Nano-SnO₂ Decorated Carbon Cloth as Flexible, Self-supporting and Additive-Free Anode for Sodium/Lithium-Ion Batteries

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Received: 28 September 2019 / Revised: 24 October 2019 / Published online: 14 January 2020
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Abstract

In this study, nano-sized SnO₂ decorated on carbon cloth (SnO₂/CC) is prepared through a simple and facile solid method. The nano-sized SnO₂ is uniformly distributed on the surface of carbon fibers in carbon cloth, providing sufficient free space to relieve volume expansion and reduce electrode pulverization during cycling. The as-prepared SnO₂/CC as a flexible, self-supporting and additive-free anode electrode for sodium-ion/lithium-ion batteries (SIBs/LIBs) can demonstrate outstanding electrochemical performance. SnO₂/CC after annealing at 350 °C (SC-350) as an anode for SIBs can deliver a reversible capacity of 0.587 mA h cm⁻² at the current density of 0.3 mA cm⁻² after 100 cycles. In addition, when cycling at 1.5 mA cm⁻², SC-350 can maintain 1.69 mA h cm⁻² after 500 cycles when used as LIB anode. These results illustrate that the as-prepared SnO₂/CC can be a promising flexible anode material for flexible SIBs/LIBs and provide a simple and practical method for designing new flexible electrode materials.

Keywords Flexible carbon cloth · SnO₂ coating · Sodium/lithium-ion batteries

Available online at <http://link.springer.com/journal/40195>.

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s40195-020-01001-7>) contains supplementary material, which is available to authorized users.

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1 Introduction

Nowadays, increasing developments of flexible electronics such as roll-up displays, wearable devices and touch screens, are creating a new era to improve our quality of life [1]. It is convenient for the flexible electronics with diverse functions to have high power efficiency. Among different energy storage systems, flexible batteries have drawn the attention of a lot of scientists due to their high flexibility, high energy density, excellent rate performance, outstanding cycle stability and so on [2–5]. In addition, there are some prototypes of flexible batteries in the market; for example, Philips propounds flexible smartphone looking like a slim strap that can be wrapped around the wrist and become a bracelet for the fashion conscious.

Among various battery systems, lithium-ion batteries (LIBs) with high energy density, high operating voltage and long cycling performance are ideal flexible energy storage systems [6, 7]. However, there is limited lithium resource in the earth crust, where content is only 0.0065% [8, 9]. To date, lithium-ion batteries are widely used in smartphone, electric vehicles (EVs) and other fields, which increase the demand of LIBs causing the price of lithium to skyrocket [10–13]. Therefore, it is urgent to develop new battery

systems with low cost and excellent performance to replace LIBs. Sodium and lithium are in same main group and are both alkali metal elements. Sodium resource is more abundant than lithium, and sodium has similar physicochemical properties compared with lithium. Hence, sodium-ion batteries (SIBs) have been regarded as promising candidates for LIBs, which have been given abroad attention for researchers. Flexible sodium-ion batteries with high energy and power density have broad application prospects in the future, such as flexible electronic displays and wearable devices. In addition, in order to meet the demands of the versatile design, it is necessary for the flexible batteries to have high mechanical strength. Among numerous flexible materials, carbon cloth is one of the most available materials which have remarkable mechanical strength, flexibility and conductivity [14–16]. Carbon cloth making up of crisscross carbon fibers is easily obtained by carbonization of cotton cloth. Cotton cloth consisted of cellulose, which is one of the most natural, biodegradable and renewable polymers. Carbon cloth not only has excellent wettability of electrolyte, but also can be directly used as electrode without binder and super carbon [17–19]. However, pure carbon cloth as an anode for SIBs/LIBs does not have a higher specific capacity compared with graphite (372 mA h g⁻¹ for LIBs). So it is necessary to modify the pure carbon cloth to attain excellent electrochemical performance. Generally, there are many ways to modify carbon cloth, such as doping sulfur, nitrogen and phosphorus heteroatoms [20], pore formation [21] and compounding with electrochemically active substances [22]. For example, Lü et al. [23] prepared flexible P-doped carbon cloth as an anode for sodium-ion batteries by a vacuum-sealed doping technology, delivering outstanding rate capability and high first coulombic efficiency of ~72%. Zhang et al. [20] reported nitrogen dual-doped porous carbon fibers as LIBs anodes, showing a high reversible areal capacity of 4.55 mA h cm⁻² at a current density of 1 mA cm⁻² and outstanding cycling performance in which capacity retention was 97.32% after 200 cycles. Gu and co-worker [24] synthesized three-dimensional (3D) TiO₂ nanotubes on carbon cloth through ALD deposition, revealing a higher charge capacity of 320 mA h g⁻¹ at 0.2 C and a capacity retention of 85.1% after 150 cycles at 0.25 C. Although the electrochemical performance of modified carbon cloth has been improved, there is no material exhibiting ideal properties with long cycling stability and high rate property. Therefore, it is important to design a reasonable structure to achieve excellent properties.

Among all kinds of anode materials, tin-based materials with high theoretical capacities and low price have been intensively investigated. For instance, Sn with a theoretical specific capacity of 847 mA h g⁻¹ can be used as excellent anode material for SIBs [25]. However, tin-based materials suffered from large volume expansion and solid electrolyte

interphase (SEI) is unstable causing them to lose electrochemical activity during charge/discharge processes [26–28]. There are many methods to solve these problems, such as building 3D carbon networks [29], preparing nanostructures [30] and constructing special shapes [31] like honeycomb [32–34]. Xu and co-workers [35] reported a Sn₄P₃-P@Graphene nanocomposite via a mechanochemical method as SIBs anode, which delivered a reversible capacity of ~585 mA h g⁻¹ at a current density of 2 A g⁻¹ and a high specific capacity of 607 mA h g⁻¹ at 1 A g⁻¹ after 800 cycles. Yang et al. [36] synthesized amorphous Sn₂P₂O₇/reduced graphene oxide nanocomposite through ball-milling method which achieved a high reversible capacity of 150 mA h g⁻¹ after 15,000 cycles at 2 A g⁻¹ and exhibited a high specific capacity of 480 mA h g⁻¹ at a current density of 0.05 A g⁻¹ and superior rate property of 250 and 165 mA h g⁻¹ at 2 and 10 A g⁻¹, respectively. Qu et al. [37] designed layer-structured SnS₂-reduced graphene oxide (SnS₂-RGO) nanocomposites, which had a high reversible capacity of 630 mA h g⁻¹ at 0.2 A g⁻¹, and more impressively, 544 mA h g⁻¹ after a ten-fold increase in a current density of 2 A g⁻¹. Although these strategies have relieved the volume expansion of tin-based materials to some extent, tin-based materials with flexible, self-supporting and additive-free are rarely reported. Tin-based materials loaded on the carbon cloth as anode for SIBs can not only increase the capacity and alleviate the volume expansion, but also reduce the usage amount of binders and super carbon to cut down the cost of practical application.

Herein, we have designed nano-sized SnO₂ decorated on the carbon cloth (SnO₂/CC) via a simple solid-phase method. Nano-SnO₂ particles are uniformly distributed on the surface of carbon fibers. On the one hand, carbon cloth provides 3D conductive network; on the other hand, there is sufficient free space on carbon fibers which relieve volume expansion and reduce electrode pulverization. The as-prepared materials can be directly used as anodes for SIBs/LIBs without binder and super carbon, and deliver outstanding electrolyte wetting to promote the transportation of Na⁺/Li⁺. When used as potential flexible anodes for SIBs/LIBs, the as-prepared SnO₂/CC reveals outstanding cycling performance and superior rate capability due to its unique structure. SC-350 as an anode for SIBs can show a reversible areal capacity of 0.587 mA h cm⁻² at the current density of 0.3 mA cm⁻² after 100 cycles. And when used as LIBs anodes, a reversible areal capacity of 1.88 mA h cm⁻² can be obtained even at 3 mA cm⁻².

2 Experimental

2.1 Materials

All raw materials are of analytical grade (Sigma-Aldrich) and are used as received without further purification,

including stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 99%) and hydrochloric acid (HCl, 36%).

2.2 Preparation of SnO_2/CC

As shown in Fig. 1, SnO_2/CC was prepared by a simple and facile solid-phase method. First, commercially available cotton cloth as raw material was carbonized at 1300°C for 3 h in argon atmosphere to obtain carbon cloth. Second, 20 mL 0.8 mol L^{-1} stannous chloride hydrochloride solutions were configured. Third, the solution was added to the carbon cloth and dried in an oven at 60°C for 5 times. Forth, the samples were annealed at 300, 350, 400 and 450°C for 3 h at the heating rate of 5°C min^{-1} in Ar atmosphere to obtain SnO_2/CC at different temperatures, named SC-300, SC-350, SC-400 and SC-450, respectively.

2.3 Material Characterization

The crystal structure of the materials was investigated by X-ray diffraction (XRD) on Rigaku Smart Lab X-ray diffractometer ($\text{Cu-K}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$, current: 30 mA, voltage: 40 kV) in the 2θ range of $5\text{--}80^\circ$. Thermal stabilities of the materials were tested by the thermogravimetric (TG, American TA Instruments, Q500) analysis at the heating rate of $10^\circ\text{C min}^{-1}$ from 25 to 800°C in air atmosphere. The scanning electron microscope (SEM, HITACHI SU8010, 20 kV) and transmission electron microscope (TEM, 2100Plus Electron Microscope) were used to characterize the morphology and microstructure of all the samples. Raman spectra of all the samples were measured on an Aramis system (Jobin–Yvon) with an incident laser light of 488 nm wavelength.

2.4 Electrochemical Measurements

Electrochemical properties of the materials were measured by assembling 2032 coin-type cells with sodium/lithium foil as the counter electrodes. The diameter of work and counter electrodes is 1.2 cm and area is 1.13 cm^2 , and the corresponding mass of each work electrode is $\sim 7 \text{ mg}$. The half-cells were assembled in a glovebox filled with high-pure argon where the concentrations of water and oxygen are below 0.1 ppm. The glass fiber from Whatman was used as separator, and the electrolytes were 1 M NaClO_4 in ethylene carbonate (EC, $\text{C}_3\text{H}_4\text{O}_3$) and propylene carbonate (PC, $\text{C}_4\text{H}_6\text{O}_3$) in a volume ratio of 1:1 with 5% fluoroethylene carbonate (FEC, $\text{C}_3\text{H}_3\text{FO}_3$) as additive and 1 M LiPF_6 in ethylene carbonate (EC, $\text{C}_3\text{H}_4\text{O}_3$) and dimethyl carbonate (DMC, $\text{C}_3\text{H}_6\text{O}_3$) with a volume ratio of 1:1. In order to ensure that the electrolyte penetrated well into all voids in the electrodes and separators, the coin cells needed to be rested for at least 8 h before testing electrochemical performance. For full cells, $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{O}_2\text{F}$ (NVPOF) was used as cathode instead of Na foil. And the slight excess capacity of anode compared with cathode was 1.4 (SC-350: NVPOF = 1.4). There was a pre-sodiation process for SC-350 before assembling full batteries. The battery test systems (LAND CT2001A) were used to measure the galvanostatic charge–discharge (GCD) tests of SnO_2/CC at 25°C . Cyclic voltammetry (CV) curves of SC-350 were tested on Versa STAT 3 (Princeton Applied Research) in a potential window of 0.01–2.5 V versus Na^+/Na at various scanning rates of 0.1, 0.2, 0.3, 0.5, 0.7 and 1 mV s^{-1} .

Fig. 1 Preparation procedures of SnO_2/CC anode

3 Results and Discussion

As shown in Fig. 1, the SnO₂/CC was prepared via a simple method. The commercially cotton cloth was used as the raw material. After carbonized at 1300 °C for 3 h in Ar atmosphere, cellulose in cotton cloth is completely converted into carbon and water ($(C_6H_{10}O_5)_n \rightarrow 6nC + 5nH_2O$) and the carbon cloth still shows flexibility as seen in Fig. S1. The conductivity of the carbon cloth is better than cotton cloth, and there are more sodium storage activity sites in carbon cloth. After drying, SnCl₂ is loaded on carbon fibers. During annealing process, SnCl₂ will gradually become SnO₂ and HCl, and SnO₂ is homogeneously loaded on the surface of the carbon cloth. The as-prepared SnO₂/CC is a highly flexible and self-standing electrode without binder for SIBs/LIBs. It is worth noting that cotton cloth is one of renewable biomass, which guarantees the possibility and sustainability of the currently proposed SnO₂/CC as a large-scale application for SIBs anodes.

Figure 2a displays the XRD patterns of the SnO₂/CC, in which all the peaks are consistent with the SnO₂ phase (PDF #72-1147, space group, P42/mnm), confirming that the SnO₂/CC in this work was successfully prepared. For SnO₂, the diffraction peaks located at 26.6°, 33.9° and 51.8° could be assigned to the (110), (101) and (211). As the annealing temperature increases, the nanocomposites remain SnO₂, indicating that the annealing temperature has no effect on the crystal form of SnO₂. In order to further confirm the content of SnO₂, the TG tests were performed and the results are shown in Fig. 2b. Carbon cloth decomposes at about 550 °C and turns into CO₂ in the air and all the samples also decompose at about 550 °C displaying that carbon cloth converts into CO₂. The SnO₂ content (sc) in SnO₂/CC decreases first and then increases with the annealing temperature increasing, and

when the annealing temperature is 400 °C, the SnO₂ content is the highest. It clearly observed the defect-induced band (D-band, 1350 cm⁻¹) and crystalline graphite band (G-band, 1584 cm⁻¹) in the Raman spectra as shown in Fig. S2 [38–40]. The intensity ratios between D-band and G-band (viz., I_D/I_G) are 1.128, 1.102, 1.070, 1.027 and 1.031 for CC, SC-300, SC-350, SC-400 and SC-450, respectively [41]. This further confirms the amorphous characteristics of the as-prepared SnO₂/CC.

In order to further characterize the morphology of the materials, SEM and TEM tests were performed. Figure 3 displays the morphology of SC-350. As shown in Fig. 3a, nano-sized SnO₂ is evenly distributed on the surface of carbon fibers, which is similar to the morphologies of SC-300, SC-400 and SC-450 (Fig. S3). From Fig. S3, it is noted that the distribution of SnO₂ nanoparticles on carbon fibers for SC-300, SC-400 and SC-450 is uniform, but the free space between each SnO₂ nanoparticle is less than that in SC-350. In addition, it is clear that the sizes of SnO₂ nanoparticles in different samples are not the same. By counting the sizes of 200 nanoparticles, it can be found that the nanoparticle sizes of SnO₂ are about 61.58, 23.62, 50.68 and 53.82 nm for SC-300, SC-350, SC-400 and SC-450, respectively. Compared to other samples, the nanoparticle size of SC-350 is smallest, revealing that there is a gap between each SnO₂ nanocrystal, which provides sufficient free space to facilitate sodium storage and reduce electrode pulverization during charge/discharge. Figure 3b is TEM image of SC-350 and inset is high-resolution TEM (HRTEM). It can be clearly observed the crystal lattice of SnO₂ in Fig. 3b, which belongs to the crystal face (110), consistent with XRD patterns in Fig. 2a. The TEM images of the other samples are displayed in Fig S3. It is noted that the crystal lattice of SnO₂ in other samples is similar to SC-350 and crystal plane spacing is 0.35 nm which is consistent with XRD patterns in Fig. 2a. In addition, the element composition

Fig. 2 Structure characterizations: **a** XRD patterns, **b** TG curves of CC, SC-300, SC-350, SC-400 and SC-450 (sc is the abbreviation of SnO₂ content)

Fig. 3 **a** SEM images of SC-350; **b** TEM and HRTEM (inset) images of SC-350; **c–f** SEM images and the corresponding element mappings of SC-350; **g** the optical photograph of SC-350

and distribution of the as-prepared SnO_2/CC were further investigated by energy-dispersive X-ray (EDAX) element mapping. Figure 3c–f shows that carbon, tin and oxygen in the materials are uniformly distributed, which is also consistent with the XRD patterns analysis. Figure 3g is the optical photograph of SC-350, showing the materials are highly flexible electrodes.

To measure the electrochemical performance of the as-prepared SnO_2/CC electrode materials as SIBs anode, the rate and cycle properties were tested and displayed in Fig. 4. The rate properties of SC-300, SC-350, SC-400 and SC-450 as SIBs anode are shown in Fig. 4a, implying that SC-350 has more outstanding rate performance than SC-300, SC-400 and SC-450. SC-350 exhibits charge capacities of 0.86, 0.67, 0.57, 0.50, 0.46, 0.32 and 0.18 mA h cm^{-2} at 0.15, 0.3, 0.45, 0.6, 0.75, 1.5 and 3 mA cm^{-2} , respectively. And when the current density returns to 0.15 mA cm^{-2} , there is still a specific capacity of 0.84 mA h cm^{-2} , which indicates that the SC-350 has better rate performance. The cycling performances of SC-300, SC-350, SC-400 and SC-450 as SIBs anode are shown in Fig. 4b. The result shows that the SC-350 has better cycling performance than

other materials at the current density of 0.3 mA cm^{-2} . After 100 cycles, there is still 0.587 mA h cm^{-2} at 0.3 mA cm^{-2} for the SC-350 while carbon cloth demonstrates a reversible capacity of 0.252 mA h cm^{-2} after 100 cycles. To gain a better understanding of the cycle life of SC-350, we have tested the long cycling performance of SC-350. As displayed in Fig. 4c, when cycled at 0.75 mA cm^{-2} , the specific capacity has still maintained 0.379 mA h cm^{-2} and has a capacity retention of 83.11% after 500 cycles with the decay of 1.54×10^{-4} mA h cm^{-2} and 0.034% per cycle, respectively. The charge/discharge curves of different current densities of SC-300, SC-350, SC-400 and SC-450 in a potential window of 0.01–2.5 V versus Na/Na^+ are displayed in Fig. S4. As shown in Fig. S4, there is a clear slope above 0.1 V and a plateau below 0.1 V, indicating that median voltage of the material is low and is an ideal anode material. In addition, it can be found that the slope above 0.1 V in SC-350 is much clearer and can offer more capacity in sodium storage than the others. According to previous reports, the slope may belong to the alloying reactions of Sn. On the basis of these results, we conclude that SC-350 has better rate and cycling properties and is an ideal anode material for SIBs.

Fig. 4 **a** Rate capabilities of SC-300, SC-350, SC-400 and SC-450 at various current densities from 0.15 to 3.0 mA cm⁻²; **b** cycling performance of CC, SC-300, SC-350, SC-400 and SC-450 at a current density of 0.3 mA cm⁻²; **c** Cycling performance of SC-350 at 0.75 mA cm⁻²

To achieve a better understanding of the electrochemical reactions of SC-350 during the charge/discharge processes, we adopted the SC-350 as an anode active material to assemble Na-half-cells and carried out cyclic voltammetry (CV) test. Figure 5a shows the CV curves of the SC-350 material at a scanning rate of 0.1 mV/s with the potential window from 0.01 to 2.5 V (vs. Na⁺/Na). As shown in Fig. 5a, there is a clear oxidation peak at 0.992 V during desodiation due

to sodium tin dealloying reaction [42–44]. And the oxidation peak at 0.201 V is Na⁺ deintercalation into carbon cloth. In addition, there is an irreversible reduction peak at 1.028 V in the first cycle of CV curves, which is caused by the formation of SEI [45, 46]. Figure 5b shows the first three galvanostatic profiles of the SC-350 at a current density of 0.15 mA cm⁻² over the potential window of 0.01–2.5 V (vs. Na⁺/Na). From Fig. 5b, we can conclude the better cycling

Fig. 5 **a** CV curves of the initial three cycles at a scanning rate of 0.1 mV/s; **b** the first three galvanostatic profiles of SC-350 at a current density of 0.15 mA cm⁻²

performance owing to the good coincidence of second and third circles. It is a large irreversible capacity in the first cycle, which is due to the formation of SEI in the anodes. This is consistent with the CV curves.

In order to deeply investigate the sodium storage mechanism and kinetic performance of the SC-350, the CV curves at a series of scanning rates from 0.1 to 1 mV/s were obtained. The result is shown in Fig. 6, indicating that the peak current of the SC-350 is not proportional to the square root of the scan rate which means that the electrochemical process of the material has faradic and non-faradic processes [47].

$$i = av^b, \quad (1)$$

$$\log(i) = b\log(v) + \log(a), \quad (2)$$

where a and b are tunable parameters. As $b = 0.5$, the electrochemical process of materials is mainly controlled by diffusion; as $b = 1$, the electrochemical process of materials is mainly controlled by pseudocapacitive behavior. According to Fig. 6a, we can find that there are three redox peaks during cycling. And Fig. 6b displays $\log(i)$ versus $\log(v)$ plots of SC-350 at three redox peaks and the slope of the plot is b -value. The b -values of SC-350 are 0.67, 0.78 and 0.69 at peak 1, peak 2 and peak 3, respectively. From the results, we can conclude that the electrochemical process of the SC-350 is controlled by diffusion and pseudo capacitive behavior.

The lithium storage performance of the SC-350 was also studied. The rate performance of the as-prepared SC-350 is shown in Fig. 7a. According to Fig. 7a, we can find that the 3rd charge capacities are 2.85, 2.59, 2.42, 2.30, 2.27, 2.13 and 1.88 mA h cm⁻² at different current densities of 0.15, 0.3, 0.45, 0.6, 0.75, 1.5 and 3 mA cm⁻², respectively. Even at 3 mA cm⁻², SC-350 still has a reversible capacity of 1.88 mA h cm⁻², far higher than pure carbon cloth (0.55 mA h cm⁻² at 3 mA cm⁻²). In addition, when

the current density returns to 0.15 mA cm⁻², the charge capacity of SC-350 is back to 2.61 mA h cm⁻², while the pure carbon cloth only obtains a lower reversible capacity of 0.894 mA h cm⁻². The results reveal that SC-350 has better rate performance. The outstanding rate performance of SC-350 is due to the gap between SnO₂ particles and nano-sized particles which are contributed to lithium-ion diffusion. Figure 7b shows the charge/discharge curves of SC-350 at various rates, revealing a slop capacity contribution. The charge/discharge curves of cloth carbon at different current densities are displayed in Fig S5. It can be found that there are differences between the two charge/discharge curves, revealing different electrochemical reactions. In order to study the mechanism of SC-350 as LIBs anode, the CV was tested by Versa STAT 3 in a voltage window of 0.01–2.5 V versus Li/Li⁺ at 0.1 mV s⁻¹. There are two clear reduction peaks at 0.796 and 0.093 V in the first cycle. The two peaks can be attributed to the SnO₂ decomposition into metal Sn and Li₂O and the formation of tin-lithium alloy, and formation of SEI, respectively [46]. The first oxidation peak at 0.523 V represents the Li-ion deintercalation into carbon cloth and the oxidation peaks at 1.242 V and 1.761 V can ascribe to the reversible formation of the Li_xSn [42, 43]. The second and third circles of the CV curves are coincidence, indicating that SC-350 has a splendid cycling performance. Figure 7d displays the first three galvanostatic charge/discharge voltage profiles of the SC-350 used as LIBs at 0.15 mA cm⁻² under a potential window of 0.01–2.5 V (vs. Li/Li⁺). The first cycle discharge and charge capacities are 4.38, 3.10 mA h cm⁻² and the first coulombic efficiency is 70.79%, demonstrating that there is a large irreversible capacity loss to be ascribed to the formation of SEI on the electrode surface at a low voltage. To further explore the long cycling performance of SC-350, the long-term cycling was tested at 1.5 mA cm⁻² for LIBs. As displayed in Fig. 7e, when cycled at 1.5 mA cm⁻², there is still 1.69 mA h cm⁻²

Fig. 6 **a** CV curves of the SC-350 at different scanning rates from 0.1 to 1 mV/s; **b** $\log(i)$ versus $\log(v)$ plots for the SC-350

Fig. 7 Electrochemical properties of SC-350: **a** rate performance; **b** galvanostatic profiles at various current densities of 0.15, 0.3, 0.45, 0.6, 0.75, 1.5 and 3 mA cm⁻²; **c** CV curves of the initial three cycles at a scanning rate of 0.1 mV/s; **d** the first three galvanostatic profiles at the current density of 0.15 mA cm⁻²; **e** cycling performance at 1.5 mA cm⁻²

after 500 cycles with the decay of 8.8×10^{-4} mA h cm⁻² and 0.041% per cycle, respectively.

To gain more insight mechanical properties of SC-350 in sodium-ion half-cells after cycling, the morphological and structural changes in SC-350 after 500 cycles were tested using XRD and SEM. As can be seen from Fig. 8a, it is obvious that the diffraction peaks are indexed to the Sn phase (PDF#65-2631), suggesting that SnO₂ is converted into Sn ($\text{SnO}_2 + 4\text{Na}^+ + 4\text{e}^- \rightarrow 2\text{Na}_2\text{O} + \text{Sn}$), and then, Sn and Na react to form tin-sodium alloy ($\text{Sn} + n\text{Na}^+ + \text{ne}^- \rightarrow \text{Na}_n\text{Sn}$) during charge/discharge processes. And this is consistent with the observation from the results of CV curves.

Figure 8b shows SEM images of SC-350 after 500 cycles in sodium-ion half-cells. From Fig. 8b, c, it is clear that the electrode remains flexible and Sn nanoparticles are evenly distributed on the surface of carbon fibers, indicating this structural design can effectively alleviate the volume expansion of Sn and be used as an excellent negative electrode material. In addition, we also study the morphological changes of SC-350 in lithium-ion half-cells after 500 cycles. The SEM image is shown in Fig. S6, demonstrating that SC-350 still has flexibility.

In order to study the practical application of SC-350, we fabricated sodium-ion full cells with the Na₃V₂(PO₄)₂O₂F

Fig. 8 SC-350 electrodes after 500 cycles in sodium-ion half-cells: **a** XRD pattern; **b** SEM image; **c** optical photographs

(NVPOF) as cathode material [48]. The XRD pattern and SEM image of NVPOF are shown in Fig. S7, suggesting that NVPOF with nano-tetraprism in shape is successfully synthesized. As displayed in Fig. S8, the rate and cycling capabilities of NVPOF are tested in half-cells, indicating the representative properties with the previous reports. The theoretical capacity of NVPOF is 130 mA h g^{-1} . The rate capability in Fig. S8a displays that the reversible capacities of NVPOF are 129.2, 123.8, 118.1, 111.4, 100.6, 87.9 and 64.4 mA h g^{-1} at 0.2, 0.5, 1, 2, 5, 10 and 20 C, respectively.

When the current density returned to 0.2 C, the discharge capacity is 129 mA h g^{-1} , suggesting that the cathode material has better rate capability. Figure S8c shows cycling performance of NVPOF in half-cells, delivering a discharge capacity of $110.9 \text{ mA h g}^{-1}$ with a capacity retention of 92% at 1 C after 100 cycles. Figure 9a shows charge/discharge curves of NVPOF and SC-350 in the Na-ion half-cells at 0.2 C and 20 mA g^{-1} ($\sim 0.15 \text{ mA cm}^{-2}$), and Fig. 9b shows the rate performance of SC-350/NVPOF full cells under a potential window of 2.0–4.3 V (vs. Na/Na⁺). As we can

Fig. 9 **a** Charge/discharge curves of NVPOF and SC-350 in the Na-ion half-cells at 0.2 C and 20 mA g^{-1} ($\sim 0.15 \text{ mA cm}^{-2}$); **b** Rate performance of SC-350/NVPOF full cells. **c** Cycling performance of SC-350/NVPOF full cells

see, the 3rd discharge capacities of SC-350/NVPOF full cells are 120.53, 118.43, 113.63, 96.76, 73.53, 54.29 and 42.21 mA h g⁻¹ at 0.2, 0.5, 1, 2, 5, 10 and 15 C, respectively. The inset in Fig. 9b is the charge/discharge curves of SC-350/NVPOF full cells and shows two voltage plateaus at about ~3.47 V and 2.88 V. As shown in Fig. 8c, the SC-350/NVPOF full cell displays excellent cycling performance at 1 C, which is still 80.68 mA h g⁻¹ after 100 cycles with the decay of 0.3307 mA h g⁻¹ and 0.29% per cycle, respectively. According to these results, SC-350 as SIBs anode shows brilliant rate and cycling performance in full cells, indicating its potential for practical application.

4 Conclusion

In summary, we show a simple repeatable method to prepare a flexible nano-sized SnO₂ decorated carbon cloth anode material. Nano-sized SnO₂ is evenly loaded on the surface of carbon fibers which is beneficial to relieve volume expansion. Compared with pure carbon cloth, SC-350 reveals splendid electrochemical performance as SIBs/LIBs anode. For instance, SC-350 manifests 0.86 mA h cm⁻² at 0.15 mA cm⁻² and maintains 0.379 mA h cm⁻² after 500 cycles at 0.75 mA cm⁻². In addition, SC-350 used as anode materials for LIBs displays 1.88 mA h cm⁻² at 3 mA cm⁻² and maintains 1.69 mA h cm⁻² after 500 cycles at 1.5 mA cm⁻². After matching with NVPOF to sodium-ion full batteries, there is still 80.68 mA h g⁻¹ after 100 cycles at 1 C, revealing its potential application. In brief, the as-prepared SnO₂/CC anode is a simple synthesis method with excellent Na/Li storage performance, suggesting great potential in practical application of flexible LIBs/SIBs.

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (No. 91963118) and the Fundamental Research Funds for the Central Universities (No. 2412019ZD010).

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