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High-performance symmetric supercapacitor based on manganese oxyhydroxide nanosheets on carbon cloth as binder-free electrodes

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HIGHLIGHTS

- Thin-wall MnOOH grows on carbon fibers as a binder-less electrode.
- The smart architecture is beneficial to fast ion and electron transfer.
- The integrated electrode shows high capacitance and excellent cycle stability.
- The fabricated SSC exhibits high energy density of 32.5 Wh kg^{-1}.

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ABSTRACT

Three-dimensional (3D) material, as a promising candidate for supercapacitor electrodes, draws great attention all the time since it exhibits the enhanced capacitive performance comparing with the low dimensional nanoscale building blocks. Herein, we grow MnOOH on carbon cloth (CC) fibers by employing electrodeposition method. The morphology, microstructure and composition of the as-obtained samples were characterized by using FESEM, XRD, XPS, Raman and FTIR. The MnOOH nanosheets are grown vertically on CC fibers to form a thin-wall cell structure with open pores (donated as thin-wall MnOOH/CC), which can be directly acted as working electrode without other binders or conductive additions. The thin-wall MnOOH/CC electrode in the three-electrode configuration reveals a high specific capacitance of 330.2 F g^{-1} under a wide potential window of 1.7 V (ranging from −0.9 V to 0.8 V) as well as excellent cycle stability (6.3% decay after 5000 cycles). Furthermore, the symmetric supercapacitor (SSC) assembled by using thin-wall MnOOH/CC as both negative and positive electrodes shows an energy density of 32.5 Wh kg^{-1} at power density of 850 W kg^{-1} with a remarkable cycle lifetime (84.6% of the initial value after 10000 cycles). The unique thin-wall structure and binder-free electrode are responsible for the enhanced electrochemical performances.

1. Introduction

To meet the ever growing demand for the environmentally friendly and renewable energy devices in the modern electronic industry, much efforts have been devoted to exploring the high-performance energy storage devices [1–3]. Supercapacitors, as one of the most important energy devices, have attached much attention because of their excellent reliability, high power density and exceptionally long cycle life, but they suffer from a relatively low energy density comparing to lithium-ion batteries [3–5]. As for a supercapacitor, the energy density (E) can be calculated on the basis of the equation $E = 1/2CV^2$ [6–9], and enlarged by realizing the maximization of the specific capacitance (C) and the cell voltage (V). Moreover, the specific capacitance is closely related to the chemical and physical properties of the electrode materials. According to the charge-storage mechanism, supercapacitors are classified into two types, that is, double-layer capacitors and pseudocapacitors [7,10–12]. It is generally considered that the pseudocapacitors based on transition metal (Ru, Co, Fe, Mn, etc.) oxides have substantially higher capacitance and energy density due to the fast and reversible faradaic reactions [13–15]. Among the transition metal oxides, manganese (Mn) compounds have evoked considerable interest because of their multi-oxidation states for charge transfer and reversible adsorption, such as MnO_2 [16–18],

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Mn_3O_4 [19–21] and MnOOH [10,22–24]. Especially, MnOOH with a stable trivalence under ambient conditions has been expended to apply in supercapacitors in recent years, due to its low cost, abundant resources and great flexibility in structure and morphology. It is regrettable that it suffers from poor electrical conductivity, which limits the advancement in energy storage [25,26]. To overcome this disadvantage, one attempts to incorporate MnOOH into carbon-based materials with the excellent conductivity and chemical stability to form composites. For instance, Mei et al. [27] reported that the MnOOH-graphene composite could achieve specific capacitances of 112 F g^{-1} in 1 M Na_2SO_4 and 165 F g^{-1} in 6 M KOH electrolyte, respectively. Recently, Fang et al. [10] have prepared multi-walled carbon nanotube/α-MnOOH coaxial nanocable films through electrophoretic deposition process, which shows a high mass specific capacitance of 327 F g^{-1} and good cycle stability. In addition, MnOOH nanorods/graphene synthesized without adding any surfactant released a specific capacitance of 268 F g^{-1} at a current density of 0.5 A g^{-1} by Cao et al. [22]. Except for graphene and carbon nanotube, carbon cloth (CC) consisting of numerous uniform carbon fibers, is regarded as a novel carbonaceous material because of its low-cost, chemical stability and desirable conductivity [21,28–30]. In this regard, it has been extensively used as current collecting substrate in the fabrication of electrode materials. What is more, compared to other carbon-based materials, CC with regular network structure could be conducive to accelerating the flow of ions and shortening the diffusion pathway of ions in the electrochemical process, leading to attractive performances for supercapacitors.

As well-known, the capacitive performances of electrode materials could be varied as a function of the microstructure. With the increasing dimensionality, a large percentage of certain facets are exposed in the electrolyte, which effectively enlarges the reactive surfaces, and accordingly enhances the capacitance of electrode materials. On this account, more and more attentions have been focused on the construction of three-dimensional (3D) hierarchical structures composed by low dimensional nanoscale building blocks [7,31–33]. The reconstructed 3D hierarchical structures could not only exhibit the advantages of the pristine building blocks, but also possess new physicochemical properties due to their secondary architecture.

In the present work, we used temperature-controlling cathodic electrodeposition to grow unique MnOOH on the CC fibers etched by mixed acid, where the MnOOH nanosheets are interlaced with each other to form the thin-wall cell vertical to the surface of the CC fibers. It has two merits as a binder-free electrode for supercapacitors. On the hand, the cell could be served as a micro-accumulator to store electrolyte, resulting in short diffusion pathway of reacting ions; on the other hand, the thin wall lets the certain facets of MnOOH expose in electrolyte solutions, providing sufficient active sites for electrochemical reactions or increasing the utilization of active species. Furthermore, the ion and electronic channels formed during the electrodeposition are favorable for electron collection and ion diffusion during charging/discharging processes. As a result, the binder-free thin-wall MnOOH/CC electrode shows excellent capacitive performances both in three-electrode and two-electrode systems. Emphatically, the symmetric supercapacitor assembled on the basis of thin-wall MnOOH/CC delivers a high energy density with outstanding cycle stability (84.6% of the initial value after 10,000 cycles).

2. Experimental

2.1. Growth of MnOOH nanosheets on CC fibers

All the reagents in the experiment are analytical grade without further purification. CC was first cleaned by continuous sonication in acetone, deionized (DI) water, and ethanol for 15 min, respectively. To enhance hydrophilicity, we appropriately etched the CC by a mixed acid oxidation as well as our previous report [7]. The electrodeposition process was performed in a three-electrode configuration, where CC (1 × 4 cm^2), platinum (Pt) mesh and Saturated Calomel Electrode (SCE) were used as the working electrode, the counter electrode and the reference electrode, respectively. MnOOH was electrochemically deposited on CC surface in an electrolyte solution including 0.5 M $MnCl_2 \cdot H_2O$ and 0.5 M $NaNO_3$ at a constant potential of −1.5 V at 50 °C, and then the substrate was rinsed several times with DI water to remove the excessive electrolyte. Finally, the resultant product was dried in a vacuum oven at 60 °C. The mass loading of MnOOH was controlled by adjusting the deposition time and measured by a microbalance before and after the materials loading.

2.2. Characterization of samples

Contact angle measurement was tested by HARKE-SPCAx3 equipment with a CMOS camera. The structure features of the samples were characterized by field emission scanning electron microscopy (FESEM; LTRA plus, Germany). The crystalline state was examined by Powder X-ray diffraction (XRD) on a diffractometer (D/Max-2400) with Cu Kα radiation (λ = 1.5418 Å) operating at 40 kV, 60 mA. X-ray photoelectron spectroscopy (XPS; PHI-5702, U.S.) was employed to investigate the valence state of metal element. The chemical components of samples were measured *via* elemental mapping (Aztee-X-80, Britain), FTIR spectrum (a Nicolet Nexus 670 FTIR instrument), and Raman spectroscopy (Bruker RFS 100/S, Germany).

2.3. Electrochemical measurement

Electrochemical measurements, such as the cyclic voltammogram (CV), galvanostatic charge/discharge test and electrochemical impedance spectroscopy (EIS), were carried out in three-electrode or two-electrode systems by employing a CHI760D electrochemical workstation (Chenhua, Shanghai) at room temperature. In the three-electrode configuration, thin-wall MnOOH/CC (1 × 1 cm^2), Pt mesh and SCE were used as working electrode, the counter electrode and the reference electrode, respectively, as well as 0.5 M $LiNO_3$ solution as electrolyte. In the two-electrode system, two identical pieces of the samples were sandwiched by polymer filtering membrane regarded as separator, and 0.5 M $LiNO_3$ solution was used as electrolyte.

3. Results and discussion

3.1. Synthesis mechanism

The fabrication of symmetric supercapacitor is shown in Scheme 1. The preparation of the thin-wall MnOOH/CC mainly includes two steps. In the first step, $Mn(OH)_2$ precursors are deposited on CC. When electric current passes electrodes, nitrate ions are reduced in the vicinity of the cathode surface to produce hydroxide ions, and $Mn(OH)_2$ precipitates immediately form *via* the combination between Mn^{2+} and OH^-. In the second step, the resultant $Mn(OH)_2$ is further oxidized by dissolved oxygen in the electrolyte, which leads to the formation of MnOOH. It notes that the hydrophilicity originated from oxygen-containing functional groups on CC fibers is a very pivotal factor for the successful fabrication of the electrode. An appropriate hydrophilicity is beneficial to formation of dispersing nucleus, which makes MnOOH sheets grow on CC uniformly. Furthermore, strong binding force between MnOOH and oxygen-