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Lithium storage capability of $CuGeO_3$ nanorods

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A R T I C L E I N F O

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Copper metagermanate ($CuGeO_3$) nanorods were synthesized through a low temperature hydrothermal method at 180 °C. The as-synthesized $CuGeO_3$ nanorods show a well crystallined nanostructure with diameters in the range from 40 to 70 nm, and a length from 250 to 350 nm. Electrochemical measurements demonstrate that the $CuGeO_3$ nanorods exhibit a first charge capacity of 924 mAh g^{-1} and 690 mAh g^{-1} after 50 cycles, which is remarkably improved than the pure nanosize GeO_2 electrode. This investigation indicates that $CuGeO_3$ nanorods could be utilized as a high capacity anode material in lithium-ion batteries by reducing particle size and metal oxide addition. The lithium storage mechanisms for the improved capacity retention were also studied.

1. Introduction

Copper metagermanate ($CuGeO_3$) is the only compound in which all GeO_4 tetrahedra lies on one side of the chain and is the first inorganic Spin–Peierls material ever discovered. Thereafter, a lot of attentions have been attracted to its magnetic properties [1].

Germanium (Ge) has a high theoretical lithium storage capacity of 1600 mAh g^{-1} by forming $Li_{22}Ge_5$ alloy, a low working potential of about 0–0.6 V vs. Li, and relatively high Li diffusivity at room temperature (400 times higher than well-studied Si). Therefore Ge and Ge compounds may be promising candidates for the applications as anodes for Li batteries [2–4]. However, the research on the Ge compounds as the anode is relatively limited compared to Si and Sn compounds [5–13]. Recently, Chowdari and co-workers [13] reported that the ternary oxides containing CuO can be used as a novel anode for the Li batteries owing to the high reversible capacities obtainable with the optimized compositions and conductivities, which is attributed to in situ electro-generated electronic conductive nano-sized metallic Cu networks.

The lithium storage mechanism can be explained through a several stages. In the first stage, Cu^{2+} from $CuGeO_3$ is first reduced to Cu metal together with formation of GeO_2 compound as indicated by Eq. (1) [6]. The newly formed GeO_2 is then reduced by forming pure Ge and Li_2O as shown in Eq. (2). Finally the pure Ge will be alloyed by Li forming Li_xGe [12,13].

$$CuGeO_3 + 2Li \rightarrow Cu + GeO_2 + Li_2O \tag{1}$$

$$GeO_2 + 4Li \rightarrow Ge + 2Li_2O \tag{2}$$

$$Ge + xLi \rightarrow GeLi_x \tag{3}$$

During charging, Li_xGe alloy will be first of all de-alloyed followed by oxidation of Ge and Cu as indicated in Eqs. (4) and (5).

$$GeLi_x \rightarrow Ge + xLi \tag{4}$$

$$Cu + Li_2O \leftrightarrow CuO + Li \tag{5}$$

It has been recognized that nanosized electrode materials can enhance electrochemical performance due to large surface area and reduced diffusion pathway [14,15]. Therefore it is worth investigating effect of nanosized $CuGeO_3$. Up to now, there are only limited studies on the formation of one dimension $CuGeO_3$ nanowires [16,17]. In this study, we have synthesized well crystallized $CuGeO_3$ nanorods with diameters of about 40–70 nm and length of about 250–350 nm by a facial hydrothermal process at 180 °C. Electrochemical characterization of the as-synthesized $CuGeO_3$ nanorods as anodes for Li rechargeable batteries shows promising results for practical applications.

2. Experimental

Nanocrystalline $CuGeO_3$ was synthesized by a hydrothermal process according to the procedure reported by Pei et al. [17] with some modifications. In a typical synthesis, 0.364 g of cetyltrimethylammonium bromide (CTAB, Aldrich, >99.9%), 0.52 g of GeO_2 (Aldrich, 99.999%), and 0.85 g of $CuCl_2{\cdot}2H_2O$ (Aldrich, >99.9%) were added to 15.0 mL of distilled water. The pH value of the resulting mixture was adjusted to 8 by adding NaOH (30 wt.%). The mixture was stirred for 1 h and then transferred to a

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stainless Teflon-lined autoclave of 25 mL inner volume with 80% fill ratio. The autoclave was heated to 180 °C and held for 24 h, followed by cooling to room temperature. The product was centrifuged, filtered, and rinsed with alcohol and deionized water for several times. Finally, the product was dried at 80 °C for 12 h in the air. A blue colored $CuGeO_3$ powder was obtained with a yield of about 90%.

The crystal structures and microstructures of the products were characterized by means of X-ray diffraction (XRD, Shimadzu 6000, λ = 1.5405 Å), and scanning electron microscopy (SEM, Hitachi, S-4300) with energy dispersive X-ray (EDX) spectroscopy.

To measure the electrochemical performance of the as-synthesized $CuGeO_3$ nanorods, the $CuGeO_3$ nanorods (80 wt.%) was mixed with PVDF (10 wt.%) (polyviyldifluoroethylene) and acetylene black (10 wt.%). The mixture of the $CuGeO_3$ nanorods was then stirred 24 h to form a uniform paste. The paste was caste onto a titanium substrate and vacuumed-dried at 120 °C for 24 h. Weight of the electrode was measured by a balance (AND GR-202) with an accuracy of 0.01 mg. The typical loading of the $CuGeO_3$ electrode is about 1–2 mg/cm^2. For SEM examination of the electrodes after charge/discharge, the electrode films were washed using tetrohydronfuran and then dried in a vacuum at room temperature before characterization [8].

To evaluate the electrochemical performance of the $CuGeO_3$ nanorods as an anode, cyclic voltammetry and battery tests were carried out using a Solartron 1287 and 1256 two terminal cell test system. A Li foil was used as both counter and reference electrodes. $LiPF_6$ (1 M) in EC:EMC:DMC (1:1:1 in volume OZARK Fluorine Specialities, Inc.) solution (1/1/1, vol.% Merck) was used as the electrolyte. The cell was assembled in the argon-filled glove box with moisture and oxygen pressure below 0.1 ppm. The galvanostatic charge/discharge cycling experiment was performed in the potential range from 0 to 3 V at a current density of 150 mA/g.

3. Results and discussion

X-ray diffraction (XRD) spectrum of the as-synthesized $CuGeO_3$ nanorods is shown in Fig. 1a. All the diffraction peaks can be assigned to the orthorhombic phase of $CuGeO_3$ (JCPDS File No. 32-0333) with lattice parameters of a = 4.805 Å, b = 8.477 Å, c = 2.946 Å, indicating the pure phase of the product. The $CuGeO_3$ nanorods are well crystallized according to the strong diffraction peaks. The inset in Fig. 1b presents the EDX spectrum of the nanorods showing the presence of Ge, oxygen and Cu in the sample with a Ge:Cu atomic ratio of about 1:1. The chemical composition of the sample derived from EDX analysis can be denoted as $CuGeO_3$ and is consistent with the chemical composition of $CuGeO_3$ consistent with report [17].

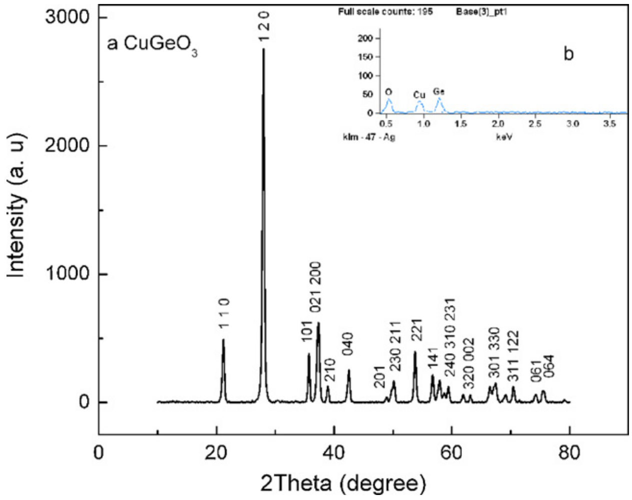

Fig. 1. XRD pattern (a) and EDX spectrum (b) of prepared $CuGeO_3$ nanorods.

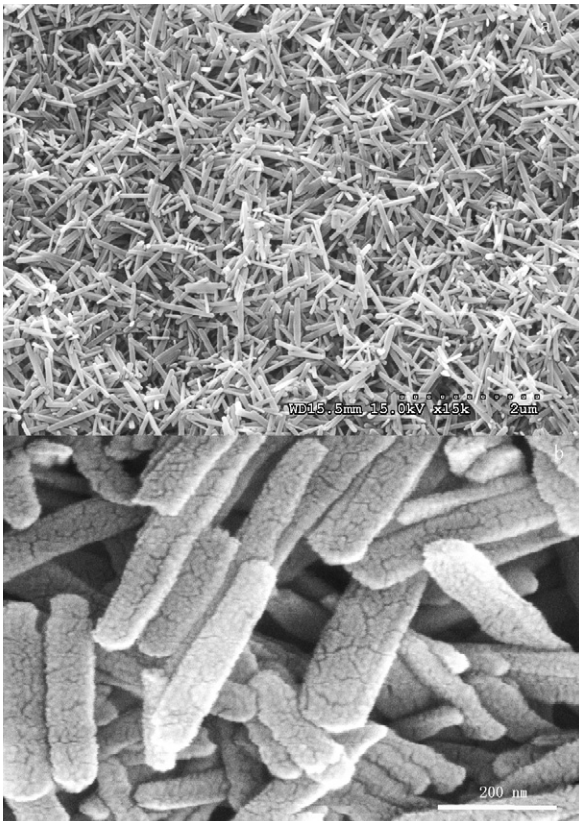

Fig. 2. SEM images of the prepared $CuGeO_3$ nanorods at low (a) and high (b) magnifications.

The morphology of the as-synthesized $CuGeO_3$ nanorods was examined by scanning electron microscopy (SEM) in the low-magnification SEM (Fig. 2a), it can be seen that the $CuGeO_3$ nanorods consist of uniform one dimension nanostructured crystals. The high-magnification SEM image in Fig. 2b shows that the one-dimensional nanorods have a length of about 250–350 nm and a diameter of about 40–70 nm.

The mechanisms for Li storage in $CuGeO_3$ are proposed through three steps. The first step is the irreversible reduction of Cu^{2+} to Cu. The second step involves the reversible reduction of Ge (IV) to Ge, and finally Ge is experienced lithiation–delithiation process. Cyclic voltammetry is an effective method to probe the mechanism of electrochemical reactions. Fig. 3 shows the first three cyclic voltammetry curves of the $CuGeO_3$ electrode at a scanning rate of 1 mV/s between 0 and 3.2 V. The first cathodic sweep started from an open circuit voltage (OCV) 3.2 V. A sharp peak starts at about 1.7 V was observed due to Cu^{2+} reduction. Another peak starting from 0.8 V is due to the Ge^{4+} reduction and Li–Ge alloying reaction. During the anodic process, an anodic peak is also present between 0 and 0.9 V, corresponding to the reversible de-lithiation of $GeLi_x$. A second peak between 1 and 2 V corresponds to Cu–Cu^{2+} and partly $Ge \rightarrow Ge^{4+}$ [7–10]. Both the peak current and the integrated area of the anodic peak in the first cycle are decreased, indicating a capacity loss during the charging process due to the formation of SEI and some irreversible reaction. It is clearly shown that two pairs of peaks are still existence in the subsequent cycles with a little potential shift. In the subsequent cycles, the two cathodic/anodic peak potentials shift to 1.2, 0.4 V and 0.6, 1.50 V, respectively. The areas under the two peaks which correspond