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Development of electrochemical supercapacitors with uniform nanoporous silver network



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ABSTRACT

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Keywords: Nanoporous silver Metallic glass Manganese dioxide Capacitance Energy storage Metal oxides such as manganese dioxide (MnO₂) are often used as electrode materials for supercapacitors due to their high specific capacitance. In practice, however, their specific capacitance is much smaller than the theoretical limit due to the low electrical conductivity and serious agglomeration. In the present work, we demonstrate that highly conductive nanoporous silver (NPS) network with uniform continuous nanoporosity and high surface area which was fabricated by dealloying Ag-Mg-Ca metallic glasses can be employed as supports and collectors for MnO₂ capacitors. By plating the MnO₂ nanocrystals into the nanopore structure, the NPS/MnO₂ composite electrode provides fast ionic conduction and excellent electron-proton transport, resulting in an ultrahigh specific capacitance of the plated active MnO₂ (~1088 F g⁻¹), which is close to the theoretical limit. The unique combination of high specific capacitance and long cycle life enhanced by the current composite structure makes the NPS/MnO₂ composite promising for electrochemical supercapacitor as electrode material. In addition, our findings suggest that the uniform NPS network is capable for improving capacitance performance of metal oxides in electrochemical supercapacitors.

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1. Introduction

Supercapacitors, also known as ultracapacitors or electrochemical supercapacitors, are passive and static electrical energy storage devices with a unique combination of high electrical power, fast charge-discharge rate and long operating lifetime [1-3]. These high-performance capacitors have attracted a great deal of attention due to their extensive applications in portable electronic devices, hybrid electric vehicles and large industrial equipments [4–7]. Currently, the supercapacitors mainly include electric double-layer capacitors and pseudocapacitors. The capacitance of the electric double-layer capacitor generally comes from the charge accumulated at the electrode/electrolyte interface. In contrast, the high energy storage in the pseudocapacitors comes from the charge transfer between electrodes and electrolytes through surface adsorption, reversible faradic redox reactions and intercalation of ions [3,8-10]. These two mechanisms (i.e., electric double-layer capacitance and pseudocapacitance) can work separately or coordinately, depending on the electrode materials used in the supercapacitors. The active electrode materials, which determine the capacitance performance of the pseudocapacitors, are currently focused on transition metal oxides and conductive polymers [11–14]. Among them, manganese dioxide (MnO_2) has been extensively studied because of its high capacitance, low cost, and environment-friendly [15,16]. The electrochemical process is a reversible change in the valance state of the MnO_2 during the charge and discharge process, while the protons and electrons are transferred between the MnO_2 and electrolytes through the following reaction [17,18]:

$$MnO_2 + H^+ + e^- - MnOOH$$
(1)

Theoretically, the above reaction resulted from MnO_2 was predicted to provide a high specific capacitance of ~1370 Fg⁻¹. However, such a high capacitance has not been achieved in practice, and experimental specific capacitances are usually much lower than the theoretical maximum by $100\sim200$ Fg⁻¹ [19,20]. The poor charge storage performance of MnO_2 is attributed to its weak conductivity and serious agglomeration [21–24]. Over the past decades, conductive supports, such as carbon nanotubes and graphene, have been utilized to improve the capacitance of the MnO_2 [25–27]. More recently, newly developed nanoporous metals have also been employed as supports and collectors for supercapacitors applications due to their open nanopore structure, high surface area, and strong interfacial affinity [28,29]. For example, Chen et al. have fabricated nanoporous gold with RuO₂

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hybrid electrodes for high performance supercapacitors, exhibiting ultrahigh specific capacitance and good cyclic stability. The three dimensional (3D) nanoporous composite architecture can evidently decrease the internal resistance while maintaining sufficient electrolyte penetration and fast ion exchange [30]. Considering the advantage of ultrahigh conductivity of silver, in the present work, we utilized the 3D nanoporous silver (NPS) fabricated by electrochemical dealloying Ag-Mg-Ca glassy ribbon as both support and collector for MnO₂-based capacitors. The synthesized NPS/MnO₂ composite electrodes offer a large interface area and excellent electronic/ionic conductivity for high energy storage, resulting in high specific capacitance and long cycle life. These newly developed composites are promising for applications in electrochemical supercapacitors as electrode/collector materials.

2. Experimental

2.1. Synthesis of NPS and NPS/MnO₂ composites

Ag45Mg35Ca20 (at.%) glassy precursors were pre-prepared by using high-frequency induction furnace and single-roller meltspinning apparatus. The NPS ribbons with dimension of $40 \text{ mm} \times 2$ $mm \times 7 \mu m$ were fabricated by electrochemical dealloying $Ag_{45}Mg_{35}Ca_{20}$ metallic glass in 0.025 mol L⁻¹ MgCl₂ aqueous electrolyte for 30 min under a potential of 0.8 V (vs. Ag/AgCl reference electrode, $3 \mod L^{-1} \text{ KCl}$ [31]. Then the dealloyed products were placed in diluted HCl aqueous solution (0.01 mol L^{-1}) for 5 min to homogenize. The residual chemical substances within pore channels were rinsed with ultrapure water and dehvdrated alcohol repeatedly. The NPS/MnO₂ composites were fabricated by an electroless plating method [32]: the clean NPS ribbons were suspended on an aqueous solution which contains 2 mmol L⁻¹ $KMnO_4$ and 5 mmol L⁻¹ KOH. MnO₂ was plated into the nanopore structure for 5, 10, 15, 20, 25 and 30 min under the reducing reagent atmosphere (Hydrazine, N_2H_4) at room temperature. Subsequently, the synthesized MnO_2 plated NPS ribbons were then rinsed in ultrapure water and dehydrated alcohol repeatedly to remove the residual chemical substances.

2.2. Microstructure characterization

Microstructure and chemical composition of the as-synthesized composites were characterized using a scanning electron microscopy (SEM, Zeiss Supra 55) equipped with an energy dispersive X-ray spectrometer (EDS) and transmission electron microscope (TEM, Tecnai G2 F30). The foils used for the TEM experiments were prepared by focused ion beam (FIB, Zeiss Auriga). X-ray photoelectron spectroscopy (XPS AXIS-ULTRA-DLD, Kratos) with an Al K α (mono, 1486.6 eV) anode at an energy of 150 W in a vacuum of 10⁻⁷ Pa was employed to investigate the surface chemical state and binding energy of the NPS/MnO₂ composite. Elementary analysis of the NPS/MnO₂ composites was also carried out by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Prodigy, Leeman).

2.3. Electrochemical measurement

The electrochemical properties and capacitance measurements of the NPS/MnO₂ composite electrodes were conducted by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) techniques in a standard three-electrode electrochemical analyzer (CHI 660D) at room temperature. The system was constructed using a platinum plate as the counter electrode, Ag/AgCl standard electrode ($3 \text{ mol L}^{-1} \text{ KCl}$) as the reference electrode and the NPS/MnO₂ composite as the working electrode. The aqueous solution of $2 \text{ mol L}^{-1} \text{ Li}_2\text{SO}_4$ was used as electrolyte. Electrochemical impedance spectroscopy (EIS) measurement was performed on the NPS/MnO₂ composite electrode with a frequency ranging from 100 kHz to 0.01 Hz with a potential amplitude of 5 mV. Before each testing, the electrolytes were deaerated by pure N₂ gas for 30 min.



Fig. 1. Schematic of the fabrication process for the NPS/MnO₂ composite by electroless plating of MnO₂ into the NPS nanopores. SEM images show the surface morphologies of the NPS before (a) and after (b) plating, respectively.

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