Amorphous SnO$_2$/graphene aerogel nanocomposites harvesting superior anode performance for lithium energy storage

Linlin Fan$^{a,b,1}$, Xifei Li$^{a,*}$, Bo Yan$^{a,1}$, Xiaojia Li$^{a,1}$, Dongbin Xiong$^{a,1}$, Dejun Li$^{a,*,1}$, Hui Xu$^c$, Xianfa Zhang$^c$, Xueliang Sun$^{b,*,2}$

$^a$ Energy & Materials Engineering Centre, College of Physics and Materials Science, Tianjin Normal University, Tianjin 300387, China
$^b$ National Key Laboratory of Power Sources, Tianjin Institute of Power Sources, Tianjin 300381, China
$^c$ Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education & School of Chemistry and Material Science, Heilongjiang University, Harbin 150080, China
$^d$ Nanomaterials and Energy Lab, Department of Mechanical and Materials Engineering, Western University, London, Ontario N6A 5B9, Canada

**Highlights**

- The amorphous SnO$_2$/graphene aerogel were successfully synthesized.
- The nanocomposites showed high reversible capacity and cycling stability.
- The study exhibited an effective strategy for anode materials of LIBs.

**Abstract**

The Sn-based materials have been hindered from practical use for lithium ion batteries due to the inherent volume change leading to poor cycling performance. To mitigate this challenge, in this study, amorphous SnO$_2$/graphene aerogel nanocomposites are fabricated via a simple hydrothermal approach. The amorphous nature of SnO$_2$ is clearly determined in detail by transmission electron microscopy, aberration-corrected scanning transmission electron microscopy, and X-ray diffraction measurement. The as-prepared material shows satisfying reversible capacity and significant cyclic stability. For instance, it delivers an excellent discharge capacity of 700.1 mA h g$^{-1}$ in 80th cycle at a current density of 100 mA g$^{-1}$, in accordance with a high retention capacity of 97.6% compared to that of the sixth cycles, which is much better than crystalline SnO$_2$/graphene aerogel. The enhanced electrochemical performance can be ascribed to the intrinsic isotropic nature, smaller size, and high electrochemical reaction kinetics of amorphous SnO$_2$, together with the graphene aerogels matrix. Therefore, this study may provide an effortless, economic, and environmental friendly strategy to fabricate high volume change electrode materials for lithium ion batteries.

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1. Introduction

Rechargeable lithium ion batteries (LIBs) emblematize state-of-the-art technology in the field of the electrochemical energy storage systems because of high energy density and good electrochemical cycling performance [1,2]. For a long time, LIBs have received great attention for energy storage applications, such as portable consumer electronics (smartphones, camera and tablet computers), power tools (electric vehicles and hybrid electric vehicles) [3–5]. Unfortunately, the LIB development for these applications is still full of challenges since the issues such as costs, safety, materials availability, and environmental friendly are addressed [6]. Especially, although graphite has been ubiquitously employed as a commercial anode material, and it is expected to play a key role in the coming process of manufacturing advanced LIBs due to good cycling performance, however, its relatively low specific capacity of 372 mA h g\(^{-1}\), limited rate capability, and low density obstruct the development of LIBs [7,8]. So far, to circumvent these hurdles, metal, metal oxides, and a number of other potential materials with high theoretical reversible capacities, abundance, and non-toxic have recently received increasing attention as alternative anode materials for rechargeable LIBs, for instance, Si [9,10], Sn [11,12], SnO\(_2\) [13], CoO\(_2\) [14], SnO\(_2\) is a n-type wide-bandgap (\(E_g = 3.6\) eV) semiconductor [15], because of relatively high theoretical capacity (782 mA h g\(^{-1}\)) according to 4.4 Li per molecule and safe lithiation potential [16,17], SnO\(_2\) has been supposed to one of the most promising electrode materials for LIBs. However, it suffers a severe capacity fading originating from its severe agglomeration, poor electrical conductivity, and volume expansion during the processes of Li\(^+\) insertion/ extraction [13].

To mitigate the aforementioned challenges, one effective strategy has been proposed to conduct the SnO\(_2\) based nanocomposites. The matrix in the composite anodes reveals high electrical conductivity as well as great tolerance of volume change [18,19]. In view of this point, various carbon-based materials such as carbon nanotubes, graphene, and porous carbon are effective candidates enhancing battery performance of SnO\(_2\) anode. Notably, due to high surface area of over 2600 m\(^2\) g\(^{-1}\), conductance quantization, remarkable structural flexibility, ultrashort pathway for Li\(^+\), and excellent electrical conductivity [20–22], graphene have been receiving tremendous attention recently. For instance, the synthesized flexible nitrogen-doped graphene/SnO\(_2\) foams [23], the dually fixed SnO\(_2\) nanoparticles on graphene nanosheets by polyol coating [24], and the designed SnO\(_2\)-reduced graphene oxide composites [25] all show enhanced electrochemical performance as anodes in LIBs. More strikingly, it’s generally known that amorphous nanoparticles own intrinsic isotropic nature, which can effectively buffer volume changes upon cycling [26,27], guaranteeing the integrity of the structure and excellent electrochemical performance. For instance, amorphous porous TiO\(_2\)@nitrogen doped graphene nanocomposites were designed to deliver outstanding high rate performance, e.g., 182.7 mA h g\(^{-1}\) (the current density is 3.36 A g\(^{-1}\)) in 100th cycle [28]. Furthermore, McDowell et al. have illustrated that amorphous silicon compared to the crystalline can resist more efficiently the large volume modifications at least for spheres with 870 nm of diameter [29]. Based on above results, it is expected that amorphous SnO\(_2\) based nanocomposites could minimize the effect of volume expansion during discharge–charge processes and improve the lithium energy storage.

Hence, in this study, we rationally proposed a facile strategy for the fabrication of amorphous SnO\(_2\)/graphene aerogel nanocomposites via a hydrothermal approach. Intriguingly, benefiting from the synergistic effects of intrinsic isotropic nature of amorphous SnO\(_2\) as well as good matrix of graphene aerogels, the resultant amorphous SnO\(_2\)/graphene aerogel nanocomposites exhibit excellent electrochemical performance and great potential application when employed as anode materials for LIBs. For instance, it maintains a high energy capacity of 700.1 mA h g\(^{-1}\) in the 80th discharge cycle, which corresponds to 97.6% of the 6th discharge capacity. To the best of our knowledge, this value is amongst the better published in the literature, and the synthetic strategy can be an effective access for the synthesis of carbon-based metal oxides with controlled amorphous structure.

2. Experiments

2.1. Synthesis of the amorphous and crystalline SnO\(_2\)/graphene aerogel nanocomposites

Graphene oxide (marked GO) was first synthesized using the Hummers method, as previously reported by our group [30]. SnO\(_2\)/graphene aerogel (SnO\(_2\)/GA) nanocomposites were synthesized by a facile hydrothermal method using SnCl\(_2\) 2H\(_2\)O (Tianjin Fengchuan Chemical Reagent Science And Technology Co., Ltd., ≥98.0%) as a precursor and GAs as a carrier. Specifically, 39 mg GO in 60 ml ethylene glycol (EG, Tianjin Jiantian Chemical Technology Co., Ltd.) was dissolved in a beaker, followed by 30 min intense ultrasonication. After that, 60 mg SnCl\(_2\) 2H\(_2\)O dispersed in 60 ml EG was mixed with the GO contained-solution using peristaltic pump to form a uniform mixture. Then, the resulting solution was transferred to three 50 ml Teflon-lined stainless steel autoclaves and kept at 160 °C for 12 h. The products were obtained via centrifuging and sequentially washing with deionized water and ethanol for several times, and then freeze-dried. Finally, amorphous SnO\(_2\)/GA (a-SnO\(_2\)/GA) nanocomposites were obtained, while, crystalline SnO\(_2\)/GA (c-SnO\(_2\)/GA) nanocomposites were synthesized by calcination at 400 °C for 4 h under Ar atmosphere. Pristine GAs were produced via the same process as for a-SnO\(_2\)/GA except that no SnCl\(_2\) 2H\(_2\)O was added. Additionally, for comparison, the bare SnO\(_2\) was synthesized by a facile reflux method. SnCl\(_2\) 2H\(_2\)O was dissolved in 50 mL ethanol, followed stirring for 30 min. Subsequently, the mixed solution was transferred to the three flask filled with distilled water drop by drop, and stirred at 100 °C for 12 h with the reflux. The resultant gel was rinsed by ethanol and deionized water using a centrifuge. The final product was dried at 80 °C for 12 h, and the products were synthesized by subsequent calcination at 500 °C for 3 h in a muffle furnace.

2.2. Physical characterization

The X-ray diffraction patterns (XRD, DX-2700) of the products were obtained with CuK\(_\alpha\) radiation in a coupled 2\(\theta\) mode at room temperature. The results were recorded at the range of 10–80°. The morphology and structure of products were characterized with scanning electron microscope (SEM, SU8010, Hitachi), transmission electron microscope (TEM, JEOL-JEM-3000F), and aberration-corrected scanning transmission electron microscopy (STEM, JEOL ARM200F, Tokyo, Japan). The microscope was equipped with a CEDOS probe aberration corrector (CEOS, Heidelberg, Germany). The binding characteristics of the materials were conducted via X-ray photoelectron spectroscopy (XPS, VG SCALAB MK II) analysis. The graphene contents in the composites were performed via thermogravimetric analysis (TGA, Pyris Diamond6000 TG/DTA, PerkinElmer Co, America) at air ranging from room temperature to 800 °C. Raman spectra were recorded on LabRAM HR800.

2.3. Electrochemical performance

Electrochemical testing was evaluated with the coin cells (CR2032), they were assembled in a glove box filled argon, where
the oxygen and moisture contents were kept below 0.1 ppm. To obtain working electrodes, typically, active materials (80%), polyvinylidene fluoride (10%), and conductive carbon black (10%) were mixed in N-methyl-2-pyrrolidinone (NMP) solvent to form an uniform slurry and pasted onto Cu foil. Afterwards, they were dried at 80°C for 12 h via a vacuum oven. Then, the electrodes were punched into 12 mm disks in diameter, and the typical electrode loading was about 0.65 mg cm\(^2\). All the cells were galvanostatically discharged and charged ranging from 0.01 V to 3.0 V using the multi-channel Land battery test system (LANHE CT2001A). Cyclic voltammetry (CV) testing data were recorded by the Princeton Applied Research VersaSTAT4 at a scan rate of 0.1 mV s\(^{-1}\) in the voltage range of 0.01–3.0 V. The electrochemical impedance spectra (EIS) were measured in a frequency range from 100 kHz to 0.01 Hz with ac signal amplitude of 5 mV. All electrochemical characterizations were performed at room temperature.

3. Results and discussion

The phase structures of a-SnO\(_2\)/GA and c-SnO\(_2\)/GA are inspected by XRD. It can be seen from Fig. 1(a) that all the diffraction peaks of c-SnO\(_2\)/GA are in good accordance with the standard diffraction data of rutile structure of SnO\(_2\) (cassiterite, JCPDS No. 41-1445). Notably, there is no characteristic peak in a-SnO\(_2\)/GA except for the broad peak around 29–31°, confirming a typical nature of amorphous SnO\(_2\) successfully designed onto GAs. X-ray photoelectron spectroscopy (XPS) provides the chemical composition of a-SnO\(_2\)/GA in comparison to c-SnO\(_2\)/GA. One can see from the insets in Fig. 1(b) and (c), C, O and Sn are clearly detected, and no other elements exist in both nanocomposites. The high resolution C 1s XPS spectra of a-SnO\(_2\)/GA and c-SnO\(_2\)/GA can be deconvolved into four peaks: 284.7 eV for graphitic carbon, 286.4 eV for carbon in

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<th>C–C 284.7 eV (%)</th>
<th>C–O 286.4 eV (%)</th>
<th>C=O 287.8 eV (%)</th>
<th>O=O=O 289.0 eV (%)</th>
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<tbody>
<tr>
<td>a-SnO(_2)/GA</td>
<td>65</td>
<td>22</td>
<td>8</td>
</tr>
<tr>
<td>c-SnO(_2)/GA</td>
<td>81</td>
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The electrochemical impedance spectra (EIS) were measured in a frequency range from 100 kHz to 0.01 Hz with ac signal amplitude of 5 mV. All electrochemical characterizations were performed at room temperature.
epoxide groups (including C—O—C and C—OH), 287.9 eV for carbonyl carbon, 289.0 eV for carboxylate carbon [31]. Meanwhile, we quantify the peak area% in the C 1 s spectra of a-SnO2/GA and c-SnO2/GA, the values are presented in Table 1. Clearly, one can see that the total area% of oxygen-containing functional groups in a-SnO2/GA and c-SnO2/GA are estimated to be 35% and 19%, respectively, confirming that the GAs in c-SnO2/GA are further reduced after annealing process [32,33]. In Fig. 1(d), a pair of peaks of Sn 3d spectra appear at 495.8 and 487.0 eV associated with Sn 3d 3/2 and Sn 3d 5/2 spinorbit peaks of SnO2, demonstrating the formation of SnO2 nanoparticles in the composites [34]. As seen in Fig. 1(e), the Raman spectra of pristine GAs, a-SnO2/GA, and c-SnO2/GA show two peaks at 1348 cm\(^{-1}\) and 1602 cm\(^{-1}\), which are in good agreement with D band causing by the presence of graphitic carbon, respectively [35–37]. Compared to the pristine GAs, both SnO2/GA exhibit an increased intensity ratio (I_D/I_G), originating from a decrease of the size of sp\(^2\) domains and the defects generated by the insertion of SnO2 nanoparticles into GAs [38,39]. Thermogravimetric analysis (TGA) is employed to measure the SnO2 contents in a-SnO2/GA and c-SnO2/GA (Fig. 1(f)). The initial weight loss is associated with the desorption of moisture. According to the weight loss of GAs, the contents of SnO2 in a-SnO2/GA and c-SnO2/GA are calculated to be 51% and 55%, respectively.

Figs. 2 and S1 show the morphology characteristics of the synthesized a-SnO2/GA and c-SnO2/GA by SEM, TEM, and high-resolution HAADF-STEM images. Obviously, in Fig. 2(a), the amorphous SnO2 particles are homogeneously and firmly anchored on GAs matrix. Meanwhile, one can observe that the size of amorphous SnO2 particles is small. In addition, it can be seen from Fig. 2(b) and (c) that no lattice fringes are found, consistent with the amorphous state of the SnO2 nanoparticles. By contrast, the particle size of crystalline SnO2 increases to 10–15 nm, and they are uniformly deposited on GAs matrix, as shown in Fig. 2(d). TEM and high-resolution HAADF-STEM images (see Fig. 2(e) and (f)) clearly exhibit the crystalline character of the SnO2 nanoparticles. For instance, the lattice fringes with d-spacings of 0.336 nm and 0.264 nm assign to the (110) and (101) planes of SnO2. Similarly, the absence of diffraction rings of SAED (see the inset of Fig. 2(b)) and the obvious concentric rings of SAED (see the inset of Fig. 2(e)) well agree with our design of a-SnO2/GA and c-SnO2/GA. As a result, the intrinsic isotropic nature and the small particle size of amorphous SnO2 guarantee increased electrochemical performance. For comparison, the bare SnO2 nanoparticles are synthesized, and the morphology and structure are confirmed by SEM, XRD, and XPS, as shown in Figs. S2–S4.

Fig. 3(a) and (b) exhibit typical CV characteristics corresponding to the lithiation/delithiation of the a-SnO2/GA and c-SnO2/GA, tested in the voltage range of 0.01–3.0 V (vs. Li\(^+\)/Li) with a scan rate of 0.1 mV s\(^{-1}\). Obviously, both nanocomposites show similar CV profiles. In the initial cycle, one can see a reduction peak around 0.85 V in both samples, which is consistent with the formation of SnO2 to Sn [33,40]. The characteristic pair of cathodic peak (at 0.05 V) and anodic peak (at 0.55 V) are assigned to reversible lithium alloying with Sn and dealloying of Li_xSn reactions, respectively [25]. Additionally, another one oxidation peak at 1.31 V is observed, which is ascribed to partially reversible reactions of Li_2O and Sn [41]. The CV curves almost overlap together from the second cycle, suggesting that the electrochemical reactions are reversible well. Fig. 3(c) and (d) depict the discharge and charge profiles of a-SnO2/GA and c-SnO2/GA in the 1st, 2nd, 20th, and 80th cycles, which are measured at a current density of 100 mA g\(^{-1}\) from 0.01 V to 3.0 V at room temperature. As can be seen, the discharge capacity of first cycle reduces rapidly compared to the second cycle. In other words, a part of initial discharge capacity can be irreversible originating from electrolyte decomposition, the formation of SEI, and the irreversible conversion from SnO2 and Li to Li_2O and Sn in lithiation process [42]. Fortunately, in the following discharge/charge cycles, a-SnO2/GA maintain a higher reversible capacity and better cyclic stability compared to c-SnO2/GA.

The cycling performances of pristine GAs, bare SnO2, a-SnO2/GA, and c-SnO2/GA electrodes under a current density of 100 mA g\(^{-1}\) are compared in Fig. 3(e). As expected, GAs matrix deliver low reversible capacity and cyclability. Meanwhile, it can be seen that the bare SnO2 exhibits poor cyclability, and the specific capacity falls to 420 mA h g\(^{-1}\) upon 40 cycles, which originates from large volume change of anode materials. With the help of GAs matrix, a-SnO2/GA and c-SnO2/GA reveal increased performance. Interestingly, one can see that the anode crystallinity significantly affects lithium storage performance of the SnO2 material. Due to the sev-
ere volume expansion, c-SnO$_2$/GA exhibit high capacity fade. Its discharge capacity only remains 571.6 mA h g$^{-1}$ in 80th cycle, and capacity retention is about 84% compared to that of the 6th cycle. By contrast, a-SnO$_2$/GA show enhanced cycling performance. For instance, the discharge capacity decreases to 716.6 mA h g$^{-1}$ in the first six cycles. After that, it remains stable at around 700.1 mA h g$^{-1}$ when the test is prolonged to 80 cycles, in accordance with a high retention rate of 97.6%. These results illustrate that the amorphous SnO$_2$ particles with the smaller size and isotropic nature demonstrate better function to relieve the volume expansion/shrinkage and make less active material lose electrical contact with the matrix, guaranteeing the excellent lithium energy storage. In order to further highlight the advantages of a-SnO$_2$/GA, the rate capability of a-SnO$_2$/GA and c-SnO$_2$/GA at various current densities: 100, 200, 400, 800, 1600 mA g$^{-1}$.

**Fig. 3.** The CV curves of (a) a-SnO$_2$/GA and (b) c-SnO$_2$/GA at a scan rate of 0.1 mV s$^{-1}$ in the voltage range of 0.01–3.0 V; The discharge/charge profiles of (c) a-SnO$_2$/GA and (d) c-SnO$_2$/GA in the 1st, 2nd, 20th, and 80th cycles; (e) Comparison of the cyclic performance of pristine GAs, bare SnO$_2$, a-SnO$_2$/GA, and c-SnO$_2$/GA at a current density of 100 mA g$^{-1}$; (f) Rate capability of a-SnO$_2$/GA and c-SnO$_2$/GA at various current densities: 100, 200, 400, 800, 1600 mA g$^{-1}$.

densities (such as 100 and 200 mA g$^{-1}$) are comparable to that of c-SnO$_2$/GA electrode. With increased current densities at 400, 800, 1600 mA g$^{-1}$, a-SnO$_2$/GAs deliver higher reversible capacities than c-SnO$_2$/GA (see Fig. S5). These results clearly demonstrate the significant advantages of designed a-SnO$_2$/GA used as anode material for LIBs.

Fig. 3(a) and (b) display the electrochemical impedance spectroscopy of a-SnO$_2$/GA and c-SnO$_2$/GA in the 1st, 5th, and 10th cycles. The equivalent circuit in Fig. 3(c) is employed to simulate the obtained EIS results. Note that both SnO$_2$/GA exhibit a depressed semicircle and an angled straight line corresponding to the high frequency and low frequency range. These features are characteristic of charge transfer resistance ($R_{ct}$) and Warburg impedance ($Z_W$) of Li ions [43]. Additionally, the $R_{ct}$ values of a-SnO$_2$/GA and c-SnO$_2$/GA in the 1st, 5th, 10th cycles are compared in Fig. 3(d). On one side, a-SnO$_2$/GA reveal lower $R_{ct}$ than c-SnO$_2$/GA, suggesting high electrochemical reaction kinetics, which attributed to the Li ions insertion/extraction into the composites anodes [44]. On the other side, the $R_{ct}$ values of both SnO$_2$/GA con-
tinually decrease upon cycling, which confirms the enhanced electrochemical activity with increasing cycles [32,45]. Since the lithium insertion and extraction reaction rates are governed by Li\(^+\) diffusion and electron conductivity, therefore, the increased electronic conductivity, that is to say, the high electrochemical reaction kinetics suggest enhanced lithium energy storage.

Based on the aforementioned discussion, we further study the morphology of a-SnO\(_2\)/GA after 80 charge/discharge cycles (see Fig. S6). Clearly, the a-SnO\(_2\)/GA structure shows some changes after repeated charge–discharge cycles to some degree. Compared to Fig. 2(b), some nanoparticles showing clear lattice fringes are observed, indicating that the resultant nanoparticles are substantially crystalline. Note that the distribution on GAs and particle size of SnO\(_2\) have no obvious change, suggesting the intrinsic isotropic nature and smaller size of SnO\(_2\), along with the GAs matrix can effectively relieve SnO\(_2\) volume changes during charge/discharge cycles, guaranteeing the structure integrity between SnO\(_2\) particles and GAs matrix. It exhibits a convincing evidence that a-SnO\(_2\)/GA are potential anode materials for LIBs.

4. Conclusions

In summary, LIBs have had remarkable success as power sources for portable electronic devices, on the basis of traditional graphite electrode. In our study, the designed electrode material with excellent performance is expected to be a good anode candidate. More strikingly, as more demand emerges for electrical vehicles and hybrid electric vehicles, and as emphasis shifts to the power grid and other large scale applications, exploring potential materials with high reversible capacity and high stability as alternative anode materials is eager. However, these materials show poor performance resulting from large volume change. Our results demonstrate that the amorphous nature of electrode materials can efficiently overcome this challenge, and enhance cycling performance. Hence, this study opens an excellent approach to improve electrochemical performance of electrode materials with large volume change for energy storage systems.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (51572194), the Key Projects of Tianjin Municipal Natural Science Foundation of China (14JCZDJC32200 and 13JCZDJC33900), LPMIT (Laboratory of Precision Manufacturing Technology), CAEP (China Academy of Engineering Physics) (KFI-4006), Academic Innovation Funding of Tianjin Normal University (52X1C404), Training Plan of Leader Talent of University in Tianjin, Scientific Research Foundation for Returned Overseas Chinese Scholars of State Education Ministry, and the Program of Thousand Youth Talents in Tianjin of China.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apenergy.2016.02.094.

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Fig. 4. The electrochemical impedance spectroscopy of (a) a-SnO\(_2\)/GA and (b) c-SnO\(_2\)/GA in the 1st, 5th, and 10th cycles; (c) The corresponding equivalent circuit used to simulate EIS curves; (d) The R\(_c\) values of a-SnO\(_2\)/GA and c-SnO\(_2\)/GA in the 1st, 5th, and 10th cycles.


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