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Extremely facile synthesis of manganese dioxide-polyaniline nano-reticulation with enhanced electrochemical properties

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ABSTRACT

MnO_2/polyaniline composite is a promising candidate for supercapacitor electrode material. However very few research has researched nano-reticulation-structured MnO_2 and polyaniline composites for supercapacitor electrode materials. Former research on MnO_2 and polyaniline composites shown very common electrochemical properties. In this manuscript, an extremely facile, low-cost and high-yielding preparation of MnO_2-polyaniline (MP) nano-reticulation composites with enhanced electrochemical properties was developed for the first time. For MP composite, the specific capacitance based on MnO_2 is 425 F g^{-1} at 0.1 A g^{-1}. The MP composite also exhibits excellent cycle stability, and the cycle retention keeps 95% after 10000 cycles. The outstanding performance is primarily attributed to improved electrical conductivity (compared to pure MnO_2) and homogenous presence of MnO_2 in the porous nano-reticulation, facilitating the fast transport of the electrolyte ions and the maximum utilization of MnO_2. For MP composite, the maximum power density is 14.3 kW kg^{-1} (energy density is 62.4 Wh kg^{-1}). Hence, the MP composites prepared by facile solution reaction of $KMnO_4$ and aniline may have a promising future in applications where durable, high energy and power density are requested simultaneously.

1. Introduction

Sustainable and renewable resources have become more and more important due to climate change and the decreasing availability of fossil fuels. Large-scale, efficient energy storage industry has been flourishing to store energy from renewable resources for human to utilize. Batteries and supercapacitors (SCs) stand at the very front of energy storage industry. SCs, also called ultracapacitors, are efficient energy storage units. They have attracted wide attention because of their higher power density, longer cycle life, safer working conditions, higher cycle retention, better environment-friendliness and wider range of working temperatures compared with secondary batteries [1]. However, the major dilemma that hinders applications of existing SCs is their low energy density. To solve this problem, metal oxides such as RuO_2 [2], MnO_2 [3], NiO [4], Nb_2O_5 [5], V_2O_5 [6], CoO_x [7], MoO_3 [8] and TiO_2 [9] were largely researched as electrode materials. The specific capacitance of these pseudo-capacitive materials (metal oxide-based materials) is much better than that of carbon-based materials in electric double-layer capacitors (EDLCs) [10], which store ions through reversible absorption in electrolyte/electrode interface.

Among pseudocapacitors, Ruthenium oxide (RuO_2) is widely recognized as the best electrode materials owing to its high specific capacitance [2]. Nevertheless, low porosity, low natural abundance, toxicity and the high cost of RuO_2 have made it unlikely candidate for commercialization of supercapacitors. MnO_2 stands out as the most promising material due to its low cost, abundance, high theoretical capacitance (about 1370F g^{-1}) and environment friendliness [3]. Overcoming the poor electrical conductivity (10^{-5}–10^{-6} S cm^{-1}) of the MnO_2 still remains an unavoidable challenge to be settled for optimization of its ion storage performance [11]. Accordingly, recent research has introduced several structural strategies for electrode design in order to improve the electrical conductivity and facilitate the full utilization of MnO_2 by incorporating carbon material, metal oxide or metal-based nanostructures as an effective electron pathway. For example, 3D graphene [12], carbon nanospheres [13] and carbon nanotube [14] have been applied as substrate and nanoscale MnO_2 accumulated on the surface to fabricate core/shell-structured hybrid electrodes.

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Similarly, a variety of metal oxide nanowires, such as SnO_2 [15], ZnO [16] and WO_3 [17] have been grown on current collector and MnO_2 nanocoating deposited on them to assemble composite materials. A fast charge transmit process and high electrode/electrolyte surface have been effectively obtained, resulting in high specific capacitance. However, these electrode materials require complex and multistep fabrication process, which would eventually increase the cost. Their corresponding energy density also remains unsatisfactory compared to common li-ion battery.

In this work, in order to subdue these drawbacks brought about by complicated synthesis process and improve energy density without impairing their high electrochemical properties, meanwhile very few research has researched nano-reticulation-structured MnO_2 and polyaniline composites for supercapacitor electrode materials, a nano-reticulation electrode with an extremely facile synthesis of MnO_2-polyaniline (MP) was developed. The $KMnO_4$ in solution is reduced to amorphous MnO_2 by aniline. During the reaction, polyaniline forms automatically which surrounds or commingles with MnO_2 nano-reticulation. This porous nano-reticulation structure enhances an enlarged electrolytic surface area of MnO_2, providing more active spots for ions during faradic reaction [38]. The width of the MnO_2-polyaniline (MP) reticulation skeleton lies between 2 and 4 nm which will largely facilitate the maximum utilization of MnO_2 during the ion adsorption/desorption process. Aniline is a reductant with regards to $KMnO_4$ while serves as raw material of synthesizing polyaniline simultaneously. An existence of polyaniline would enhance the electrical conductivity, leading to impressive improvement of specific capacitance and energy density. Consequently, high values of specific capacitance (425 F g^{-1}), energy and power density (62.4 Wh kg^{-1} and 14.3 kW kg^{-1} respectively) have been achieved in MnO_2-polyaniline nano-reticulation supercapacitors. More than 95% retention is acquired after 10000 cycles at a current density of 5 A g^{-1}. This functionalized nano-reticulation is fairly inexpensive, powerful and durable that it is highly expected to be applicable to auxiliary power supply (APS) or microelectromechanical systems (MEMs) where extraordinary performance is requisite.

2. Experimental

2.1. Synthesis of MnO_2-polyaniline nano-reticulation

All of chemical reagents were analytically pure and used without any further purification. 3.16 g $KMnO_4$ (Sinopharm Chemical Reagent Co., Ltd) were dispersed in 150 mL deionized water by magnetic stirring for 5 min at room temperature until uniform transparent purple aqueous solution was obtained. 1 mL aniline ($C_6H_5NH_2$) (Sinopharm Chemical Reagent Co., Ltd) was added to the above solution by magnetic stirring for 20 min. The dark brown precipitates and puce suspension were isolated by centrifugation at a rate of 10000 r min^{-1} for 10 min. The separated precipitates were rinsed with deionized water and alcohol respectively for 3 times. The finally obtained precipitates were dried at 70 °C for 3 h in air.

2.2. Synthesis of polyaniline

10 ml aniline ($C_6H_5NH_2$) (Sinopharm Chemical Reagent Co., Ltd), 10 ml hydrochloric acid (HCl) (Sinopharm Chemical Reagent Co., Ltd) and 20 ml hydrogen peroxide (H_2O_2) (Sinopharm Chemical Reagent Co., Ltd) were mixed under magnetic stirring for 20 min. The as-resulted grey blue precipitates were isolated by centrifugation a rate of 5000 r min^{-1} for 5 min. The separated precipitates were rinsed in deionized water and alcohol for 1 time respectively. The obtained precipitates were dried at 70 °C for 5 h in air.

2.3. Prepare of pure MnO_2

The MP composites were rinsed with acetone for 6 times to remove polyaniline completely. The precipitates were dried at 70 °C for 4 h in air.

2.4. Microscopic characterization

Microstructure of the MnO_2-polyaniline nano-reticulation was examined using a transmission electron microscope (Tecnai $G^2$20) in bright field at 200 kV for medium- and high-resolution imaging, as well as the selected-area electron diffraction (SAED) of the samples. Scanning transmission electron microscopy mode was applied for EDS mapping. Oxygen K_{a1} (0.525 keV), nitrogen K_{a1} (0.392 keV), carbon K_{a1} (0.285 keV) and manganese K_{a1} (5.899 keV) lines are used to generate the elemental maps of oxygen, nitrogen, carbon and manganese, respectively. The X-ray diffraction (XRD) data were collected using a Bruker X-ray diffractometer (D8 ADVANCE A25) with Cu K_α (λ = 0.154178 nm) radiation. The diffraction patterns were recorded from 10° to 90° at a scanning rate of 5° min^{-1}. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALAB 250 Xi electron spectrometer from VG Scientific using 300 W Al K_a radiation. The base pressure was about 3×10^{-9} mbar. The Mn 2p spectra were calibrated with the C 1s photoemission peak for sp^2-hybridized carbons centered at 284.6 eV. The Brunauer-Emmett-Teller (BET) surface area and pore structure analysis were measured on an Autosorb-iQ2-MP surface area and porosimetry analyzer. The thermogravimetric analyses (TGA) were performed on a Q5000 IR thermogravimetric analyzer (TA Instruments, USA) in the temperature range from ambient temperature to 300 °C at a heating rate of 10 °C min^{-1} under oxygen atmosphere. Fourier transformed infrared (FTIR) spectra were measured using a spectrophotometer (VERTEX 70V) by pressed KBr pellets.

2.5. Electrochemical properties measurement

The working electrode materials were prepared by mixing the MnO_2-polyaniline, acetylene black and polytetrafluoroethylene (PTFE) in a weight ratio of 80:10:10 with ethanol. Then the electrode slurry was coated on nickel foam round sheet (r = 7 mm) and dried at 70 °C for 3 h. The typical mass of the loaded MnO_2-polyaniline electrode materials in each nickel foam sheet is about 5 mg. All electrochemical measurements were carried out in a three-electrode system: A Ni foam coated with MnO_2-polyaniline composites as the working electrode, a platinum foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The measurements were carried out in a 1 mol L^{-1} Na_2SO_4 (Sinopharm Chemical Reagent Co., Ltd) aqueous electrolyte at room temperature. Voltammetry (CV) measurements and galvanostatic charge/discharge tests were performed on a CHI 760E electrochemical workstation (Chenhua, Shanghai). The specific capacitance (C) was calculated according to the following equation:

$$C = \frac{I \times \Delta t}{\Delta V \times m}$$

where C (F g^{-1}) is the specific capacitance, I (A) is the discharge current, m (g) is the designated mass of active materials, ΔV(V) is the potential drop during discharge, Δt(s) is the discharge time.

3. Results and discussion

The MP material with nano-reticulation structure was synthesized via just one reaction between $KMnO_4$ and aniline. The facile