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Tin–indium/graphene with enhanced initial coulombic efficiency and rate performance for lithium ion batteries

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ABSTRACT

Tin is an attractive anode material replacing the current commercial graphite for the next generation lithium ion batteries because of its high theoretical storage capacity and energy density. However, poor capacity retention caused by large volume changes during cycling, and low rate capability frustrate its practical application. In this study, a new ternary composite based on tin–indium alloy (Sn–In) and graphene nanosheet (GNS) was prepared via a facile solvothermal synthesis followed by thermal treatment in hydrogen and argon at 550 °C. Characterizations show that the tin–indium nanoparticles with about 100 nm in size were wrapped between the graphene nanosheets. As an anode for lithium ion batteries, the Sn–In/GNS composite exhibits a remarkably improved electrochemical performance in terms of lithium storage capacity (865.6 mAh g^{-1} at 100 mA g^{-1} rate), initial coulombic efficiency (78.6%), cycling stability (83.9% capacity retention after 50 cycles), and rate capability (493.2 mAh g^{-1} at 600 mA g^{-1} rate after 25 cycles) compared to Sn/GNS and Sn–In electrode. This improvement is attributed to the introduction of lithium activity metal, indium, which reduces the charge transfer resistance of electrode, and the graphene nanosheet which accommodates the volume change of tin–indium nanoparticles during cycling and improves electrical conductivity of material.

1. Introduction

Tin-based alloys, as one of the most promising materials to replace graphite for the next generation lithium ion batteries, have been extensively studied as anode materials because of their high theoretical storage capacities on both the gravimetric and volumetric bases [1–4]. However, the poor cycle performance arising from large volume expansion/contraction during Li^+ insertion/extraction leading to the pulverization of the electrode and the electrical disconnection from current collectors impedes its practical application. Many researchers have made great efforts in order to resolve those existing problems. One of the successful strategies is to fabricate core–shell nanostructure, such as metals and alloys with carbon shells [5,6]. This structure can offer a more expansion space, enhanced electronic transport framework, a good isolator layer between the high-activity metal sites and electrolytes, hence improved cycling stability [5,6]. The other approach is the incorporation of lithium inactive element, such as, Sn–Cu [7–10], Sn–Co [11–15], Sn–Ni [16,17], Sn–Fe [18], and Sn–Al [19,20] into tin active material to form a Sn-based alloy electrode. These hybrid systems provide distinct advantages, especially in mechanics, such as buffering the volume expansion of Sn phase during cycling, and higher electrical conductivity. These are beneficial for achieving enhanced cycle performance compared to the single metal systems, but at the expense of the battery capacity. The introduction of lithium active metal material into tin to form alloy electrode has been reported rarely [21,22]. Indium metal is reactive towards lithium and has higher electrical conductivity compared to tin [23–26]. The reported heterostructured SnO_2–In_2O_3 nanowires showed improved reversible capacity compared to single SnO_2 nanowires because of indium lithium activity after first cycle [27]. However, the thermal evaporation synthesis process of SnO_2–In_2O_3 nanowires usually has some serious drawbacks, such as, high cost (requirement for (100) Si substrate and gold coating) and very low productivity. Therefore, it is very significant to synthesize Sn–In nanoparticles composites via a low cost and mass production method for extensive application in high performance lithium ion batteries. Until now, there is no report about tin–indium alloy anode in the application of lithium ion batteries.

On the other hand, it was found that the introduction of a conductor buffer such as carbon [28], carbon nanotube [29,30], carbon fibres [31], or graphene nanosheet [32–34], could lead to an improvement in electrochemical performance. Especially, graphene nanosheet (GNS) with a two-dimensional structure of carbon atoms packed into planar honeycomb lattice, has been proposed as a potential electrode material for energy storage devices because of its superior electrical conductivity, high surface area,

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structural flexibility, and chemical tolerance [35–39]. GNS as buffering matrix not only accommodate the large volume change of Sn during the cycling process, but also enhance the electron transport properties of the electrode due to their excellent electronic and mechanical properties [32–34]. Recently, the reported SnO_2–In_2O_3/GNS composite improved the rate and cycle performances, but the initial coulombic efficiency is relatively lower due to the irreversible reaction between SnO_2–In_2O_3 and lithium ion [40]. This inspired us to design and prepare Sn–In/GNS as anode for lithium ion batteries with enhanced initial coulombic efficiency. To our knowledge, Sn–In/GNS composite has not been reported, yet.

Herein, we intend to combine the advantages of indium and graphene nanosheet to synthesize a new ternary composite of tin–indium (Sn–In)/graphene nanosheet (GNS) through a facile solvothermal synthesis following annealing method. Indium, as lithium activity metal, not only delivers higher capacity, but also has higher electrical conductivity compared to tin which reduces the charge transfer resistance of electrode. GNS in the Sn–In/GNS could accommodate the volume change of tin–indium nanoparticles during cycling and improve electrical conductivity of material. It could be expected that Sn–In/GNS electrode for lithium ion batteries could achieve better capacity retention and enhanced capability.

2. Experimental section

2.1. Synthesis of graphene oxide

In a typical synthesis method, graphene oxide (GO) was synthesized by a modified Hummers method [40–42]. Briefly, 80 mL concentrated H_2SO_4 was added into a flask containing 1 g graphite powder and 0.5 g $NaNO_3$ with an ice bath. Under vigorous stirring, 3 g $KMnO_4$ was added gradually at below 20 °C. After removing the ice bath, the mixture was stirred at 35 °C for 2 days. Successively, 50 mL of H_2O was slowly added to the pasty mixture. Addition of water into the concentrated H_2SO_4 medium will release a large amount of heat; therefore, water should be added while keeping the mixture in an ice bath to keep the temperature below 35 °C. After dilution with 350 mL of H_2O, 5 mL of 30% H_2O_2 was added to the mixture, and the diluted solution color changed to brilliant yellow along with bubbling. After continuously stirring for 2 h, the mixture was centrifuged and washed with 10% HCl aqueous solution, distilled water, and ethanol to remove other ions. Finally, the resulting solid was dried by vacuum at 35 °C for 2 days.

2.2. Synthesis of Sn–In/GNS composites

50 mg GO was dispersed in 60 mL ethanol under ultra-sonication for two hours as Part A. A mixture of 0.285 g $SnCl_2 \cdot 2H_2O$ and 0.096 g $InCl_3$ was dissolved in 10 mL ethanol solution as Part B. Part A and Part B were then mixed under stirring to form a uniform suspension. Then, the suspension was transferred to 100 mL autoclave at 150 °C for 10 h. The solvothermal product was centrifuged and washed using ethanol for three times, and dried under vacuum at 80 °C for overnight. To get Sn–In/graphene composite, the obtained SnO_2–In_2O_3/graphene powder was reduced at 550 °C for 6 h within a mixture Ar (50%)/H_2 (50%). For comparison, Sn–In nanoparticles were also synthesized at similar conditions without the presence of graphene oxide. Sn/graphene composites were synthesized at similar conditions without the presence of In.

2.3. Characterizations and measurements

The Sn–In/GNS composites were characterized by a field emission scanning electron microscope (FE-SEM, JEOL JSM-7600F), field emission transmission electron microscope (FE-TEM, JEOL JEM-2100F), X-ray diffraction analyser (XRD, Rigaku D/MAX RINT-2000), and Raman Spectra (Raman Microprobe, Renishaw Instruments, England). Elemental analyses (C) were carried on an Elementar Vario EL III analyzer. Sn and In were determined by a Jobin Yvon Ultima2 ICP atomic emission Spectrometer.

The working electrodes were prepared by mixing 80 wt% active material, 10 wt% Super P, and 10 wt% polyvinylidene fluoride binder dissolved in N-methyl-2-pyrrolidinone. The resulting slurry was pasted onto copper foil and dried in a vacuum oven at 90 °C for overnight, and the electrodes were then pressed under a pressure of approximately 180 kg cm^{-2}. Coin-type half cells (2032 R type), the as-prepared composites as working electrode, pure lithium metal as counter electrode and 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 vol%) as the electrolyte, were fabricated to evaluate the electrochemical properties using a battery cycle tester (TOSCAT 3000, Toyo System, Tokyo, Japan). Cyclic voltammetry (CV) measurements were performed on a Sn–In/GNS working electrode using an electrochemical workstation (Parstat 2273) between 2 and 0.01 *vs* (Li/Li^+)/V at a sweep rate of 0.2 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) tests were also measured on an electrochemical workstation (Parstat 2273) operating in the frequency range of 0.1 Hz to 10^6 Hz with ac amplitude of 10 mV.

3. Results and discussion

3.1. Characterizations of Sn–In/GNS composite

Fig. 1 illustrates the synthesis of Sn–In nanoparticles on graphene nanosheet via solution-phase reaction method followed by thermal treatment in hydrogen and argon. Fig. 2 shows the scanning electron microscope (SEM) and transmission electron microscope (TEM) images of Sn–In/GNS composite. As can be seen in Fig. 2a and b, Sn–In/GNS composite composed of graphene nanosheets and nanoparticles. These nanoparticles are wrapped between graphene nanosheets. TEM images of the Sn–In/GNS composite are exhibited in Fig. 2c and d. The mean particle size of Sn–In nanoparticles was found to be 100 nm according to TEM images. TEM characterization further confirms the intimate contact between the graphene nanosheets and Sn–In nanoparticles. It is believed that, on the one hand, the presence of graphene nanosheets is favorable to improve the dispersion and growth of Sn–In nanoparticles. On the other hand, the assembly of nanoparticles on the graphene surface to some extent prevents the stacking of graphene nanosheets due to van der Waals interactions, leading to a large available surface area for energy storage.

Fig. 3a shows the typical X-ray diffraction pattern of the as-prepared Sn–In/GNS composite. From its XRD patterns, the as-prepared composite consists of β and γ phases, including Sn and In composition. The weight ratio between Sn and In was found to be 75:25 via the ICP atomic emission Spectrometer, corresponding to the Sn weight content of 67.5% and In weight content of 22.5%. This result is in accordance with the binary In–Sn equilibrium phase diagram ([43], Fig. S1). The carbon content of 10% is determined by the element analyses. Raman spectra for Sn–In/GNS and graphene oxide were also investigated. It is well known that the intensity ratio of the D to G band (I_D/I_G) reflects the graphitization degree of carbonaceous materials and the defect density [39]. The I_D/I_G for Sn–In/GNS (1.72) is much larger than that for graphene oxide (1.04), showing the transformation of graphene sheets from graphene oxide sheets after the solvothermal treatment. Based on above data, SEM and TEM images of the as-prepared material, it can be concluded that the Sn–In/GNS composite has been successfully synthesized.

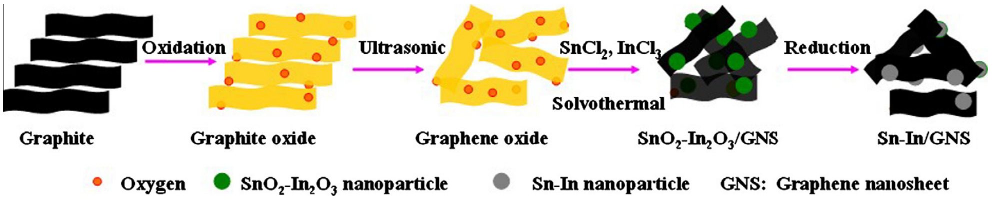

Fig. 1. Synthesis process of Sn–In/GNS composite.