Enhanced cyclic performance of SnO₂-CuO-graphite nano-sheets as anode for Li-ion battery

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Abstract

A ternary nanocomposite of SnO₂, CuO and graphite is prepared by bead milling in alcohol, during which the graphite is greatly thinned to form graphite nano-sheets that wrapping the SnO₂ and *in-situ* formed CuO nanoparticles. This unique microstructure of SnO₂-CuO-graphite nanocomposite benefits the reversible formation of SnO₂ and CuO in the repeatedly charging process, and thus significantly improves the cyclic stability and rate capability. The reversible capacity of this ternary nanocomposite remains 561.2 mAhg⁻¹ at 0.1 A g⁻¹ after 150 cycles, much higher than that of the SnO₂-graphite, and CuO-graphite hybrids.

Key words: Tin oxide; Copper oxide; Composite materials; Energy storage and conversion

1. Introduction

As a representative type of metal oxides for potential negative electrode material of lithium ion batteries, SnO_2 has attracted much research attention because of its high theoretical specific capacity of $\sim 1494 \text{mAhg}^{-1}$ [1-3]. It is generally regarded that the conversion reaction of SnO_2 in the initial discharge to form Sn and Li_2O is irreversible. Hence, the lithium storage in SnO_2 is substantially similar to that of pure Sn, which normally suffers fast capacity fading due to the huge volume change occurring in the Li-alloying of Sn [4-6]. In addition, serious aggregation of Sn particles during the repeated alloying reactions could also lead to poor cycling performance [7-9].

Many strategies have been proposed to alleviate the volume change of the SnO_2 anodes, while the most effective approach is to composite nanosized SnO_2 with carbonaceous materials, such as graphite, graphene, carbon nanotube [10-12]. These soft carbon materials can improve the conductivity, and also act as a buffer matrix to maintain the stability of the SnO_2 . Additionally, transition metal oxides (M_xO_y) have also been proven good components to composite with SnO_2 [13-16], showing synergistic effect on lithium storage for SnO_2 - M_xO_y hybrids. On one hand, the M_xO_y could maintain the highly dispersion of nanosized SnO_2 and thus benefit its reversible conversion reactions. On the other hand, the stepwise lithiation of SnO_2 and M_xO_y at different potentials could accommodate the volume change [13, 15-17]. Consequently, the cyclic performance of SnO_2 - M_xO_y was significantly improved.

Herein, we synthesized a new multi-phase composite containing SnO_2 , *in-situ* formed CuO and graphite nano-sheets by bead milling in alcohol. The as-synthesized SnO_2 -CuO-graphite nanocomposite demonstrates much higher capacity and markedly improved cycling stability.

2. Experimental

Firstly, the powder mixture of SnO₂, Cu (99.9%) and graphite (99.9%) with the weight ratio 38:32:30 were milled on a planetary mill to obtain the SnO₂-Cu-graphite (SnO₂-Cu-G) mixture. After that, the SnO₂-Cu-G mixture was further grinded in alcohol on a bead mill at 2500 rpm for 4 hours to form a SnO₂-CuO-graphite (SnO₂-CuO-G) nanocomposite. For comparison, the SnO₂-graphite (SnO₂-G) and CuO-graphite (CuO-G) with a weight ratio of 70:30 were also prepared.

X-ray diffractometer (XRD, Philips X'Pert MPD), a scanning electron microscope (SEM, Zeiss supra40) equipped with energy-dispersive X-ray spectroscopy (EDS), a transmission electron microscope (TEM, JEOL-2100), and a laser Raman spectrometer (Raman, HORIBA Labram) were used to characterize the microstructure of samples. Thermogravimetry analysis (TG, Netzsch 209F3) was conducted in oxygen. The electrochemical properties were measured using coin-type half-cells (CR2016). The working electrode was prepared by dissolving 80 wt.% active powders, 10 wt.% conductive agent, and 10 wt.% binder in solvent. Lithium metal foils were used as counter and reference electrodes, and polyethylene membranes as separators. The electrolyte was LiPF₆ (1M) in a mixture of ethylene carbonate/diethyl carbonate/ethyl methyl carbonate (1:1:1, v/v/v). Galvanostatic charge–discharge measurements were performed with battery testers (CT2001A, Land) at various current densities in the range of 0.01–3.0 V vs. Li/Li⁺. Cyclic voltammetry (CV) was performed on an electrochemical workstation (Interface 1000, Gamry).

3. Results and discussions

Figure 1 XRD pattern (a), TG profile (b), and Raman spectra (c, d) of the as-synthesized SnO₂-CuO-G composite.

Figure 1a shows the XRD pattern of the as-prepared composite, in which the SnO₂ and CuO phases are clearly observed. The formation of CuO is due to the oxidation of Cu during bead milling in alcohol. The notably broadening diffraction peaks imply the greatly decreased crystallite sizes of the SnO₂ and the *in-situ* formed CuO, which are roughly estimated to be 11 nm and 22 nm respectively by using profile fitting. **Figure 1b** shows the TG result of this composite, the weight loss is ca. 29.7%, which is due to the oxidation of carbon in the oxygen atmosphere, suggesting almost all the carbon remained in the composite during milling.

Figure 1c and **1d** show the Raman spectra of SnO₂-CuO-G composite at different Raman shift ranges. Only the distinct CuO peaks at 285 cm⁻¹ and 619 cm⁻¹ are shown in Figure 1c, while the SnO₂ could not be detected. As shown in Figure 1d, three characteristic peaks of carbon at ~1331 cm⁻¹ (D band), ~1586 cm⁻¹ (G band) and ~2718 cm⁻¹ (2D band) are observed. For the 2D band, it is approximately symmetric, and there is a blue shift in comparison to the standard value 2700 cm⁻¹ of

single layer graphene, implying the notable thinning of graphite during bead milling. The absence of Raman peaks of SnO_2 could be due to the coating of graphite nano-sheets and CuO on the surface of SnO_2 in the nanocomposite.

Figure 2 Microstructure of SnO_2 -CuO-G composite. SEM micrographs (a, b) , EDS spectrum (c), elemental mapping images (d) , and TEM (e, f) micrographs, the inset in (e) is the electron diffraction pattern of selected area as marked by red circle.

SEM image in **Figure 2a** shows the agglomerated micro-sized particles of the as-prepared composite, while the **Figure 2b** shows that SnO_2 and CuO nanoparticles are highly dispersed within

thinned graphite sheets. The EDS spectrum (**Figure 2c**) and elemental mapping images (**Figure 2d**) indicates the existence of Sn, Cu, O and C elements, showing that the SnO₂ and CuO nanoparticles mixed together quite uniformly. TEM results (**Figure 2e, 2f**) further demonstrate the crystallite size and dispersion state of SnO₂, CuO in the nanocomposite. In **Figure 2e**, the continuous diffraction rings confirms the nanocrystalline structure of SnO₂ and CuO. In particular, the abnormally large diffraction spot of graphite (002) plane indicates its typical two-dimension structure. According to the lattice fringes shown in the high-resolution TEM image (**Figure 2f**), the grain sizes of SnO₂ and CuO are less than 20 nm. Therefore, it is demonstrated that, by bead milling in alcohol, the SnO₂ and *in-situ* formed CuO nanoparticles are interconnected and wrapped by soft graphite nano-sheets.

Figure 3a shows the CV curves of SnO₂-CuO-G composite anode in the initial cycles, several pairs of anodic and cathodic peaks at different potentials are observed. As marked in detail, a pair of redox peaks (A, A') are related to Li insertion and extraction in the graphite, while the cathodic peaks at 0.2 ~ 0.6 V (C) and anodic peaks (C') at 0.3~ 0.8 V represent the alloying and de-alloying of Sn with Li, respectively. With respect to the two anodic peaks (B₁', B₂') at 1.0 V ~ 2.2 V, they originates from the reversible formation of SnO₂ from the Sn/Li₂O. In addition, the anodic peak above 2.6V (D') is coupled with the cathodic peak (D) at 1.9V, which should be due to the oxidation and reduction of CuO, respectively. The reversible formation of SnO₂ in the charging process indicates its high activity, which is related to the nanosizing effect and the increased conductivity in the SnO₂-CuO-G nanocomposite.

Figure 3 The Electrochemical performances of SnO₂-CuO-G electrode: (a) CV curves at scanning rate of 0.2 mV s⁻¹, (b) the discharge-charge profiles at 100 mA g⁻¹ between 0.01 and 3 V vs. Li/Li⁺; (c) charge capacity vs. cycle number at 100mA g⁻¹, (d) rate capability with current density range from 0.1 to 1.0 A g⁻¹.

Figure 3b shows the charge-discharge profiles of the SnO₂-CuO-G composite anode at 100 mA g⁻¹. The initial discharge and charge capacity is 1172.8 mAhg⁻¹ and 764.5 mAhg⁻¹, respectively, much higher than the theoretical value 628.3 mAhg⁻¹ if only considering the contribution of the single component SnO₂ ($\text{Sn} \leftrightarrow \text{Li}_{4.4}\text{Sn}$, 782mAhg⁻¹), CuO (672 mAhg⁻¹) and graphite (372 mAhg⁻¹) in this composite. This also confirms that the extra capacity comes from the reversible conversion reaction of SnO₂ and CuO. **Figure 3c** shows the cycling performance of the SnO₂-CuO-G composite anode. After 150 cycles, the charge capacity remains 561.2 mAhg⁻¹, slightly lower than its theoretical capacity of 628.3 mAhg⁻¹. Nevertheless, this capacity retention is much better than that of the SnO₂-Cu-G mixture, which just delivered a charge capacity of 450.8 mAhg⁻¹ after 80 cycles.

Furthermore, the cycleability of the SnO₂-CuO-G composite is also superior to those of the milled SnO₂-G and CuO-G hybrids, indicating by the fact that the SnO₂-G just delivers a lower capacity of 200 mAh g⁻¹ after 100 cycles. As shown in **Figure 3d**, the multi-phase SnO₂-CuO-G composite also present obviously superior rate-capability. Specifically, after three activation cycles, the SnO₂-CuO-G composite maintained a stable reversible capacity of 440 mA h g⁻¹ at a high current density of 1.0 A g⁻¹ (equal to ca. 2C). A capacity of 630 mA h g⁻¹ could be restored when the current density was reduced to 0.1 A g⁻¹ (equal to ~0.2C). The good rate capability was attributed to the enhanced kinetics resulted from the short diffusion distance for Li⁺ intercalation in the nanoparticles of SnO₂, CuO, and the interconnected graphite nano-sheets.

4. Conclusions

A new multi-phase anode composed with SnO₂, *in-situ* formed CuO and graphite nano-sheets has been prepared by wet-phase bead milling, in which the SnO₂ and CuO nanoparticles are wrapped by interconnected graphite nano-sheets. This unique nanocomposite microstructure contributes to the significant improvement of cyclic stability and rate capability of SnO₂-CuO-G anode. This work demonstrates the feasibility of bead milling for preparing the high-performance metal oxide composite electrode materials.

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Graphic Abstract