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Declaration of interests

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N-doped silk wadding-derived carbon/ SnO_x @reduced graphene oxide film as an ultra-stable anode for sodium-ion half/full battery

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Abstract

Achieving high-stability, long span-life, and fast sodiation reaction kinetics in sodium ion battery (SIB) can significantly promote its practical application. Here, we use freeze-drying and carbonization to prepare a flexible N-doped silk wadding-derived carbon/SnO_x@reduced graphene oxide (N-SWC/SnO_r(α rGO) film as an ultra-stable anode for a half/full SIB. A superior capacity of 572.2 mA h g⁻¹ at 0.1 A g⁻¹ and long span-life over 1000 cycles are obtained in the N-SWC/SnO_x@rGO film anodes. Moreover, a super-stable capacity of 245.7 mA h g⁻¹ can be secured in the assembled SIB full cell, outperforming the current studies. After the detailed structural and performance characterization, we attribute these superior capacities to the following unique structural characteristics: 1) SnO_x nanoparticles (<100 nm) are attached to the surface of SWC to provide more active sites for Na⁺; 2) rGO and SWC form a double-layer conductive system, which can tremendously promote the transmission efficiency of electrons in N-SWC/SnO_x@rGO film, thereby greatly accelerating the reaction kinetics of SIB; 3) the N- $SWC/SnO_x(a)$ rGO film contains a conductive network with voids, which can increase the contact area between electrolyte solution and SnO_x and in turn effectively shorten the transmission path of Na⁺. This work provides a new perspective for the preparation of ultra-stable flexible SIB anodes.

Keywords: Self-standing; Silk Wadding; Anode; Flexible; Film.

1 Introduction

Given the superior energy density and high energy conversion efficiency, Lithium-ion batteries (LIBs) have become indispensable devices for electric vehicles, smart phones, and wearable electronic devices [1]. However, the scarcity of Li makes LIBs unable to meet the ever-growing needs of the energy storage markets [2, 3]. Sodium-ion battery (SIB) has been selected as an alternative for replacing LIB due to the elemental abundance of sodium and low cost [4]. However, compared to Li⁺, Na⁺ has a large radius of 1.02 Å and may result in huge volume change during insertion reaction, which seriously reduces the cycle stability and cycle-life of SIBs [5, 6]. Therefore, it is a great significance to search an ultra-stability and long span-life material for SIBs.

Currently, SIB cathodes have shown great progress [7], while the research on SIB anodes is still in the early stage [7, 8]. A few SIB anode materials, such as carbonaceous materials [2], alloy-based materials [5], molybdenum-based compounds [8], have been explored [9]. Among them, Sn-based materials such as Sn, SnS₂, SnO₂, with the high theoretical specific capacity of 847 mA h g⁻¹, 1136 mA h g⁻¹, and 1378 mA h g⁻¹ respectively, which have shown a great potential as competent and efficient anode materials for SIB [10]. However, intrinsic Sn-based materials suffer ~520 % huge volume changes during the intercalation process of Na, which can cause structure fractures and reduced span-life [11, 12]. Therefore, carbonaceous materials, such as carbon nanotubes (CNTs), reduced graphene oxide (rGO), biomass carbon, expanded graphite (EG), have been used to be compounded with Sn-based materials to form a composite as SIB anodes [13, 14]. For example, Zhou and his co-workers report a core-shell structured carbon nanotube (CNT)@SnO₂ composite as SIB anode, which has a high discharge capacity of 323 mA h g⁻¹ after 100 cycles [15]. These carbonaceous materials in SIB anodes can effectively alleviate

the volume expansion of SIB anodes [16], and simultaneously increase the transmission rate of electrons to accelerate the reaction kinetics of SIB anode and improve the cycle stability and span-life of SIB [17]. Moreover, environment-friendly and low-cost biomass materials, such as rice, crop straw and wood, have been used to be precursors for the fabrication of carbonaceous materials [18-20]. For example, a binder-free SIB anode has been fabricated by Sn nanoparticles loaded wood fiber (Sn@WF) prepared by electrodeposition. An stable cycled performance of 400 cycles and a specific capacity of ~150 mA h g⁻¹ were witnessed [21]. Comparing with other biomass materials, silk wadding (SW) is easier to peel into thin sheets than cotton, and maintain a good self-standing film after carbonized, while other biomass is mostly powder [22, 23]. Furthermore, SW has excellent liquid absorption ability, and can be easily attached to the fiber surface by impregnation process. However, many challenges in the span-life and electrochemical performance of SIB anodes exist in biomass carbon/Sn-based composite materials as SIB anodes [20]. Particularly, the structural compound design of Sn-based materials and biomass carbon materials still faces many challenges. Therefore, it is urgent to search a biomass carbon/Sn-based anode with low cost, high-performance and long span-life for SIBs.

Here, we report a flexible N-doped silk wadding-derived carbon/SnO_x@reduced graphene oxide (N-SWC/SnO_x@rGO) film as a binder-free SIB anode **by using** freeze-drying method and carbonization process. In the fabricated film, ultra-small SnO_x nanoparticles are attached to the surface of SWC to provide more contact points for Na⁺, and rGO wrapped in the outer layer is used to accommodate the volume change of SnO_x particles. Moreover, rGO and SWC form a double-layer electron transport layer, so that electrons can travel unimpeded in the whole film. Consequently, N-SWC/SnO_x@rGO film as a SIB half-cell anode possesses a long span-life with a capacity of 488.2 mA h g⁻¹ over 1000 cycles. Our assembled SIB full cell also exhibits a high

capacity of 245.7 mA h g⁻¹. Our method can be used to prepare other biomass carbon/Sn-based anodes.

2. Experimental

2.1. Specification of GO and $Na_3V_2(PO_4)_3$.

GO (2.0 mg mL⁻¹) and Na₃V₂(PO₄)₃ were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of N-SWC/SnO_x@rGO film.

Firstly, silk wadding (SW) films were pretreated and cleaned with ethanol, acetone, and deionized water to remove surface impurities, and then dried at 25 °C. Secondly, 3.5 g $SnCl_2 \cdot 2H_2O$ was dispersed in 100 ml deionized water and stirred for 2 h. The dried SW films are immersed in the solution and ultrasonically dispersed for 5 h to obtain SW with Sn^{2+} (SW/Sn²⁺). Due to the strong physical adsorption capacity of SW, Sn^{2+} are easily adsorbed on the surface of SW. SW/Sn²⁺ film was freeze-dried to maintain the structural integrity and further heated at 280 °C for 2 h, and then calcined to 800 °C at N₂ for 5 h to form N-SWC/SnO_x film. Finally, N-SWC/SnO_x films were added into GO dispersion with excess ascorbic acid for 1 h under ultrasonic irradiation, and then dried in an oven at 90 °C to obtain N-SWC/SnO_x@rGO film.

2.3. Characterization of samples

The crystal phase of the product is determined by a Cu $K\alpha$ X-ray diffraction (XRD) equipment of model D/max2200PC. X-ray photoelectron spectroscopy (XPS, AXIS SUPRA) was carried to analyze the binding energy and bond energy of the compounds in the film. A Tecnai F20 S-TWIN of Transmission electron microscopy (TEM) and a Verios 460 of scanning electron microscopy (SEM) was used to further character the morphology of the film. A model Vario EL

of Element analyzer (EA) was used to further determine the accurate content of C and N element.

2.4. Assembly and testing of SIB half cell and full cell

With SnO_x carrying of about 0.3~1.5 mg cm⁻², self-standing SWC, N-SWC/SnO_x and N-SWC/SnO_x@rGO film were directly as SIB anodes. The salt 1M NaPF₆ was dissolved in Ethylene carbonate (EC) and Dimethyl carbonate (DMC) to form an electrolyte solution and EC:DMC has a volume ration of 1:1. Considering that N-SWC and rGO can also storage sodium ions, the whole film was used as an active material to evaluate the electrochemical performance of SIB. Ar-filled glove box was used to fabricate CR2032 SIB half cells at the moisture and oxygen values of below 1 ppm. The cathode of Na metal and the anode of SWC, N-SWC/SnO_x and N-SWC/SnO_x@rGO film were carried to assemble half cells. On a suitable potential of 0.01~3.0 V, a LAND-CT2011A test system was carried to record alloy and de-alloy of half cell at 0.05~2 A g⁻¹. A CHI618D electrochemical station with three-electrode cells was used for Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) testing at room temperature. CV was measured within 0.01~3.0 V at 0.1 mv s⁻¹. The EIS was performed with an Alternating current (AC) voltage of 5 mV under the frequency range from 100 kHz to 10 mHz.

Na₃V₂(PO₄)₃ was used as a SIB cathode material for full cell. Its preparation and assembly process were listed followings. Firstly, Na₃V₂(PO₄)₃, polyvinylidene fluoride (PVDF) and carbon black were mixed into N, N-Dimethylformamide (DMF) at a mass ratio of 8:1:1 to fabricate the slurry. After that, the coating equipment was used to coat the slurry on the Al foil, and then the Al foil was dried at 60 °C for 24 hours. Finally, a Na₃V₂(PO₄)₃ carrying of 0.5~1.5 mg cm⁻² of Al foil was cut as SIB full cell cathodes. Na₃V₂(PO₄)₃ (cathode) and N-SWC/SnO_x@rGO film (anode) were coupled as CR2032 SIB full cells.

3. Results and discussion

Fig.1a illustrates the fabrication of N-SWC/SnO_r@rGO flexible film. As an environmentally friendly biomass material, SW film was firstly processed with ethanol, acetone, and deionized water to remove impurities attached to the surface of the SW. Then, SW film was put into the SnCl₂•2H₂O aqueous solution and sonicated for 5 h to obtain SW/Sn²⁺ film. It is noteworthy that SW film has a strong liquid absorption capacity and Sn²⁺ is easily adsorbed on the surface of SW film. Next, SW/Sn²⁺ film was freeze-dried and carbonized in N₂, and N-SWC/SnO_x (x = 0, 2) film was obtained. Finally, under the action of ascorbic acid, N-SWC/SnO_x film was added into GO dispersion and self-standing at 90 °C for 1 h to form N-SWC/SnO_x@rGO film. The used renewable natural SW and our simple preparation process provide a low-cost method to fabricate N-SWC/SnO_x@rGO film. Fig. 1b-d are the schematical model and SEM images of SWC. As can be seen, the surface of the carbon fiber (SWC) is very smooth without any attachments. After the SWCs are immersed in SnCl₂•2H₂O aqueous solution and carbonated treatment under N₂, SnO_x particles are formed on the surface of SWC, as shown in Fig. 1e-f. Due to the strong liquid absorption capacity of SW, SnO_x particles can be evenly distributed along the carbon fiber. rGO was further used to wrap the outer layer to prevent the SnO_x particles to falling off the fiber surface during charging and discharging process, and their typical morphologies are shown in Fig. 1h-j. These tightly packed rGO can simultaneously accommodate the volume change of SnO_x particles and accelerate the transmission efficiency of electrons in the outer layer of the fiber, thereby increasing the cycle stability of the N-SWC/SnO_x@rGO film.



Fig. 1. (a) Illustration of the preparation process for N-SWC/SnO_x@rGO film. Model of SWC (b) and SEM images of SWC (c, d); Schematic diagram of N-SWC/SnO_x (e) and SEM images of N-SWC/SnO_x (f, g); N-SWC/SnO_x@rGO model (h) and SEM images of N-SWC/SnO_x@rGO (i, j).

Energy dispersive X-ray spectroscopy (EDS) was used to analyze the content of each element in N-SWC/SnO_x@rGO film and the results are shown in Fig. 2a. As can be seen, C, O, Sn and N elements exist on the surface of single carbon fiber (green area in illustration). The proportion of Sn, O, C and N elements in N-SWC/SnO_x@rGO can be calculated to be ~13.99 %, 22.61 %, ~52.33 % and ~11.07 %, respectively. Under a temperature ramp of 10 °C min⁻¹, thermal gravimetric analysis (TGA) was used to confirm the exact ratio of SnO_x in the whole N-SWC/SnO_x(a)rGO film and the results are plotted in Fig. 2b. The chemically adsorbed water in N-SWC/SnO_x@rGO film is volatilized in 100~300 °C (ΔW_1). An obvious mass loss occurs in 300 °C~600 °C (ΔW_2) due to the combustion products of the SWC matrix and N source in the airflow environment [24, 25]. According to TGA curve, the mass percentages of SnO_x in N-SWC/SnO_x@rGO film can be calculated ~63.5 wt%, while carbon matrix and N source can be calculated ~33.9 wt%. An elemental analyzer (EA) was used to further determine the accurate content of C and N element in N-SWC/SnO_x@rGO film. The results showed that the proportion of C and N element in the film was ~67.24 % and 8.47 % respectively. The crystal structure of SWC, N-SWC/SnO_x and N-SWC/SnO_x(α)rGO film was determined by XRD. As depicted in Fig. **2c**, peaks of SWC are well indexed as C (JCPDS 46-0945), and no other diffraction peaks are found, indicating that no impurities exist on the surface of SWC. N-SWC/SnO_x and N-SWC/SnO_x(a)rGO film have similar XRD diffraction peaks, and all peaks can be indexed to Sn

(JCPDS 04-0673) and SnO₂ (JCPDS 72-1147) [26, 27]. Raman spectra of SWC, N-SWC/SnO_x, and N-SWC/SnO_x@rGO film were measured to investigate the changes of N-doped carbon with SnO_x , and shown in Fig. 2d. Two strong peaks were observed at 1351 and 1589 cm⁻¹ corresponds to the disordered (D) and graphitic (G) bands of carbonaceous materials, respectively [28-30]. The D peak reflects the defect induced and disordered structure of carbon, while the G peak reflects the existence of SP²-hybridized graphite carbon structure [31, 32]. The intensity ratio of ID:IG of N-SWC/SnO_x (I_D :I_G = 0.88) is higher than that of SWC (I_D :I_G = 0.74), and this high ratio may result from the N-doped. The N-doped can also increase the electrical conductivity of the carbon matrix and improve the performance of the material [33]. The intensity ratio of ID:IG of N-SWC/SnO_x@rGO film increased to 0.98, indicating that rGO could further increase the defects in the carbon matrix. A large number of defects are conducive to the rapid diffusion of Na⁺, which could maintain excellent electrochemical properties of N- $SWC/SnO_x(a)$ rGO film. Noteworthy, N-SWC as biomass carbonaceous material can affect the peaks of Sn and SnO₂ in the composite, which could make the XRD peaks is not sharp enough [34, 35]. Fig. 2e-f shows the N₂ adsorption and desorption isotherm of N-SWC/SnO_x@rGO film, which shows a type-IV isotherm, demonstrating the existence of mesopores. The specific surface area (Fig. 2e) and a pore volume (Fig. 2f) of N-SWC/SnO_x@rGO film can be calculated from the Brunauer-Emmett-Teller (BET) method. The results reveal a large specific surface area of 38.9 m² g⁻¹ and a pore volume of 0.15 cm³ g⁻¹, which can provide more Na⁺ active sites for the electrolyte solution. The four characteristic peaks of Sn 3d, O 1s, C 1s and N 1s are clearly displayed in the surveyed XPS spectra of N-SWC/SnO_x@rGO film, as shown in **Fig. 2g**. Peaks at 487.7 eV and 496.1 eV belong to Sn $3d_{5/2}$ and Sn $3d_{3/2}$ in the Sn 3d XPS spectrum (Fig. 2h) of N-SWC/SnO_x@rGO film [<u>36</u>, <u>37</u>]. Fig. 2i shows the O 1s XPS spectrum of the N-

SWC/SnO_x@rGO film. From which, peaks at 531.9 eV, 533.2 eV, and 534.3 eV can be seen and assigned to *Sn-O*, *C=O*, and *C-O* bond, respectively [38, 39]. The C 1*s* XPS spectrum of the N-SWC/SnO_x@rGO film (**Fig. 2j**) can be peak-fitted to three peaks, which are attributed *C-C* (284.7 eV), *C=N* (286.6 eV), and *C=O* (288.7 eV) bond [25, 40]. As can be detected in the N 1*s* XPS spectrum of N-SWC/SnO_x@rGO film (**Fig. 2k**), three peaks located at 384.4 eV, 399.3 eV, and 402.1 eV are indexed to *Pyridinic N*, *Pyrrolic N*, and *Graphitic N* bond, respectively [24, 41]. The literature demonstrated that N-doped species in carbon fibers simultaneously improves the storage capacity of sodium and accelerates the transport of ions and electrons [42, 43].



Fig. 2. EDS profile (a) and TGA curves (b) of N-SWC/SnO_x@rGO film; (c) XRD patterns of SWC, N-SWC/SnO_x and N-SWC/SnO_x@rGO film; (d) Raman spectra of SWC, N-SWC/SnO_x

and N-SWC/SnO_x@rGO film; N₂ adsorption/desorption isotherms (e) and the corresponding pore size distribution curve (f) of the N-SWC/SnO_x@rGO film; (g) The full survey XPS spectrum of N-SWC/SnO_x@rGO film and (h) Sn 3*d*, (i) O 1*s*, (j) C 1*s* and (k) N 1*s* spectrum of N-SWC/SnO_x@rGO film.

To further analyze the morphology and element mapping of the N-SWC/SnO_x(a)rGO film, SEM and TEM were carried. Fig. 3a and Fig. 3b are typical SEM and TEM images of the N- $SWC/SnO_x(\alpha)$ rGO film, which clearly show that the film has a three-dimensional (3D) carbon fiber conductive network structure, which can be used as a fast transport channel for electrons in the film. Moreover, the voids in N-SWC/SnO_x@rGO film provide sufficient space for the contact between SnO_x particles and electrolyte. rGO as an electronic channel is wrapped in the outermost layer, which can transport electrons throughout the whole film. rGO can also accommodate the volume change of SnO_x and prolong the cycle-life of N-SWC/SnO_x@rGO film. Fig. 3c is a bright-field TEM image of N-SWC/SnO_x@rGO film. From which, the size of SnO_x particles can be seen to be ~80 nm. Further high-resolution TEM analyses at Spot 1 and Spot 2 in Fig. 3c are carried and shown in Fig. 3d. The interlayer distance of the stripe in Spot 1 can be measured to be 0.280 nm, which can be indexed as (101) crystal of Sn (JCPDS:04-0673). The fringe at Spot 2 is verified to be 0.334 nm, which can be assigned to the (110) plane of SnO_2 (JCPDS: 72-1147). Fig. 3e is a selected area electron diffraction (SAED) pattern at this area. From these polycrystalline rings, both Sn (JCPDS:04-0673) and SnO₂ (JCPDS: 72-1147) can be indexed, which match with the XRD analysis, indicating the presence of Sn and SnO₂ in N-SWC/SnO_x@rGO film. Fig. 3f is a TEM image of a carbon faber in N-SWC/SnO_x@rGO film and its corresponding EDS elemental maps of C, Sn, O and N elements, the dispersive

spectroscopy (EDS) mappings are shown in **Fig. 3g-j**. Obviously, C, Sn, O and N elements are distributed evenly. **Fig. 3k** shows an optical photograph of the film before and after carbonization. Although the size of the film is significantly reduced after carbonization, its structure can remain intact. Particularly, the film can return to its original state when bending at different angles, showing excellent flexibility and self-standing. Such a self-standing film can be directly used as SIB anodes, which avoids the interference of adhesive with poor conductivity on SIB performance.



Fig. 3. SEM (a) and TEM (b) images of N-SWC/SnO_x@rGO film; (c, d) High magnification TEM and high-resolution lattice fringe patterns of N-SWC/SnO_x@rGO film; (e) Lattice diffraction ring at one point of N-SWC/SnO_x@rGO film; (f-j) Elemental mapping of N-SWC/SnO_x@rGO film in Fig. (f); (k) Optical photos of films before and after carbonization; (l) Optical photos of flexible film bending in different degrees.

Cyclic behaviors of half cells were evaluated at SIB anodes by using the as-prepared SWC, N-SWC/SnO_x and N-SWC/SnO_x(a)rGO film. Fig. 4a and b shows the first two cyclic voltammograms (CV) of SWC and N-SWC/SnO_x@rGO film in a suitable voltage range of $0.01 \sim 3.0$ V at 0.1 mV s⁻¹. Without SnO_x attached to the surface, SWC has no obvious oxidation and reduction peaks, as shown in Fig. 4a. During the cathodic scan of N-SWC/SnO_x@rGO film (Fig. 4b), a clear reduction peak at 0.50 V disappears in the next scan, representing the conversion reaction of reduction from SnO_x to Sn with the formation of Na₂O, and the solid electrolyte interface (SEI) is formed in this process [44, 45]. In the anodic scan with the dealloying process, three peaks at 0.23 V, 0.25 V, 0.59 V, and 0.60 V are assigned to the desodiation of $Na_a Sn_b$ [46, 47]. Fig. 4c shows the rate capability of SWC, N-SWC/SnO_x and N-SWC/SnO_x(a)rGO film anodes in 0.05~2 A g⁻¹. The yield charge/discharge capacities of 646/737, 577.8/602.4, 484.0/465.8, 413.1/421.0, 380.7/384.7 and 322.5/342.5 mA h g⁻¹ can be maintained at 0.05, 0.1, 0.2, 0.5, 1 and 2 A g⁻¹, respectively. The capacity of 22.5/342.5 mA h g⁻¹ can be still observed at 2 A g⁻¹, illustrating that N-SWC/SnO_x@rGO film maintains excellent structure stability. As the current returns to 0.05 A g⁻¹, the specific charge/discharge capacity of the N-SWC/SnO_x@rGO film restores to 609.4/619.4 mA h g⁻¹, which shows better electrochemical behavior than SWC and N-SWC/SnO_x. This result indicates that N-SWC/SnO_x@rGO film can

withstand the impact of high current density and has strong structure stability. At any stage of current density, the capacity of SWC and N-SWC/SnO_x are all less than that of N-SWC/SnO_x(α)rGO film. rGO can effectively accommodate the volume change of SnO_x nanoparticles, avoids particle shedding, and maintain the integrity and stability of N- $SWC/SnO_x(a)$ rGO film. Besides, the double-layer electron running channel formed by the combination of SWC and rGO, which provides the rapid transmission of electrons in N- $SWC/SnO_x(a)$ rGO film. Fig. 4d presents the cycling performances of rGO, SWC, N-SWC, N-SWC/SnO_x, and N-SWC/SnO_x@rGO film at 0.1 A g⁻¹ to cycle 100 cycles. The N-SWC/SnO_x@rGO film maintains a discharge capacity of 572.2 mA h g⁻¹ after 100 cycles with high Coulombic efficiency of ~99.8 %, which is significantly higher than rGO (22.7 mA h g⁻¹), SWC (97.2 mA h g⁻¹) N-SWC (115.1 mA h g⁻¹) and N-SWC/SnO_x (488.6 mA h g⁻¹). It should be noted N-doped improves the conductivity of carbon matrix and the cycle stability of film [48]. Fig. 4e shows the discharge-charge voltage cycles of N-SWC/SnO_x@rGO film. As can be seen, N-SWC/SnO_x@rGO film shows the Coulombic efficiency of 84.1 %, a charge capacity of 984.0 mA h g⁻¹, and discharge capacity of 1169.9 mA h g⁻¹. Notably, the discharge-charge curves almost overlap from the 10 to 100 cycles, indicating that N-SWC/SnO_x@rGO film has excellent cycle stability. The Coulombic efficiency of N-SWC/SnO_x@rGO film fluctuation range is ~99.1-100.1% (Fig. 4f), which indicates that the N-SWC/SnO_x@rGO film has a relatively stable and high Coulombic efficiency. To further illustrate the cycle stability of SWC, N-SWC/SnO_x and N-SWC/SnO_x@rGO film, SIB half cell was cycled at a high current of 1 A g⁻¹ for 1000 cycles, as plotted in Fig. 4g. The reversible capacity of N-SWC/SnO_x@rGO film can still be maintained at 473.1 mA h g⁻¹, and the Coulombic efficiency is up to 99.3%. For comparison, the reversible capacity of N-SWC/SnO_x@rGO is 195.9 mA h g⁻¹ after 1000 cycles, and that of SWC is only

77.0 mA h g⁻¹ after 724 cycles. It should be noted that due to the impact of high current density 1 A g⁻¹, some SnO_x particles were separated from the carbon fiber surface, which could provide more Na⁺ active sites and resulting in the improvement of electrochemical performance. The separated SnO_x particles are easier to break, so the electrochemical performance shows a downward trend in 250 to 350 cycles. At high current density, the activation system of N-SWC/SnO_x@rGO film will be more violent, and the subsequent side reactions are easier to increase the capacity. Therefore, films with high current density may have higher sodium storage capacity than those with low current density. However, after several subsequent cycles, the side reactions will be reduced and the capacity of the film tends to be stable.



Fig. 4. CV curves of SWC (a) and N-SWC/SnO_x@rGO film (b) in the range of $0.01 \sim 3.0$ V at 0.1 mV s⁻¹; (c) Cycle curves of SWC, N-SWC/SnO_x and N-SWC/SnO_x@rGO film at $0.05 \sim 2$ A g⁻¹; (d) Cycling behavior of rGO, SWC, N-SWC, N-SWC/SnO_x and N-SWC/SnO_x@rGO film at 0.1 A g⁻¹ for 100 cycles; (e) The charge and discharge curve of N-SWC/SnO_x@rGO film at 0.1 A g⁻¹; (f) Coulombic efficiency of N-SWC/SnO_x@rGO film; (g) Cycling stability of SWC, N-SWC/SnO_x and N-SWC/SnO_x@rGO film over 1000 cycles;

SIB half cell was further coupled to test the internal resistivity of SWC, N-SWC/SnO_x and N-SWC/SnO_x@rGO film, and the results are displayed in **Fig. 5a.** Obviously, the ohmic resistance of N-SWC/SnO_x@rGO film is smaller than that of SWC and N-SWC/SnO_x, indicating that N-SWC/SnO_x@rGO film has a faster electron transport mechanism. This is mainly attributed to the fact that carbon fiber conductive network and rGO provides an efficient electron transmission channel for the whole N-SWC/SnO_x(a)rGO film. Fig. 5b shows the Nyquist plots of N-SWC/SnO_x@rGO film before, after 100th, after 300th, and after 1000th cycles. As can be seen, N-SWC/SnO_x@rGO film has smaller impedance before cycles, and the impedance increases gradually with increasing cycling numbers. The film has a similar radius of medium and high frequency after 300th and 1000th cycles, indicating that the resistance change range of the film after multiple cycles is small. This is mainly derived from the double-layer electron running channel that greatly increases the transmission rate of electrons in N-SWC/SnO_x@rGO film. Electrochemical properties of N-SWC/SnO_x@rGO film were compared with the reported values in Sn-based SIB anodes [6, 9, 17, 25, 49-56], as summarized in Fig. 5c and d. Cycling at the same current density of 1 A g⁻¹ (Fig. 5c), our N-SWC/SnO_x(a_r GO film shows higher specific capacity, ultra-stable cyclability and longer span-life. Even after different current density cycles (Fig. 5d), our N-SWC/SnO_x@rGO film still has excellent cycling performance when compared with the previous reports [24, 47, 49, 50, 57, 58].



Fig. 5. (a) Nyquist plots of SWC, N-SWC/SnO_x and N-SWC/SnO_x@rGO film; (b) Nyquist plots of N-SWC/SnO_x@rGO film before, after 100th, after 300th and after 1000th cycles; The cycle performance of N-SWC/SnO_x@rGO film is compared with the previously reported performance of Sn-based materials in terms of long cycle (c) and different current density cycles (d).

In order to deeply understand the electron/Na⁺ transport mechanism of N-SWC/SnO_x@rGO film, we schematically illustrated charge transports in Fig. 6a. The N-SWC/SnO_x@rGO film is composed of 3D carbon fiber network, and electrons can be effectively transported along the carbon fiber in the whole film. SnO_x nanoparticles are uniformly distributed on the surface of SWC, which can not only avoid the excessive agglomeration of the nanoparticles, but also rely on the carbon fiber for the rapid transmission of electrons between the particles. Meanwhile, N doping can also effectively disperse the agglomeration of nanoparticles and accelerate the electron transport between nanoparticles. Besides, the SWC network has enough voids to provide sufficient contact for the alloying reaction of Na⁺ in the electrolyte solution with SnO_x nanoparticles, thereby greatly accelerating the progress of the electrochemical reaction kinetics. For a single fiber structure, rGO is wrapped as an electronic layer, which effectively accommodate the volume change of SnO_x nanoparticles, avoids particle shedding, and maintains the integrity and stability of N-SWC/SnO_x@rGO film. The double-layer electron running channel formed by the combination of SWC and rGO, which provides conditions for the rapid transmission of electrons in N-SWC/SnO_x(a)rGO film. Fig. 6b shows the simulation diagram of N-SWC/SnO_x@rGO film during alloying reaction process. N-SnO_x nanoparticles are located between the double conductive electronic layer composed of SWC and rGO. Besides, N-doped improves the conductivity of SnO_x and increases the cycle stability of N-SWC/SnO_x@rGO film. In the charging process, Na^+ in the electrolyte is alloyed with N-SnO_x to form N-SWC/Na_aSn_b@rGO, thereby destroying the original crystal structure of SnO_x. It should be noted that flexible rGO can effectively accommodate the volume change of SnO_x and avoid crushing and shedding. In the discharging process, Na⁺ can be separated from N-SWC/Na_aSn_b@rGO to form N-SWC/SnO_x@rGO and re-enter the electrolyte solution, and some undeleted Na⁺ causes

irreversible loss of capacity, resulting in low coulomb efficiency of SIB for the first cycling. The prediction test of low current density can effectively improve the first coulomb efficiency of SIB.



Fig. 6. (a) Electron and Na⁺ transport mechanism of N-SWC/SnO_x@rGO film; (b) Simulation diagram of N-SWC/SnO_x@rGO film in alloying process.

To further verify the advantages of the double electron transport layer of N-SWC/SnO_x@rGO film, SEM images of the pristine film (**Fig. 7a**), after 100 cycles (**Fig. 7b**),

after 300 cycles (**Fig. 7c**) and after 1000 cycles (**Fig. 7d**) are compared. As can be seen, after cycling with different circles at 1 A g⁻¹, the skeleton of N-SWC/SnO_x@rGO film can remain intact, showing excellent cycle span-life. To observe the distribution of elements after cycling, EDS mapping was tested on the N-SWC/SnO_x@rGO film after 1000 cycles, as shown in **Fig. 7e-i**. Obviously, C, Sn, O and N elements are still uniformly distributed on the surface of SWC, indicating that the N-SWC/SnO_x@rGO film has excellent cycle stability. As well, the uniform distribution of Na element can not only prove the traces left by the charge and discharge process, but also show that N-SWC/SnO_x@rGO film has more contact sites for Na⁺, which can accelerate the reaction kinetics of SIB.



Fig. 7. (a-d) SEM images of N-SWC/SnO_x@rGO film before the cycle, after 100 cycles, after 300 cycles and after 100 cycles at 1 A g⁻¹; (e-i) The element mapping of N-SWC/SnO_x@rGO film after 1000 cycles.

As a potential cathode material, $Na_3V_2(PO_4)_3$ has the characteristic of rapid Na^+ diffusion and suitable potential platform, and can provide conditions for the marketization of SIB [59-61]. To further illustrate the practical value of our developed N-SWC/SnO_x@rGO film, SIB full cell is coupled by using Na₃V₂(PO₄)₃ cathode and N-SWC/SnO_x@rGO film anode, as shown in Fig. **8a.** Fig. 8b shows an optical photo of the assembled SIB full cell, which lights LED light, proving the practicability of the SIB full cell. Fig. 8c shows the rate capability of SIB full cell in the current range from 0.01 to 1 A g⁻¹. A discharge capacity of 1028.3, 655.4, 458.8, 273.8, 192.1, and 150.1 mA h g⁻¹ was obtained in SIB full cell at 0.01, 0.02, 0.05, 0.1, 0.5 and 1 A g⁻¹, respectively. When the rate is restored to 0.1, 0.05, and 0.02 A g⁻¹, the specific discharge capacity of SIB full cell can return to 225.5, 327 and 443.7 mA h g⁻¹, respectively. This result indicates that SIB full cell can withstand the impact of high current density and has strong structure stability. Fig. 8d shows the electrochemical behavior of SIB full cell after 100 cycles at 0.1 A g⁻¹. The specific capacity of SIB full cell hardly fluctuated after the fifth cycles, showing excellent cyclic behavior. A discharge capacity of 245.7 mA h g⁻¹ still can be reserved in SIB full cell after 100 cycles. As can be seen in Fig. 8e, the Coulombic efficiency of SIB full cell is as high as ~98-101%, indicating that it has excellent cycle stability. The cyclic performance of SIB full cell is compared with the previously reported SIB full cells at the same current 0.1 A g^{-1} [62-66], as shown in Fig. 8f. Our assembled SIB full cell shows higher specific capacity and more stable cyclic behavior.



Fig. 8. (a) Na₃V₂(PO₄)₃ (Cathode) *vs.* N-SWC/SnO_x@rGO film (Anode) was coupled; (b)Photos of LEDs lights lit by SIB full cell; (c) Cycle curves of SIB full cells at different current densities; (d) SIB full cell cycle 100 cycles at 0.1 A g⁻¹; (e) Coulombic efficiency of SIB full cell; (f) Comparison of the cyclic performance of our assembled SIB full cells with that reported previously.

4. Conclusion

In this study, a flexible N-SWC/SnO_x@rGO film was prepared by using freeze-drying and carbonization and used as a self-standing SIB anode. N-SWC/SnO_x@rGO film has a 3D carbon fiber conductive network that can promote electron transport in electrochemical reactions and shorten the distance of electron transfer. Moreover, rGO wrapped in the outer layer of the fiber can simultaneously accommodate the volume change of SnO_x nanoparticles to avoid the

shedding of SnO_x nanoparticles, and act as a channel for outer electron transport. Benefitting from the unique structure, N-SWC/SnO_x@rGO film as SIB half cell anode possesses a superior reversible capacity of 572.2 mA h g⁻¹ at 0.1 A g⁻¹ and prolong span-life over 1000 cycles. More importantly, SIB full cell exhibits a capacity of 245.7 mA h g⁻¹ over 100 cycles. This work not only shows a great useful of our products in portable electronic devices, but also provides inspiration for the preparation of Sn-based/biomass materials in SIB anodes with low-cost.

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Highlights

- Silk wadding-derived carbon was used as a conductive substrate.
- A flexible self-standing film for cost-effective has been proposed.
- Constructed a double-layer conductive system in the film.
- 473.1 mA h g⁻¹ reversible capacity after 1000 cycles has been realized.

TOC

