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Preparation of tin oxide/graphene composite for lithium-ion batteries' application

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Abstract. Tin oxide/graphene (SnO_2/GO) composites were successfully fabricated by a facile hydrothermal method with the seeding crystal method. The results of SEM and TEM observations strongly suggest that the excellent dispersibility of the product is influenced by the solution pH value. If the solution is pre-treated by the seeding crystal method before applying the hydrothermal method, the number of nanoparticles on the GO surface will be larger and the distribution of the product will be better, as compared to the product without such pre-treatment. The as-prepared SnO_2/GO also exhibits a reversible capacity of 750 mAh g^{-1} at the current density of 100 mA g^{-1} . It is mainly because nanomaterials facilitate the transfer of Li^+ between the active materials and the electrolyte. Besides, GO can act as a buffer during the charge/discharge process, which can effectively reduce the electrode damage during the volume change and ensure the electrochemical performance stability of the materials.

1. Introduction

Lithium-ion batteries (LIBs), as advanced energy storage devices, are among the most preferred power sources for electronic devices by the advantages of high energy density, high voltage and good life cycling [1-2]. In the composition of the LIBs, the selection of anode materials is critical for the electrochemical performance of the devices. The common use of anode materials is based on the graphite, because of its price and high electrochemical stability. However, their theoretical capacity can reach only 372 mAh g^{-1} [3], which restricts their promotion in the energy market. To meet the application demands, many researchers switch their focus to the transition metal oxide (TMO) materials, such as Fe_2O_3 [4-5], Co_3O_4 [6-7], SnO_2 [8-9], which have high theoretical capacity and can replace graphene as anode electrode materials. Among these materials, SnO_2 who is environmental friendliness, owns low intercalation potential, and high theoretical capacity (792 mAh g^{-1}) [10], has become one of the most preferred materials. However, its volume expansion is significant, and the volume change of tin particles could reach 300% during the charge-discharge process, which is similar to other pure TMOs. Most of the bulk materials will be damaged during the reactions. What's worse, leading self-discharge is also a general problem for SnO_2 materials, which is caused by the fragmented nanoparticles travel through the separator. In addition, further degrading the anodic also can happen at the same time after cycling [11]. Therefore, many researches came to focus on combining TMOs with carbon materials, like carbon, nanotube, graphene oxide, or reducing the size to nanoparticles. For example, Li et al. [12] synthesized SnO_2 nanoparticles with carbon coated and composite with graphene nanoribbons and carbon nanotubes, which have significantly improved the conductivity and improved its performance. As shown in the articles, the reversible capacity can reach 1038 mAh g^{-1} at the current density of 100 mAh g^{-1} . After



cycling 1000 cycles, the capacity can still remain about 500 mAh g⁻¹. Zhang et al.[13] fabricated phosphorus bridging SnO₂ and graphene composite electrodes by covalent bonding for LIBs. At the current density of 100 mA g⁻¹, the specific capacity can reach about 550 mAh g⁻¹ over 200 cycles. The electrochemical experiments showed that carbon materials used as component of the composites are helpful for the improvement of the performance. The widely used graphene oxide serve as the support materials to buffer the volume changes. Its high conductivity improves the transition of the ions as well. Moreover, the nano-scaled materials also provide more active points on the surface to improve the usage of the materials.

In this work, SnO₂ nanoparticles/graphene oxides composites are selected as anodes materials. The morphology of SnO₂ was adjusted by adjusting the pH of hydrothermal system in seed crystal-hydrothermal method, and the alkalinity solution is benefit for the formation of the composite with good distribution. And the number of the nanoparticles on the surface of the GO is also improved by the seed crystal method. When tested electrochemical performance of SnO₂/GO composites, it shows that the first charge / discharge capacity is 1420 mAh g⁻¹ at the current density of 100 mA g⁻¹. After 11 cycles, the capacity remains about 750 mAh g⁻¹.

In this work, SnO₂ nanoparticles/graphene oxides composites are selected as electrode materials for lithium-ion LIBs. The morphology of SnO₂ was adjusted by adjusting the pH of the hydrothermal system in seed crystal-hydrothermal method, and the alkalinity solution is beneficial for the formation of the composite with a proper distribution. Moreover, the number of nanoparticles on the surface of the GO is also improved by the seed crystal method. When the electrochemical performance of SnO₂/GO composites was tested, it was found that the first charge/discharge capacity was 1420 mAh g⁻¹ at the current density of 100 mA g⁻¹. After 11 cycles, the capacity remained at the level of 750 mAh g⁻¹.

2. Experimental

2.1. Materials

Tin (IV) chloride pentahydrate (SnCl₄·5H₂O, 99%), sodium hydroxide (NaOH, 99%), sodium dodecyl sulfate (C₁₂H₂₅SO₄Na, SDS, 99%), ethanol, N-methyl-2-pyrrolidone (NMP, C₅H₉NO, 99.0%) PVDF (C₅H₉NO, 99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Carbon black was supplied by Hefei Kejing Material Technology Co., Ltd, China.

2.2. Synthesis of SnO₂/graphene composite

It is prepared by seed crystal method and hydrothermal method. 3 mg GO was dissolved in 0.05 M 100 ml SnCl₄·5H₂O aqueous solution and then left it for 12 h at the room temperature. Due to the hydrolysis reaction of SnCl₄·5H₂O, there would be some SnO₂ nanocrystals on the surface of the graphene. After that, the precipitation was collected after centrifugation and dried at 200°C. The final product was prepared by the hydrothermal method. The above precipitation was added into 35 ml aqueous solution with 0.1 M SnCl₄ · 5H₂O, 0.1 M NaOH (0.5 M NaOH or 0.1 M HCl) and 0.3 M SDS, stirring about 30 min. Then the 100 mL Teflon-lined stainless-steel autoclave is used as the reaction container, which was added with the above solution and kept at 220 °C for 20 h. The products were centrifuged and washed with deionized water and ethanol for several times, respectively. After that, dry at 60 °C overnight for characterization and further usage. The product was named sample 1 in the following passage.

Another synthesise method was mainly based on the hydrothermal method. 50 mg SnCl₄·5H₂O was dissolved in 40 ml GO solution (1mg ml⁻¹), which was added 10 ml SDS (0.3 M) and 10 ml NaOH (0.1 M). And then the above solution treated the same as above at 220 °C for 20 h. After that, collect the product by centrifugation and dry in the oven. Hereinafter, the product is referred to as “sample 2”.

2.3. Characterizations

Rigaku Dmax-ray X-ray diffractometer is used to collect X-ray powder diffraction (XRD) pattern at a scanning rate of 4° min⁻¹, And a JSM-6700F field emission scanning electron microscope (SEM) is used

for structure examination. The transmission electron microscope (TEM) images are obtained by a JEOL JEM-2100 high-resolution TEM. Raman spectrometer was recorded on a LabRAM HR800.

2.4. Electrochemical measurement

Working electrodes were prepared as follows: mix the active material, PVDF, and carbon black at a weight ratio of 8: 1: 1. Then add NMP as the solution to form a homogenous slurry. After that coat slurry to a copper foil substrate and dried in a vacuum oven at 120 °C for 12 h. Li foil was used as the counter and reference electrode and 1MLiPF₆ was used as electrolyte, with Celgard 2300 as separator. The cells were assembled in a glove box filled with argon atmosphere. As the active material, the performance of the cell was evaluated galvanostatically in the voltage range from 0.02 to 3 V at various current densities on a LAND CT2001A battery test system.

3. Results and discussion

3.1. Characterizations of SnO₂/graphene composite

The morphology and microstructure of the SnO₂/GO have been studied by SEM and TEM. As shown in Figure 1(a), the SEM image shows there are many nanoparticles on the surface of the GO, and the size of the particle is nanoscale. But the particles are all agglomerated with an uneven dispersion. When improving the concentration of the NaOH to 0.5 M, the number of particles on the surface of the GO is growing, showing in Figure 1(b). And the size of the particles stays the same as the product prepared in 0.1 M NaOH. The dispersion is also better, and most of the particles are located on the surface of the GO. However, in the product synthesized only by the hydrothermal method (as shown in figure 1(c) and (d)), the distribution of particles on the GO surface is uneven. Worse still, there are few particles on some of the GO surface. While in another place, there are more particles, but they are bonded in agglomerations.

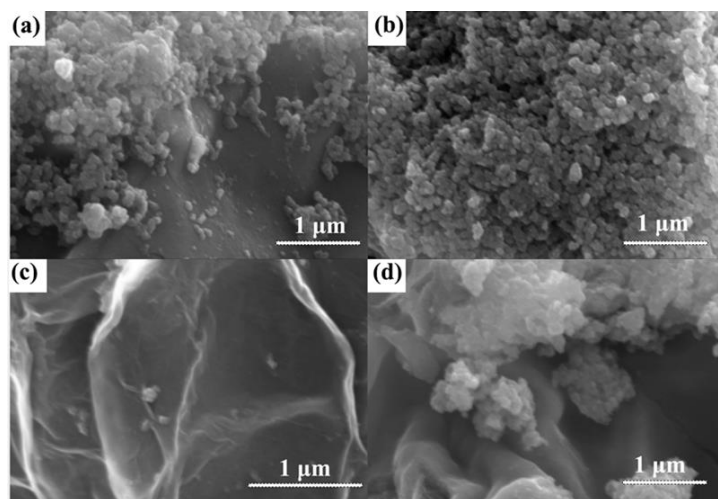


Figure 1. SEM images of sample 1 at concentration of (a) 0.1 M NaOH, (b) 0.1 M NaOH; and images of sample 2 (c), (d).

The PH of the solution during the solvothermal and hydrothermal method has a significant effect on the structure formation of the products, which is widely used to control the morphologies of nano-/micro-scale materials [14-15]. Therefore, when the solution pH is transformed into acidity, by adding HCl, the structure of the product will be different. As shown in figure 2, there are no particles on the surface of GO, and the surface is much smoother than a product prepared in alkalinity solution. At the edges of the GO, some wrinkles are appearing on the surface, which may be caused by the erosion of the acid and the sedimentation of the irregular SnO₂. It means the SnO₂ particles cannot be formed and

deposit on the GO surface in the acid environment. These results also indicate the combination of the seed crystal and hydrothermal method can fabricate product with good dispersibility, and the different concentration of the NaOH will affect the dispersibility of the particles on the GO surface. The 0.5 M of the NaOH can obtain the largest number of the nanoparticles on the GO surface.

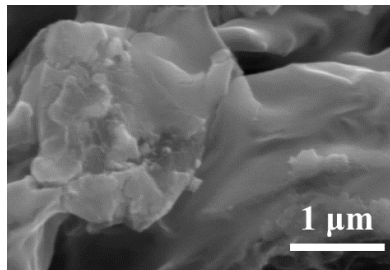


Figure 2. SEM image of SnO₂/GO composite prepared in acid solution.

Figure 3(a) shows the TEM image of SnO₂/GO composites prepared by seed crystal and hydrothermal method at high magnification. It can be found that the size of the particles is about 10 nm, and the lattice fringe can be observed. The typical lattice fringe spacing is measured about 0.48 and 0.68 nm, which were corresponded to the (200) and (100) crystal plane of SnO₂. Under low magnification image (figure 2(b)), the dispersibility can be studied, and the number of the particles is large. The product synthesized only by the hydrothermal method is displayed in figure 3(c), and there are few nanoparticles on the surface of the GO. It indicates that the size of the SnO₂ nanoparticles obtained by two different methods is almost the same. It proved that the crystal-hydrothermal method can effectively improve the number of nanoparticles on the surface of GO and can still maintain the morphology of the particles.

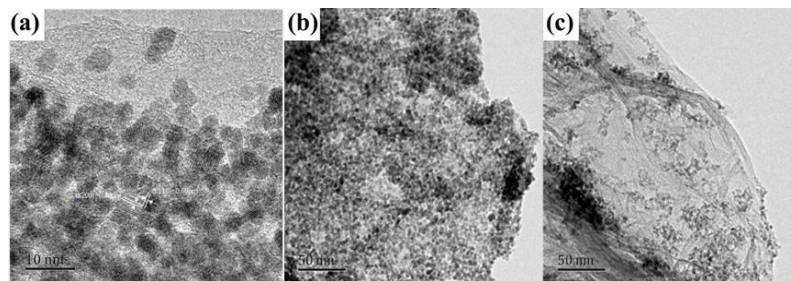


Figure 3. TEM images of (a), (b) sample 1 and (c) sample 2 SnO₂/GO composite.

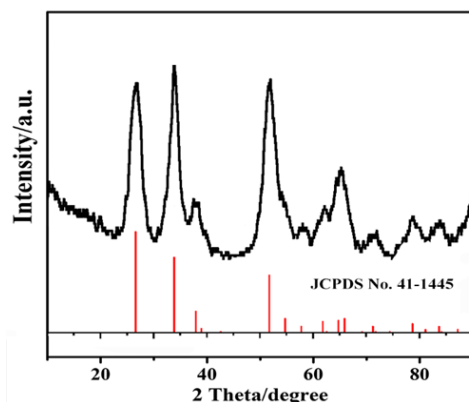


Figure 4. XRD patterns of the SnO₂/GO composite.

The crystalline phase and purity of products obtained by seed crystal and hydrothermal methods were studied by XRD. In figure 4, the diffraction patterns can be indexed to tetragonal SnO_2 (JCPDS No. 41-1445), and the peaks at 26.72° , 33.92° , 37.95° , and 51.77° are indexed to the crystallographic planes of (110), (101), (200), (211), (112). There are still some small peaks that are fitted well with the JCPDS card, which means the prepared product is not purity, and efforts still need to be made to improve the purity. It may be caused during the washing process. The time for purifying should be prolonged.

Raman spectra are shown in figure 5. There are two peaks at about 1350 cm^{-1} (D band) and 1590 cm^{-1} (G band) observed in the composites, which are ascribed to the graphene substrate [16]. Besides, there is broad band from 360 to 960 cm^{-1} corresponding to the vibration modes of SnO_2 nanoparticles. Therefore, the Raman results are consistent with the TEM and SEM results, indicating the formation of the SnO_2/GO composite [17].

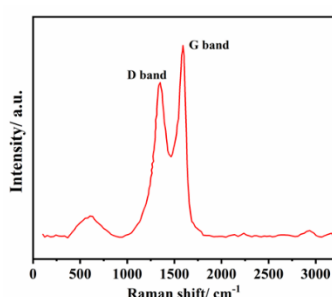
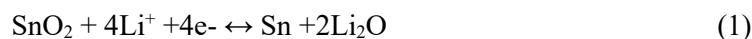


Figure 5. Raman spectra of SnO_2/GO composite.

3.2. Electrochemical performance of the SnO_2/GO composite

In figure 6, the cycling performance of the SnO_2/GO is presented, which is obtained by seed crystal and hydrothermal methods, at the current density of 100 mA g^{-1} . The first discharge capacity can reach 1420 mAh g^{-1} , which is higher than theoretical capacity of 782 mAh g^{-1} . But the first Li^+ insertion capacity can only be reach 800 mAh g^{-1} . There is an obvious capacity loss, which is caused by the irreversible reaction and the formation of solid electrolytes interface. After 11 cycles, the specific capacity still maintains at 750 mAh g^{-1} . The coulombic efficiency of the product remains stable after 8 cycles, even though the number of the cycles is small. The reactions during charge and discharge process should be as below:[18]



It is assumed that nanomaterials facilitate the reactions between the electrolyte and the electrode, and the addition of the GO can buffer the volume change during the lithiation/delithiation process.

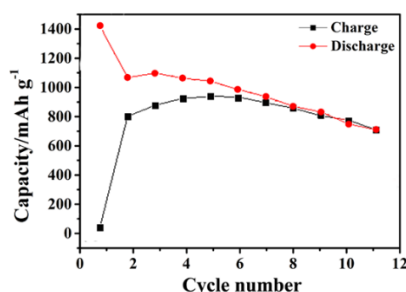


Figure 6. Cyclic performance of SnO_2/GO composite at the current density of 100 mA g^{-1} .

4. Conclusions

In conclusion, a simple method has been demonstrated to prepare the SnO₂/GO composite, and the SnO₂ is presented in the form of nanoparticles on the GO surface. In case of pre-treatment of the solution of SnCl₄ and GO before hydrothermal method, the dispersibility of nanoparticles on the GO surface will be better, and the number of the particles will be larger. Besides, the alkalinity solution is beneficial for the formation of the structure. When used as the anode materials, SnO₂/GO shows an excellent performance. At the current density of 100 mA g⁻¹, specific capacity can reach 750 mAh g⁻¹ after 11 cycles, due to the nanostructure and addition of GO buffering the volume change during the reactions.

Acknowledgments

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