 6](image_url)

**Figure 6.** Digital photographs of the (a) SnO$_2$@Sn/NGA and (e) SnO$_2$/NGA. SEM images of the (b, c, d) SnO$_2$@Sn/NGA and (f, g, h) SnO$_2$/NGA electrodes after 200 discharge-charge cycles at 2000 mA g$^{-1}$ at different magnification.

| Table 1. The fitted EIS parameters and the ionic diffusion coefficient of SnO$_2$@Sn/NGA and SnO$_2$/NGA. |
|---------------------------------|-----------------|-----------------|-----------------|
| Electrode                        | Rs (Ω)          | Rct (Ω)         | $D_{Na^+}$ (cm$^2$ s$^{-1}$) |
| SnO$_2$@Sn/NGA                  | 12.7            | 21.8            | 1.03$\times 10^{-11}$ |
| SnO$_2$/NGA                     | 9.0             | 39.0            | 1.88$\times 10^{-12}$ |

| Table 2. Comparison of rate performances of tin oxide based anodes for SIBs. |
|---------------------------------|-----------------|-----------------|-----------------|
| Samples                         | Current density (mA g$^{-1}$) | Capacity (mAh g$^{-1}$) | References |
|---------------------------------|-----------------|-----------------|-----------------|
| SnO$_2$@Sn/NGA                  | 600             | 1000            | 2000            | This work |
|                                 | 448.5           | 315.0           | 241.7           | Cheng 2016$^{[5]}$ |
| Sn/SnO$_2$/C                    | 50              | 100             | 1000            | Zhao 2018$^{[6]}$ |
|                                 | 252             | 229             | 152             | 120         |
| SnO$_2$@CEM                     | 100             | 500             | 1000            | Zhang 2018$^{[5]}$ |
|                                 | 629             | 467             | 409             | 213         |
| SnO$_2$/NC                      | 100             | 500             | 1000            | Li 2017$^{[7]}$ |
|                                 | 455             | 325             | 285             | 236         |
| PCS@SnO$_2$/C                   | 100             | 400             | 800             | 1600        |
|                                 | 331             | 189             | 136             | 88          |
| NC@SnO$_2$                      | 100             | 400             | 800             | 1000        |
|                                 | 300             | 247             | 202             | 193         |
| SnO$_2$@G                       | 100             | 500             | 1000            | 2000        |
|                                 | 472             | 307             | 260             | 222         |
| SnO$_2$-Ni foam                 | 100             | 400             | 800             | 1600        |
|                                 | 480             | 336             | 249             | 143         |
Conclusion

In summary, a ternary SnO$_2$@Sn/NGA SIB anode was successfully fabricated by converting from SnO$_2$/NGA using a microwave plasma enabled process. The SnO$_2$@Sn core-shell structure ensures that Na$_2$O can improve the anode performance in several ways, specifically to prevent agglomeration, stabilize the structure, improve Na$^+$ ion diffusion pathways, and ensure the reversible Sn$^4+$ ↔ SnO$_2$ conversion. Consequently, the SnO$_2$@Sn/NGA anode shows outstanding electrochemical performance, i.e., high specific capacity, excellent rate capability, and long cyclic stability. On the other hand, the improved graphene quality further contributed to the high rate performance. Importantly, this unique nanohybrid design can be extended to other alloy-type anode materials for both lithium- and sodium-ion batteries, and potentially to other battery types.

Experimental Section

Materials. Graphene oxide (GO) was produced from natural graphite flakes by a modified Hummer’s method. The SnO$_2$@Sn/NGA was synthesized by a two-step fabrication. Concentrated ammonia water (1.5 mL, GR 25 – 28 %) and GO aqueous dispersions (100 mL, 3 mg/mL) were mixed by stirring for 60 min. SnCl$_4$·5H$_2$O (800 mg) was added and stirred for another 60 min. Then, the solution was transferred to a Teflon-lined autoclave and kept at 180 °C for 12 h. Then, the resulting hydrogel was washed thoroughly with de-ionized water and then subjected to freeze-drying at -60 °C and 20 Pa for 24 h to generate SnO$_2$/NGA.

The as-prepared SnO$_2$/NGA was ground to powder and then processed in a microwave plasma fluidized bed (800 W, Ar 40 sccm, H$_2$O 40 sccm, ~650 °C, 20 min) to generate SnO$_2$/Sn/NGA. Temperature in the reactor was detected using an infrared thermometer.

The SnO$_2$/GA was synthesized by the same method without ammonia and microwave plasma annealing.

Structural and physical characterization. The crystal structure and phases of the as-prepared materials were characterized by X-ray diffraction (XRD, Bruker D8 Advance A25) using Cu Kα radiation in the range from 20 to 90°. A field-emission scanning electron microscope (SEM, Hitachi S-4800) equipped with a Bruker Quantax energy-dispersive X-ray spectrometry (EDS) system was used to observe the morphology and element distribution. The crystal structure details were further characterized by transmission electron microscopy (TEM, Hitachi HT7700) and high-resolution transmission electron microscopy (HRTEM, Talos F200X). Simultaneous thermal-gravimetric analysis and differential thermal analysis (TGA/DTA) were performed with a STA8000 system to analyze the weight ratio of SnO$_2$ at a heating rate of 10 °C/min in air from room temperature to 800 °C. X-ray photoelectron spectroscopy (XPS) was conducted by a KRATOS Axis Supra XPS System. All of the binding energies were calibrated by C 1s as the reference energy (C 1s = 284.6 eV). Raman spectra were collected using a Renishaw RM2000 system and a Renishaw He-Ne laser source producing 17 mW at λ= 532 nm.

Cell assembly and electrochemical testing. The electrodes were prepared by dispersing the as-prepared material (80 wt. %), carbon black (10 wt. %), and poly (vinylidene fluoride) binder (PVDF, 10 wt. %) in N-methyl-2-pyrrolidone (NMP). The resultant slurry was poured onto copper foil and dried in a vacuum oven for 12 h at 100 °C. Electrochemical measurements were conducted in two-electrode coin cells with Na metal as counter and reference electrodes and glass fiber separator (Whatman GF/D). The CR2016-type coin cells were assembled in an argon-filled glove box. The electrolyte solution was 1 M NaNO$_3$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1 with a 5 vol. % addition of fluoroethylene carbonate (FEC). The cells were galvanostatically cycled at various current densities between 0.01 and 3.0 V (vs. Na/Na$_x$) on a LAND battery tester (Wuhan, China). All the capacities were calculated based on the mass of the composites. CV tests were performed using a CHI660E electrochemistry workstation at a scan rate of 1 mV s$^{-1}$ in the potential range 0.01 – 3.0 V. EIS measurements were also performed using the CHI660E electrochemistry workstation in the frequency range 10$^{-2}$ - 10$^{6}$ Hz. The charge-discharge measurements were performed in the voltage range from 0.01 and 3 V vs. Na/Na$_x$.

Acknowledgements

This work is financially supported by the Program of Distinguished Professor of Jiangsu Province. We thank Zhenhai Wen at Fujian Institute of Research on the Structure of Matter Chinese Academy of Sciences for the instruction of cell assembly, Chunyuan Song at Nanjing University of Posts and Telecommunications for technical support of Raman spectroscopy. K.O. thanks the Australian Research Council for partial support.

Keywords: Tin • graphene • core-shell structure • plasma • sodium-ion battery

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