Preparation of Nanometer Cu$_2$Sn$_6$ and Its Application in Lithium-Ion Batteries Anode for Mass Production

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Abstract Cu$_2$Sn$_6$ 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$_2$Sn$_6$ composites were also prepared by the similar method for the reason that the presence of RGO alleviated the aggregation of Cu$_2$Sn$_6$ nanoparticles. Therefore, RGO/Cu$_2$Sn$_6$ nanoparticles showed more superior electrochemical performance compared with Cu$_2$Sn$_6$ nanoparticles. The results showed that RGO/Cu$_2$Sn$_6$ nanoparticles exhibited promising cycling stability (461 mAh·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$_2$Sn$_6$ nanocomposites, which is suitable for mass production.

Keywords Cu$_2$Sn$_6$ nanoparticles, reduced oxide graphene/Cu$_2$Sn$_6$ 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 mAh·g$^{-1}$). Therefore, to develop new anode materials as replacements for graphite is more important. As the most promising substitute, Sn$_n$$^{+}$ has attracted considerable attention due to its high theoretical capacity (993 mAh·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. 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$_2$Sn$_6$. During lithiation/delithiation process, Cu$_2$Sn$_6$ shows small volume change. Many preparation method of Cu$_2$Sn$_6$ nanoparticles have been reported, such as spray pyrolysis, high energy ball-milling, high temperature oil bath method, electodeposition, ultrasonic dispersion method, solid-phase reaction and liquid phase chemical reduction method. Polat et al. reported that Cu and Sn were deposited simultaneously on copper substrate by electron beam evaporation to form nano-porous anode films. The charge/discharge tests show that the electrochemical performance of nano-porous Cu$_2$Sn$_6$ films is enhanced significantly. In this work, Cu$_2$Sn$_6$ nanoparticles have been prepared via chemical reduction method in aqueous solutions.

In addition, many reports about graphene, which could inhibit aggregation of Cu$_2$Sn$_6$ nanoparticles and improve cycling stability, had been published. Wang et al. used a soft chemical process to immobilize nanoscale Cu$_2$Sn$_6$ on a multi-layer graphene sheet to obtain a composite of graphene and Cu$_2$Sn$_6$. The electrochemical performance of RGO/Cu$_2$Sn$_6$ composites was excellent and the reversible capacity was 450 mAh·g$^{-1}$. 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$_2$Sn$_6$ nanoparticles. Herein, we develop a simple and environmentally friendly approach to prepare Cu$_2$Sn$_6$ nanoparticles and RGO/Cu$_2$Sn$_6$ composites. We try to combine the excellent electrochemistry performance of RGO and Cu$_2$Sn$_6$. The result shows great cycling stability (461 mAh·g$^{-1}$ after 18 cycles) and superior rate capability.

Experimental

Cu$_2$Sn$_6$ nanoparticles were prepared via chemical reduction of aqueous solutions. For this process, solution A and solution B were prepared, respectively. For obtaining Solution A, CuCl$_2$·2H$_2$O and SnCl$_2$·5H$_2$O were dissolved in 20 mL deionized water with a molar radio 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 CuCl$_2$·2H$_2$O. For obtaining Solution B, surfactant CH$_3$(CH$_2$)$_n$OSO$_3$Na or (CTAB, C$_{16}$H$_{33}$)N(CH$_3$)$_2$Br were added to deionized water and moderate amounts of NaOH (reducing agent) were dissolved in the above solution, stirred at constant temperature. The schematic diagram of preparation of Cu$_2$Sn$_6$ 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 Cu$_2$H$_2$O$_4^-$ 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$_2$Sn$_6$ nanoparticles. After that, the resulting Cu$_2$Sn$_6$ nanoparticles
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$_5$Sn$_5$ 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$_5$Sn$_5$ was formed on the surface of graphene to produce RGO/Cu$_5$Sn$_5$.

The phase composition was analyzed by X-ray diffraction (XRD, Rigaku D/max2200VPC, Japan). The morphology of Cu$_5$Sn$_5$, Sn and graphene/Cu$_5$Sn$_5$ 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$_5$Sn$_5$ prepared by chemical reduction method in aqueous solutions. It can be apparently found that the reaction product was Cu$_5$Sn$_5$ without the impurities of Sn, Cu and oxides.

![Figure 2 XRD pattern of Cu$_5$Sn$_5$.](image)

The morphology of Cu$_5$Sn$_5$ nanoparticles is characterized by TEM in Figures 3a and 3b. It can be not seen clearly that the boundary between Cu$_5$Sn$_5$ 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$_5$Sn$_5$ has an amorphous coating and the grain size of Cu$_5$Sn$_5$ 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$_5$Sn$_5$ nanocomposites is characterized by SEM in Figure 4. Cu$_5$Sn$_5$ nanoparticles are not aggregated together but dispersed on graphene nanosheets, indicating the formation of RGO/Cu$_5$Sn$_5$ nanocomposite (Figure 4a). From Figure 4b, it can be seen that Cu$_5$Sn$_5$ nanoparticles are coated with graphene that is nearly transparent in the high magnification image. In the preparation process, Cu$_5$Sn$_5$ 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 °C in Figure 5, which corresponds to the evaporation of water contained in the nano-powder. At temperature is about 100 °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 °C due to the happening of sintering and appearing of sintering neck. At about 300 °C, the absorbed heat of decomposition is less than the heat release of sintering. The exothermic peak appeared at 375 °C corresponds to the crystallization during sintering.

![Figure 3 TEM image of Cu$_5$Sn$_5$ (a, b) and Sn (c, d).](image)

![Figure 4 SEM image of RGO/Cu$_5$Sn$_5$ nanocomposites.](image)

![Figure 5 TG/DSC curves of Cu$_5$Sn$_5$ nanoparticles.](image)

To further understand the reaction mechanism of charge and discharge process, the initial discharge/charge curves of RGO/Cu$_5$Sn$_5$ were measured in Figure 6. In the first discharge curve, the Cu$_5$Sn$_5$ nanoparticles electrode has a discharge platform at a potential of 0.5 V, which shows an initial lithiation capacity of 1027.4 mAh·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 mAh·g$^{-1}$. The initial coulombic efficiency is 45.8%. This poor coulombic effi-
Efficiency 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$_6$Sn$_5$ and metallic lithium. The electrochemical cycling performances of Sn, Cu$_6$Sn$_5$, RGO, RGO-Sn and RGO-Cu$_6$Sn$_5$ as control samples are investigated by discharge/charge measurements at a current density of 100 mA·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 mAh·g$^{-1}$ and charge capacity is 647.6 mAh·g$^{-1}$, the coulombic efficiency of Sn is 55.3%. The initial discharge capacity of Cu$_6$Sn$_5$ is 1027.4 mAh·g$^{-1}$, charge capacity is 442.4 mAh·g$^{-1}$ and the coulombic efficiency is 45.8%. The capacity of Sn is higher than that of Cu$_6$Sn$_5$ in the initial discharge/charge process. Because the theoretical capacity of Sn is 960 mAh·g$^{-1}$, the theoretical capacity of Cu$_6$Sn$_5$ is 584 mAh·g$^{-1}$, the capacity of Sn nanoparticles in the first few cycles is much higher than that of Cu$_6$Sn$_5$. 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 mAh·g$^{-1}$. The capacity of Cu$_6$Sn$_5$ decreases slower than Sn and get a stable value of 265 mAh·g$^{-1}$ after 45 cycles. It can be concluded that Cu$_6$Sn$_5$ 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$_6$Sn$_5$.

**Figure 7** Cycling performances of Sn, Cu$_6$Sn$_5$, RGO, RGO/Cu$_6$Sn$_5$.

The electrochemical cycling performances of RGO/Sn nanoparticles were also investigated by discharge/charge measurements. The initial discharge capacity of RGO/Sn nanocomposites is as high as 1208 mAh·g$^{-1}$, and the charge capacity is 741 mAh·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 mAh·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$_6$Sn$_5$ is lower than the theoretical capacity (584 mAh·g$^{-1}$). The main reason is that Cu$_6$Sn$_5$ 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$_6$Sn$_5$ nanoparticles could increase the diffusion channels of lithium ions and has a higher lithium ions packing density. As for RGO/Cu$_6$Sn$_5$ nanocomposite, the initial discharge capacity is as high as 1380 mAh·g$^{-1}$, charge capacity is 1180 mAh·g$^{-1}$ and the coulombic efficiency is 85%. The stable capacity is 461 mAh·g$^{-1}$ after 18 cycles, indicating the excellent cycling stability. After comparison, RGO/Cu$_6$Sn$_5$ nanocomposite exhibits best cycling performance. That is because Cu$_6$Sn$_5$ nanoparticles have 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$_6$Sn$_5$ nanoparticles have a smaller volume effect during charge and discharge process. In addition, Cu$_6$Sn$_5$ nanoparticles were uniformly dispersed on the surface of graphene, and the interaction between graphene and Cu$_6$Sn$_5$ nanoparticles makes Cu$_6$Sn$_5$ nanoparticles very stable. This nanocomposites structure of RGO/Cu$_6$Sn$_5$ inhibits the volume change effectively during electrochemical cycling. Therefore, RGO/Cu$_6$Sn$_5$ nanocomposites have high lithium storage capacity and excellent cycle stability.

Furthermore, RGO/Cu$_6$Sn$_5$ nanocomposites also exhibit excellent rate performance in Figure 8. The test was carried out at 100 mA·g$^{-1}$ and 20 cycles and the current density were 100, 200, 500 and 1000 mA·g$^{-1}$, respectively. The corresponding average capacity were 646, 447.35, 400.9 and 334.6 mAh·g$^{-1}$, respectively except first cycle, and the capacity recovered to 448.35 mAh·g$^{-1}$ when the current density returned to 1000 mA·g$^{-1}$. Compared with the stable capacity (461 mAh·g$^{-1}$), the RGO/Cu$_6$Sn$_5$ nanocomposites has excellent capacity retention (448.35 mAh·g$^{-1}$) and good stability after large rate charge/discharge cycling process. The results of test show that the RGO/Cu$_6$Sn$_5$ 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$_6$Sn$_5$ nanocomposites have high conductivity, which can provide fast and stable transport channel for electrons and ions.

**Figure 8** The rate performances of RGO/Cu$_6$Sn$_5$.
In this paper, Cu$_4$Sn$_5$ and graphene/Cu$_4$Sn$_5$ nanoparticles were prepared via chemical reduction method in aqueous solutions. Cu$_4$Sn$_5$ nanoparticles could inhibit the volume expansion and graphene could prevent the aggregation between Cu$_4$Sn$_5$ nanoparticles. Due to this structure, RGO/Cu$_4$Sn$_5$ composites exhibit the best cycling performance (461 mAh·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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