Preparation of Nanometer Cu_6Sn_5 and Its Application in Lithium-Ion Batteries Anode for Mass Production

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Abstract Cu_6Sn_5 nanoparticles have been synthesized successfully via chemical reduction method in aqueous solutions, which is a kind of intermetallic compound (IMC) with active/inert Sn-Cu interfaces. The active layer reacted with Li^+ and the inert layer inhibited the volume change effectively. Meanwhile, reduced oxide graphene (RGO)/ Cu_6Sn_5 composites were also prepared by the similar method for the reason that the presence of RGO alleviated the aggregation of Cu_6Sn_5 nanoparticles. Therefore, RGO/ Cu_6Sn_5 nanoparticles showed more superior electrochemical performance compared with Cu_6Sn_5 nanoparticles. The results showed that RGO/ Cu_6Sn_5 nanoparticles exhibited promising cycling stability (461 $\text{mAh}\cdot\text{g}^{-1}$ after 18 cycles), high rate capability and prominent capacity retention, which can be extensively used in the field of lithium-ion battery anode. Herein, we also develop a simple and environmental friendly fabrication approach to prepare Cu_6Sn_5 nanocomposites, which is suitable for mass production.

Keywords Cu_6Sn_5 nanoparticles, reduced oxide graphene/ Cu_6Sn_5 nanoparticles, chemical reduction method, electrochemical performance

Introduction

With the popularization of portable electronic devices and electric vehicles, the demands on the capacity of lithium-ion batteries get more pressing in recent years. As the main anode material of lithium-ion batteries, the capacity of graphite has reached the theoretical limit ($320 \text{ mAh}\cdot\text{g}^{-1}$).^[1] Therefore, to develop new anode materials as replacements for graphite is more important.^[2-5] As the most promising substitute, $\text{Sn}^{[6-9]}$ has attracted considerable attention due to its high theoretical capacity ($993 \text{ mAh}\cdot\text{g}^{-1}$). During lithiation/delithiation process, Sn anode produce volume expansion so that it cannot form a stable SEI film (solid electrolyte interface film), resulting in low coulombic efficiency, poor cycle life ability and rapid capacity fading.^[9-12] These problems limit the application of Sn in the field of lithium-ion battery anode. In order to overcome above problems, IMC has been brought into focus such as Cu_6Sn_5 . During lithiation/delithiation process, Cu_6Sn_5 shows small volume change. Many preparation method of Cu_6Sn_5 particles have been reported, such as spray pyrolysis,^[13] high energy ball-milling,^[14] high temperature oil bath method, electrodeposition,^[15] ultrasonic dispersion method, solid-phase reaction^[16] and liquid phase chemical reduction method.^[17] Polat *et al.* reported that Cu and Sn were deposited simultaneously on copper substrate by electron beam evaporation to form nano-porous anode films.^[18,19] The charge/discharge tests show that the electrochemical performance of nano-porous $\text{Cu}_{6.26}\text{Sn}_5$ films is enhanced significantly.^[20-26] In this work, Cu_6Sn_5 nanoparticles have been prepared via chemical reduction method in aqueous solutions.

In addition, many reports about graphene, which could inhibit aggregation of Cu_6Sn_5 nanoparticles and improve cycling stability, had been published.^[27-29] Wang *et al.* used a soft chemical process to immobilize nanoscale Cu_6Sn_5 on a multi-

layer graphene sheet to obtain a composite of graphene and Cu_6Sn_5 . The electrochemical performance of RGO/ Cu_6Sn_5 composites was excellent and the reversible capacity was $450 \text{ mAh}\cdot\text{g}^{-1}$.^[30] The graphene layer has superior electrical conductivity and the core shell has good elasticity, which can buffer volume change effectively in lithiation process and prevent the aggregation between Cu_6Sn_5 nanoparticles. Herein, we develop a simple and environmentally friendly approach to prepare Cu_6Sn_5 nanoparticles and RGO/ Cu_6Sn_5 composites. We try to combine the excellent electrochemistry performance of RGO and Cu_6Sn_5 . The result shows great cycling stability ($461 \text{ mAh}\cdot\text{g}^{-1}$ after 18 cycles) and superior rate capability.

Experimental

Cu_6Sn_5 nanoparticles were prepared via chemical reduction of aqueous solutions. For this process, solution A and solution B were prepared, respectively. For obtaining Solution A, $\text{CuCl}_2\cdot\text{H}_2\text{O}$ and $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ were dissolved in 20 mL deionized water with a molar ratio of 6 : 5 and a certain amount of sodium citrate as a coordinating agent was added to the above solution, sonicated 5 min. In this solution, Sn^{4+} and Cu^{2+} were effectively disperse by electrostatic effect of $\text{C}_6\text{H}_5\text{O}_7^{3-}$. For obtaining Solution B, surfactant $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$ or (CTAB, $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$) were added to deionized water and moderate amounts of NaBH_4 (reducing agent) were dissolved in the above solution, stirred at constant temperature. The schematic diagram of preparation of Cu_6Sn_5 is shown in Figure 1. Firstly, Solution A was added into solution B, Sn^{4+} and Cu^{2+} are reduced to Sn and Cu by NaBH_4 . The surface of Cu and Sn were surrounded by $\text{C}_6\text{H}_5\text{O}_7^{3-}$ group to form a charged ion layer. The amino of CTAB interacts with the ion layer on the surface of Cu and Sn nanoparticles, which promotes the formation of Cu_6Sn_5 nanoparticles. After that, the resulting Cu_6Sn_5 nanoparticles

Figure 1 Fabrication procedure for Cu_6Sn_5 .

were centrifuged with deionized water and ethanol for three times and dried in an oven. Sn nanoparticles were prepared by the same process as above, but this process didn't need precursor of Cu. In addition, the RGO/ Cu_6Sn_5 nanocomposites were prepared by self-assembly method because of the self-assembly effect of graphene oxide (GO). GO was added into the mixed solution (Cu^+ and Sn^{4+}). In this process, GO was reduced to graphene and Cu^+ and Sn^{4+} were absorbed on the surface of graphene. Cu_6Sn_5 was formed on the surface of graphene to produce RGO/ Cu_6Sn_5 .

The phase composition was analyzed by X-ray diffraction (XRD, Rigaku D/max2200VPC, Japan). The morphology of Cu_6Sn_5 , Sn and graphene/ Cu_6Sn_5 nanoparticles were characterized by scanning electron microscopy (SEM, Hitachi S-4700, Japan) and transmission electron microscopy (TEM, TALOS F200X). The phase transition temperature of nanoparticles was analyzed by TG-DSC device (Netzsch STA449F3 Jupiter, Germany). The charge/discharge performance was carried on a Land blue-electricity test system.

Results and Discussion

Figure 2 shows the XRD pattern of Cu_6Sn_5 prepared by chemical reduction method in aqueous solutions. It can be apparently found that the reaction product was Cu_6Sn_5 without the impurities of Sn, Cu and oxides.

Figure 2 XRD pattern of Cu_6Sn_5 .

The morphology of Cu_6Sn_5 nanoparticles is characterized by TEM in Figures 3a and 3b. It can be not seen clearly that the boundary between Cu_6Sn_5 particles in Figure 3a. The reason is that the dispersants of CTAB with protection dissolve in alcohol, which led to an agglomeration phenomenon with more bare particles. From Figure 3b, it can be seen that the surface of Cu_6Sn_5 has an amorphous coating and the grain size of Cu_6Sn_5 nanoparticle vary from 18 to 48 nm. Figures 3c and 3d show the TEM image of pure Sn nanoparticles. As can be seen from Figures 3c and 3d, Sn nanoparticles have two shapes: one is spherical and the other is cubic. The Sn nanoparticles were well dispersive and have no obviously agglomeration.

The surface morphology of RGO/ Cu_6Sn_5 nanocomposites is characterized by SEM in Figure 4. Cu_6Sn_5 nanoparticles are not aggregated together but dispersed on graphene nanosheets, indicating the formation of RGO/ Cu_6Sn_5 nanocomposite (Figure 4a). From Figure 4b, it can be seen that Cu_6Sn_5 nanoparticles are coated with graphene that is nearly transparent

Figure 3 TEM image of Cu_6Sn_5 (a, b) and Sn (c, d).

Figure 4 SEM image of RGO/ Cu_6Sn_5 nanocomposites.

in the high magnification image. In the preparation process, Cu_6Sn_5 nanoparticles are effectively dispersed without the addition of polymer dispersant due to the graphene sheet structure.

It can be seen that the TG curve drops to 85% rapidly at 25–110 $^{\circ}\text{C}$ in Figure 5, which corresponds to the evaporation of water contained in the nano-powder. At temperature is about 100 $^{\circ}\text{C}$, there is an endothermic peak appeared in the DSC curve as a result of the large amount of heat absorbed in evaporation process. Then the exothermic peak is appeared when the temperature up to about 300 $^{\circ}\text{C}$ due to the happening of sintering and appearing of sintering neck. At about 300 $^{\circ}\text{C}$, the absorbed heat of decomposition is less than the heat release of sintering. The exothermic peak appeared at 375 $^{\circ}\text{C}$ corresponds to the crystallization during sintering.

Figure 5 TG/DSC curves of Cu_6Sn_5 nanoparticles.

To further understand the reaction mechanism of charge and discharge process, the initial discharge/charge curves of RGO/ Cu_6Sn_5 were measured in Figure 6. In the first discharge curve, the Cu_6Sn_5 nanoparticles electrode has a discharge platform at a potential of 0.5 V, which shows an initial lithiation capacity of 1027.4 $\text{mAh}\cdot\text{g}^{-1}$. There is a charging platform at a potential of 0.8 V, which corresponds to the delithiation process and shows an initial delithiation capacity of 442.4 $\text{mAh}\cdot\text{g}^{-1}$. The initial coulombic efficiency is 45.8%. This poor coulombic effi-

ciency is related to the pulverization of the active material and the large loss of lithium ions during the lithium intercalation process, which is an irreversible electrochemical reaction between Cu_6Sn_5 and metallic lithium. The electrochemical cycling performances of Sn, Cu_6Sn_5 , RGO, RGO-Sn and RGO- Cu_6Sn_5 as control samples are investigated by discharge/charge measurements at a current density of $100 \text{ mA}\cdot\text{g}^{-1}$, 100 of cycles, test voltage range of 0.01–1.2V in Figure 7. The initial discharge capacity of Sn is as high as $1145.4 \text{ mAh}\cdot\text{g}^{-1}$ and charge capacity is $647.6 \text{ mAh}\cdot\text{g}^{-1}$, the coulombic efficiency of Sn is 55.3%. The initial discharge capacity of Cu_6Sn_5 is $1027.4 \text{ mAh}\cdot\text{g}^{-1}$, charge capacity is $442.4 \text{ mAh}\cdot\text{g}^{-1}$ and the coulombic efficiency is 45.8%. The capacity of Sn is higher than that of Cu_6Sn_5 in the initial discharge/charge process. Because the theoretical capacity of Sn is $960 \text{ mAh}\cdot\text{g}^{-1}$, the theoretical capacity of Cu_6Sn_5 is $584 \text{ mAh}\cdot\text{g}^{-1}$, the capacity of Sn nanoparticles in the first few cycles is much higher than that of Cu_6Sn_5 . However, the capacity of Sn has been dropped rapidly within 50 cycles without a stable value. The main reason is that the initial alloying process of Sn is accompanied by huge volume change and tremendous structural strain, which causes immediate pulverization of the Sn nanoparticles. Due to such severe pulverization, the capacity of Sn dropped very rapidly within 50 cycles. After 50 cycles, the value of capacity got stable only $125 \text{ mAh}\cdot\text{g}^{-1}$. The capacity of Cu_6Sn_5 decreases slower than Sn and get a stable value of $265 \text{ mAh}\cdot\text{g}^{-1}$ after 45 cycles. It can be concluded that that Cu_6Sn_5 has better cycling performance than Sn. The main reason is that Sn undergoes huge volume change during lithiation/delithiation process that produce tremendous structural strain, resulting in cracking and pulverization of Sn particles, and then leading to rapid capacity fading.

Figure 6 The initial discharge/charge curves of RGO/ Cu_6Sn_5 .

Figure 7 Cycling performances of Sn, Cu_6Sn_5 , RGO, RGO/ Cu_6Sn_5 .

The electrochemical cycling performances of RGO/Sn nanoparticles were also investigated by discharge/charge measurements. The initial discharge capacity of RGO/Sn nanocom-

posites is as high as $1208 \text{ mAh}\cdot\text{g}^{-1}$, and the charge capacity is $741 \text{ mAh}\cdot\text{g}^{-1}$, so the coulombic efficiency is 55.3%. Compared with Sn nanoparticles, the capacity of RGO/Sn nanocomposites drops much slowly and improves capacity fading. After about 50 cycles, the capacity has a stable value of $402 \text{ mAh}\cdot\text{g}^{-1}$. Compared with the graphene, the capacity has a slight rise since the nanocomposites contain Sn, which has high lithium storage capacity. There is one notable thing the practical capacity of Cu_6Sn_5 is lower than the theoretical capacity ($584 \text{ mAh}\cdot\text{g}^{-1}$). The main reason is that Cu_6Sn_5 has a lower coulombic efficiency, which is caused by the pulverization and disconnection of the active material during lithiation process, resulting in larger lithium-ion loss. The RGO on the surface of Cu_6Sn_5 nanoparticles could increase the diffusion channels of lithium ions and has a higher lithium ions packing density. As for RGO/ Cu_6Sn_5 nanocomposite, the initial discharge capacity is as high as $1380 \text{ mAh}\cdot\text{g}^{-1}$, charge capacity is $1180 \text{ mAh}\cdot\text{g}^{-1}$ and the coulombic efficiency is 85%. The stable capacity is $461 \text{ mAh}\cdot\text{g}^{-1}$ after 18 cycles, indicating the excellent cycling stability. After comparison, RGO/ Cu_6Sn_5 nanocomposite exhibits best cycling performance. That is because Cu_6Sn_5 nanoparticles has an inert and active two-layer structure compared to pure Sn, and the presence of inert phase Cu acts as a buffer layer. Meanwhile, due to the influence of nanometer scale, Cu_6Sn_5 nanoparticles have a smaller volume effect during charge and discharge process. In addition, Cu_6Sn_5 nanoparticles were uniformly dispersed on the surface of graphene, and the interaction between graphene and Cu_6Sn_5 nanoparticles makes Cu_6Sn_5 nanoparticles very stable. This nanocomposites structure of RGO/ Cu_6Sn_5 inhibits the volume change effectively during electrochemical cycling. Therefore, RGO/ Cu_6Sn_5 nanocomposites have high lithium storage capacity and excellent cycle stability.

Furthermore, RGO/ Cu_6Sn_5 nanocomposites also exhibit excellent rate performance in Figure 8. The test was carried out at $100 \text{ mA}\cdot\text{g}^{-1}$ and 20 cycles and the current density were 100, 200, 500 and $1000 \text{ mA}\cdot\text{g}^{-1}$, respectively. The corresponding average capacity were 646, 447.35, 400.9 and $334.6 \text{ mAh}\cdot\text{g}^{-1}$, respectively except first cycle, and the capacity recovered to $448.35 \text{ mAh}\cdot\text{g}^{-1}$ when the current density returned to $100 \text{ mA}\cdot\text{g}^{-1}$. Compared with the stable capacity ($461 \text{ mAh}\cdot\text{g}^{-1}$), the RGO/ Cu_6Sn_5 nanocomposites has excellent capacity retention ($448.35 \text{ mAh}\cdot\text{g}^{-1}$) and good stability after large rate charge/discharge cycling process. The results of test show that the RGO/ Cu_6Sn_5 nanocomposites have a great rate performance, excellent capacity retention and good stability. The material does not pulverize or agglomerate during charge/discharge cycling process. RGO/ Cu_6Sn_5 nanocomposites have high conductivity, which can provide fast and stable transport channel for electrons and ions.

Figure 8 The rate performances of RGO/ Cu_6Sn_5 .

Conclusions

In this paper, Cu_6Sn_5 and graphene/ Cu_6Sn_5 nanoparticles were prepared via chemical reduction method in aqueous solutions. Cu_6Sn_5 nanoparticles could inhibit the volume expansion and graphene could prevent the aggregation between Cu_6Sn_5 nanoparticles. Due to this structure, RGO/ Cu_6Sn_5 nanocomposites exhibit the best cycling performance ($461 \text{ mAh}\cdot\text{g}^{-1}$ after 18 cycles) and high rate capability by charge/discharge test.

Supporting Information

Supporting information for this article is available on the WWW under www.genchemistry.org/EN/10.21127/yaoyigc20180028.

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