Facile preparation of hierarchical CuO nanostructures as an integrate binder-free anode for high-performance lithium-ion batteries

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Abstract. Novel CuO hybrid nanostructures composed of one-dimensional (1D) porous carbon nanofibers and two-dimensional (2D) graphene nanosheets have been fabricated with the help of electrospinning technique, which is denoted as CuO@PCNF/GN. The microstructure and morphology of the CuO@PCNF/GN were investigated by X-ray diffraction and transmission electron microscopy. The electrochemical performances of the as-prepared materials as a novel bind-free anode for lithium ion battery (LIB) were investigated. The CuO@PCNF/GN electrode exhibited high discharge capacity of 665 mAh g⁻¹ after 60 cycles at the current density of 100 mA g⁻¹. Even at 800 mA g⁻¹, the discharge capacity of the anode could still maintained at 443 mAh g⁻¹. The excellent electrochemical properties of CuO are greatly related to the unique 3D interconnected structure of continuous PCNF and GN, which enables efficient electron/ion transport and migrate the volume change of active CuO materials.

Keywords: electrospinning; 3D interconnected structure; CuO@PCNF/GN; bind-free anode; lithium-ion battery.

1. Introduction

The rapid development of portable electronics and electric vehicles requires high capacity and energy lithium-ion batteries (LIB). As the significant component of a battery system, the anode plays a vital role for high-performance LIBs. However, the commercial graphite anode material cannot meet this growing energy-demand due to its low capacity of only ~372 mAh g⁻¹. Therefore, it is urgent to develop advanced anode materials with high capacity [1-3], such as metal oxides, sulfides, etc.

Among various oxide anodes, CuO has received particular attention due to its relatively high capacity, low cost, natural abundance and environmental benignity [4-5]. However, the shortage of CuO electrode material is the large volume change during the Li⁺ insertion/extraction processes, which would induce huge damage to the mechanical stability of electrode and rapid capacity decay. Recently, various strategies have been explored to improve the electrochemical properties of CuO electrodes such as constructing CuO/conductive carbon hybrids and tailoring the size and morphology of CuO. It is well known that the electrochemical properties of electrode materials are strongly depended on the
microstructure and morphology. One-dimensional (1D) and two-dimensional (2D) nanostructures have been considered as promising materials for energy storage applications because of their high specific surface area and efficient transport pathways for both electrons and ions [6-7]. As one of the simple and efficient technologies, electrospinning is used to prepare (1D) nanostructures with high surface area and porous structures, such as nanofibers and nanobelts, and they are successfully used as electrode materials for energy storage and conversion devices [8-9]. More importantly, with the combination of 2D materials, novel 3D interconnected hierarchical nanostructures can be effectively constructed to enable efficient electrode/ion transport for high performance electrode.

In this work, we report a 3D hierarchical CuO-based nanostructures composed of porous carbon nanofibers (PCNF) and graphene nanosheets (GN), denoted as CuO@PCNF/GN, by a simple electrospinning technology followed by an annealing process. As a novel bind-free anode for LIB, the novel CuO@PCNF/GN electrode exhibits excellent cycling stability and rate performance.

2. Experimental

All reagents were of analytical grade and used without any further purification, graphene oxide (GO) powders were synthesized from natural graphite flakes by a modified Hummers method [10]. In a typical synthesized process, 30 mg GO powders and 0.3 g of polyacrylonitrile (PAN) were dissolved in 3 mL N, N-dimethyl formamide under ultrasonication for 3 h to form a homogeneous solution. 0.2 g Cu(CH₃COO)₂ was added into the above solution and ultrasound for 2 h, then the mixed solution was kept stirring for 10 h at room temperature. Electrospinning was carried out with a high voltage of 19 kV, the distance between needle tip and aluminum collector is 14 cm with a flow rate of 1.0 mL h⁻¹. Then the as-spun web-like PAN-GO-Cu(CH₃COO)₂ precursor was annealed in air at 350 °C for 2 h with a heating rate of 2 °C min⁻¹.

Morphologies and structure of the samples were characterized by a field emission scanning electron microscope (SEM; Hitachi S-4800) and Bruker D8 X-ray Diffractometer using Cu Kα radiation. CR 2025 coin-type cells with pure lithium foil as the counter electrode and electrolyte of 1 M LiPF₆ in ethylene carbonate (EC)-dimethyl carbonate (DMC) with the volume ratio of 1 : 1 assembled in a glove box filled with highly pure argon gas. Galvanostatic charge-discharge cycles were carried out on the LAND CT2001A multi-channel battery testing system. Cyclic voltammetry (CV) measurements were conducted on a BioLogic VMP3 electrochemical workstation. All tests were performed at room temperature.

3. Results and discussion

The microstructure and morphology of the as-prepared electro-spun samples was investigated by SEM. As shown in Figure 1(a-b), the electro-spun PAN-GO-Cu(CH₃COO)₂ precursor shows a web-like structure. The nanofibers have a smooth surface with diameter of about 300-800 nm and length of several millimeters. Some GO nanosheets closely entangle the surface of nanofibers, and others are distributed uniformly among crossed nanofibers to form a web-like structure. After annealing, Cu(CH₃COO)₂ decompose into CuO nanoparticles, while PAN nanofibers and GO change into porous carbon nanofibers (PCNF) and reduced graphene nanosheets (GN). As displayed in Figure 1(c-d), the length of nanofibers changes from several millimeters to several micrometers, while the size of the nanosheets remains with almost no change. Besides, the surface of the nanofibers and nanosheets becomes coarse owing to the decomposition of Cu(CH₃COO)₂ to CuO and combustion of PAN and GO. The 3D web-like structure of PCNF and GN can enable efficient electron/ion transport and migrate the large volume change of CuO.
The annealing temperature is the key factor to form the pure phase of CuO. The TG-DSC curve of the PAN-GO-Cu(CH₃COO)₂ precursor from 25 °C to 800 °C in air is shown in Figure 2(a). The first weight loss of about 12.5 wt.% between 25 °C and 150 °C is ascribed to the removal of adsorbed and coordinated water molecules. Subsequent weight loss of ~17 wt.% is related to the combustion of PAN and GO. When the temperature is above 340 °C, a steep weight loss of 56 wt.% takes place, which attributes to decomposition of Cu(CH₃COO)₂ to CuO. Based on the TG-DSC results, 350 °C was chosen as the calcination temperature.

Figure 2(b) is the XRD pattern of the CuO@PCNF/GN achieved after annealed at 350 °C for 2 h. All the diffraction peaks can be indexed to standard monoclinic CuO (standard JCPDS card no. 48-1548) belonging to the space group of C2/c. The result demonstrates the phase purity of the as-prepared product.

Figure 3(a) shows the galvanostatic charge-discharge voltage profiles of the CuO in the voltage range of 0.05-3.0 V at a current density of 0.1 mV s⁻¹. During the first discharge process, there are three obvious potential ranges at 2.2-1.6 V, 1.4-1.0 V and 1.0-0.05 V, separately. Which are ascribed to the multistep electrochemical reductions of CuO with Li intercalation [11-13]. The first stage is
related to the intercalation of Li\(^+\) into CuO to form the Cu\(^{11-}\)\(_{1-x}\)Cu\(^{1-}\)\(_{1-x}\)O\(_{1-x/2}\) (0<x<0.4) phase. The second stage is the formation of Cu\(_2\)O, and the third stage is the conversion of Cu\(_2\)O into Cu and Li\(_2\)O. The first discharge and charge capacities are 964 mAh g\(^{-1}\) and 643 mAh g\(^{-1}\), respectively. The large capacity loss during the first cycle is common for transition oxides, which might be ascribed to the decomposition of electrolytes and the formation of a solid electrolyte interface (SEI) layer on the surface of the electrode materials [14-15]. In the subsequent 20 cycles, the shapes of the charge-discharge curves almost do not change, indicating good capacity retention and excellent cycling stability of the CuO@PCNF/GN electrode. Figure 3(b) shows the initial four CV curves of the CuO@PCNF/GN electrode in the voltage window of 0.05-3 V at a scan rate of 0.1 mV s\(^{-1}\). In the first negative scan, the peaks at 1.1 V and 0.7 V agree well with the discharge curve potential stage II and III, corresponding the multi-step reduction of CuO to Cu\(_2\)O and Cu, respectively. From the second scan, the cathodic peaks shift to 1.7 V and 1.3 V with obvious capacity decay, which should be attributed the initial activation and the irreversible processes in the electrode materials. In the positive scan, only one pronounced anodic peak at around 2.1 V can be observed which attributes to the oxidation of Cu to CuO, which is in good agreement with the potential stage of charge curves. It can be seen that the curves overlap in the subsequent cycles, which suggests good cycle stability of the CuO@PCNF/GN electrode.

The cycling performance of the as-obtained CuO@PCNF/GN electrode evaluated at the current density of 100 mA g\(^{-1}\) is shown in Figure 4(a). The reversible capacity still remains 665 mAh g\(^{-1}\) after 40 cycles and shows almost no decay counted from the 2\(^{nd}\) cycle, demonstrating excellent cycling stability. Figure 3(b) shows the rate capability of the CuO@PCNF/GN electrode at various current densities from 100 mA g\(^{-1}\) to 800 mA g\(^{-1}\). The CuO@PCNF/GN electrode delivers a high average discharge capacity of 620, 580, 538, 506 mAh g\(^{-1}\) at the current densities of 100, 200, 400, 600 mA g\(^{-1}\), respectively. Even after 20 cycles at a high current density of 800 mA g\(^{-1}\), the reversible discharge capacity of 443 mAh g\(^{-1}\) could still be delivered. What’s more, when the current density returns back to 100 mA g\(^{-1}\), the high average discharge capacity of 574 mAh g\(^{-1}\) can be recovered. The results vividly indicates the excellent rate capability of the as-prepared CuO@PCNF/GN electrode.
According to the above results, it is clear that the CuO@PCNF/GN electrode exhibit high reversible capacity, and remarkable cycling life and outstanding rate capability. The excellent electrochemical properties are credited to the synergistic effect of 1D continuous PCNF and 2D GN, which interconnect with each other to form a 3D hierarchical structure. Such a structure benefits for enabling fast electron transport to improve the utilization of CuO, and migrating the large volume change to enhance the integrity of the electrode during long-term cycling. In addition, the electro-spun web-like CuO@PCNF/GN product can serve as a binder-free electrode for LIB, which also contribute the improved performance.

4. Conclusions
Novel CuO hybrid nanostructures composed of 1D nanofibers and 2D nanosheets were facilely fabricated via electrospinning of PAN-GO-Cu (CH3COO)2 precursor and post annealing. When used as a bind-free anode for LIB, the novel CuO@PCNF/GN electrode exhibits high reversible discharge capacity, good cyclic stability and excellent rate performance. The much improved electrochemical properties can be attributed to the 3D interconnected structure of 1D PCNF and 2D GN, which enables fast electron transport to improve the utilization of CuO, and migrates the large volume change to enhance the integrity of the electrode during long-term cycling. The results suggest that the as-prepared CuO@PCNF/GN sample is a promising anode material for high performance LIB, and the strategy of synthesizing 1D and 2D hybrid structure can be extended to other metal oxides based electrode materials.

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