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Mesoporous Manganese Oxide with Large Specific Surface Area for High-performance Asymmetric Supercapacitor with Enhanced Cycling Stability

Jianmin Gu,[‡,a] Xiaoyong Fan,[‡,c] Xin Liu,[a] Siheng Li,*[,b] Zhuang Wang,[a] Shoufeng Tang[a] and Deling Yuan[a]

Abstract: Boosting the energy density of supercapacitors without sacrificing their power capability and cyclability is highly desired. Herein, we reported high-performance asymmetric supercapacitor device with high cycling stability using mesoporous manganese oxide nanococoons (MONCs) as positive electrode, and activated carbon (AC) as negative electrode. The mesoporous manganese oxide nanococoons exhibit excellent electrochemical performances because of their large surface area. The optimized asymmetric supercapacitor could be cycled reversibly in the high voltage range of 0-1.7 V in aqueous electrolyte, which exhibits a maximum energy density of 32 Wh kg^{-1} at a power density of 185 W kg^{-1} and still remains 21 Wh kg^{-1} at a power density of 1630 W kg^{-1}. Importantly, such asymmetric supercapacitor exhibits superior long cycle life with ~100% specific capacitance retained after ~2700 cycles and ~98% after 5000 cycles.

1. Introduction

The development of novel clean energy storage device becomes more and more pressing to meet the growing demands for portable electronic device and green transportation.[1] Supercapacitors (SCs), also known as electrochemical capacitors, are receiving tremendous research interest for application in hybrid electric vehicle, portable electronic device, and backup power supply[2-10] because of their high power density, fast charging/discharging rate, exceptionally long cycle life and low maintenance cost,[11-16] which might fill the gap between batteries and conventional dielectric capacitors. However, the energy density of supercapacitors (normally less than 10 Wh kg^{-1}) is inferior to that of batteries,[17] which has limited the widespread application. It is imperative to boost energy density of supercapacitors without sacrificing the power capability and cyclability. The key solution is to construct the "hybrid cell" or "asymmetric cell",[18-20] which is explored to deliver high energy and power simultaneously by utilizing the high energy density of a battery-like faradic electrode as energy source and high power density of a capacitive electrode as power source.[21]

As energy density is proportional to specific capacitance (F/g) and square of potential window (V), which demonstrates that the energy density could be improved by selecting appropriate electrode materials and electrolyte.[22] In aqueous electrolyte, asymmetric supercapacitors could deliver much higher power density than those in nonaqueous electrolytes because of the high ionic conductivity,[23] therefore, building an asymmetric supercapacitor in aqueous system is a preferred choice. Pseudocapacitive materials,[24] as important electrode materials, have been promising for realizing next-generation high-efficient energy storage devices, whose performance are highly dependent on the surface structure of electrode materials.[25] Porous nanostructured materials[26-28] have been demonstrated as pseudocapacitive materials for higher capacity and higher power/energy storage because of the large specific surface area (S_{BET}), which could offer high electrode/electrolyte contact area and short ions diffusion distance during the faradic redox reactions.[29] Manganese oxide has been one of the most promising pseudocapacitive materials due to high theoretical specific capacitance value (1370 F/g), low toxicity, environmental benignity and earth abundance.[30-34] Moreover, the large specific capacitance values can almost be achieved from pure manganese oxide with large surface areas.[7, 35, 36] Here, over-reduction (OR) potassium permanganate and subsequent annealing treatment strategy could be a green process without using extra additives or toxic reagents for the preparation of porous manganese oxide with large specific surface area.

Herein, we demonstrate an asymmetric supercapacitor device with high cycling stability operable in neutral electrolyte using mesoporous manganese oxide nanococoons (MONCs) as positive electrode, and activated carbon (AC) as negative electrode. The MONCs were synthesized through a green over-reduction annealing treatment (called ORA) without using extra additives or toxic reagents. The N_2 adsorption-desorption measurements indicate the mesoporous structures of the MONCs with large specific surface area, contributing to the pseudocapacitive reaction and thus improving the electrochemical performance. The corresponding cyclic voltammetry and galvanostatic charge-discharge tests indicate that the mesoporous MONCs are excellent supercapacitor electrode materials, which can be used as a positive electrode to construct an asymmetric supercapacitor. The asymmetric supercapacitor can be cycled reversibly between 0 and 1.7 V in 1 M Na_2SO_4 or Li_2SO_4 solution and exhibits a maximum discharge capacity of 37.7 mAh/g (based on the total mass of active materials in both electrodes) at a current density of 0.25 A g^{-1}. The energy density of asymmetric supercapacitor can reach up to 32 Wh kg^{-1} at a power density of 185 W kg^{-1} and still remains 21 Wh kg^{-1} at a power density of 1630 W kg^{-1}. The asymmetric supercapacitor exhibits superior long cycle life with ~100 % specific capacitance retained after 2700 cycles and

[a] Dr. J. Gu, X. Liu, Z. Wang, Dr. S. Tang, Dr. D. Yuan
Hebei Key Laboratory of Applied Chemistry, School of Environmental and Chemical Engineering,
Yanshan University,
Qinhuangdao 066004, China.
[b] Dr. S. Li
Shenzhen Institute of Advanced Graphene Application and Technology (SIAGAT),
Shenzhen, 518106, China.
E-mail: lish051@163.com
[c] Dr. X. Fan
School of Materials Science and Engineering,
Chang'an University,
Xi'an 710061, China.
‡ These authors contributed equally to this work.

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