Available online at www.sciencedirect.com

SciVerse ScienceDirect

Chinese Chemical Letters 23 (2012) 623–626

CHINESE CHEMICAL LETTERS

www.elsevier.com/locate/cclet

Performance of PbO_2/activated carbon hybrid supercapacitor with carbon foam substrate

Wu Zhang [a], Yao Hui Qu [a], Li Jun Gao [b,*]

[a] *Department of Chemistry, Nanchang University, Nanchang 330031, China*
[b] *School of Energy, Soochow University, Suzhou 215006, China*

Received 18 November 2011
Available online 19 April 2012

Abstract

PbO_2/activated carbon (AC) hybrid supercapacitor in H_2SO_4 with a carbon foam current collector is studied. The PbO_2/AC hybrid is designed with electrodeposited PbO_2 thin film as positive electrode to match with AC negative electrode. The discharge curve shows capacitive characteristics between 1.88 V and 0.65 V. The hybrid system exhibits excellent energy and power performance, with specific energy of 43.6 Wh/kg at a power density of 654.2 W/kg. The use of carbon foam current collector ensures stability of the PbO_2 electrode in H_2SO_4 environment. After 2600 deep cycles at 15 C high rate of charge/discharge, the capacity remains nearly unchanged from its initial value.

Keywords: Hybrid supercapacitor; Lead dioxide; Activated carbon; Carbon foam

Supercapacitors have many attractive characteristics, such as low equivalent series resistance (ESR), long cycle life, and high power density [1]. Hybrid supercapacitors usually consist of a battery-type electrode and a capacitor-type electrode, which offers combined advantages of both capacitors (rate, cycle life) and batteries (energy density). Studies of hybrid supercapacitors with metal oxides and activated carbon as positive and negative electrodes become a high interest [2–4]. So far various metal oxides, such as MnO_2, RuO_2 and IrO_2, have been used as pseudo-capacitance electrode materials [5–7]. Applications of these materials have, however, been hindered by their high costs. The PbO_2/AC replaces the negative electrode of Pb in a lead acid battery with activated carbon (AC) material in H_2SO_4. Such a system is considered to be more economically viable [8,9], and the hybrid cell displays improved performance in power and lifespan over the lead acid battery. In this work, we studied electrochemical performance of PbO_2/AC supercapacitor using carbon foam as current collector. Carbon foam has large surface area and good electrical conductivity [10,11], and importantly it is stable in H_2SO_4 solution. PbO_2 thin films were prepared by electrodeposition method [12–15]. Such prepared PbO_2/AC system has exhibited long cycle life and high rate performance.

* Corresponding author.
E-mail address: gaolijun@suda.edu.cn (L.J. Gao).

1001-8417/$ – see front matter
doi:10.1016/j.cclet.2012.03.013

1. Experimental

Galvanostatic deposition of PbO_2 thin film was carried out on carbon foam substrate, its mass density is 0.6 g/cm^3, there are many pores, with the size of hundreds of micrometers, distributed on the surface. These pores provide holding place for PbO_2 deposits. The carbon foam electrode of 1 cm^2 apparent surface area was mounted in a Teflon holder and immersed in nitric acid solution containing 0.5 mol/L $Pb(NO_3)_2$. Electrodeposition of PbO_2 films was performed in an electrochemical cell, with a saturated calomel electrode (SCE) as reference electrode and a Pt gauze as counter electrode, and the deposition current density was 30 mA/cm^2. The AC electrodes were prepared by mixing the activated carbon powder (YP17, Kuraray) with 10 wt.% carbon nanotubes and 5 wt.% PVDF in NMP solvent to form slurries. The slurries were pressed onto the Ti foil (20 μm in thickness), and then dried and roll pressed, with the thickness of AC layers ranging from 85 to 240 μm at various PbO_2 to AC mass ratio.

The morphology of the PbO_2 thin films was examined using a field emission SEM (Hitachi S4800) machine. The hybrid cell was assembled with PbO_2 thin film as positive electrode and AC as negative electrode separated by a porous cellulosic separator in the 1.28 g cm^{-3} density or 5.3 mol/L H_2SO_4 solution. EIS measurements on the hybrid cell (0.012 g PbO_2 film and 0.024 g AC film) were carried out using Zahner-IM6ex electrochemical workstation, and charge/discharge tests were performed using a LAND battery measurement system.

2. Results and discussion

Fig. 1(a) shows SEM photograph of the carbon foam, of which the surface is covered with microcells. The pore structure of the carbon foam plays a role of confining $PbO_2/PbSO_4$ reactants and products, allowing full utilization of active electrode material. Fig. 1(b) presents the picture of PbO_2 particles, which are tightly coated on microcell walls. Fig. 1(c) displays the photograph of AC with 10 wt.% carbon nanotubes and 5 wt.% PVDF, it is clearly seen that the carbon nanotubes acting as conductive carbon are coated on the AC.

Fig. 2 shows charge/discharge profile of the PbO_2/AC hybrid cell at 300 mA/g in voltage range of 1.88V–0.65 V. The iR drop at the beginning of discharge curve is mainly due to the high currents applied [16], since the internal resistance was measured to be rather small being $<1.1\ \Omega$ for the cell. A linear variation of voltage is observed during discharge process, indicating that the performance of the hybrid cell is mostly dominated by capacitor characteristics at these high rates. The specific capacitance of the hybrid supercapacitor was evaluated according to $C_S = I/(m \times dV/dt)$, where I is the discharge current, m is the mass of two active electrode materials and dV/dt is the rate of voltage change obtained from the discharge curves. For a discharge current of 300 mA/g (about 15 C rate), C_S is calculated to be 101 F/g for the hybrid system from Fig. 2.

Fig. 3a shows the Ragone plot of the PbO_2/AC hybrid cell in comparison with an AC/AC capacitor. The specific energy E and specific power P are calculated from $E = (1/2)CV^2$ and $P = E/t$, where C is the specific capacitance of the cell, V is the adopted upper end of the operating voltage (1.88 V), and t is the time duration for the cell to discharge from 1.88 V to 0.65 V for the PbO_2/AC and from 1.2 V to 0 V for the AC/AC cell. For instance, at high end of power density of 1400.0 W/kg, the specific energy was 35.3 Wh/kg. Thus comparing to the AC/AC supercapacitor the PbO_2/AC capacitor

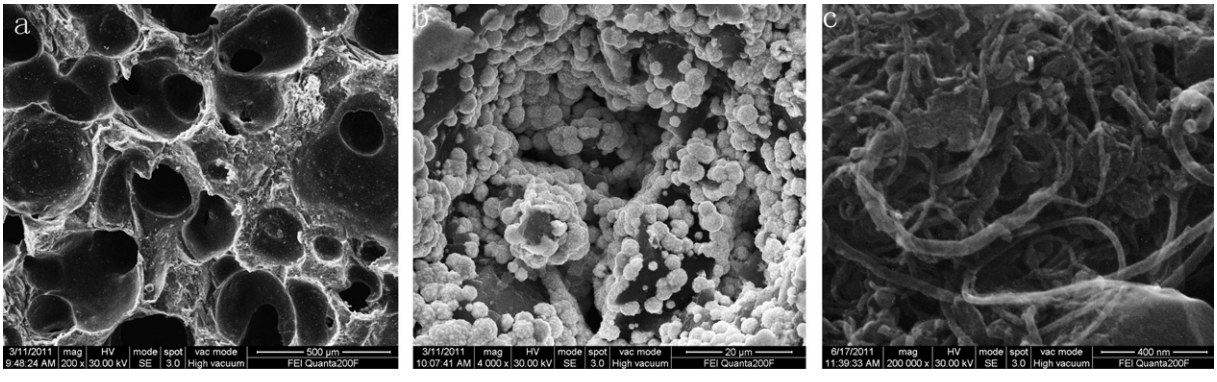

Fig. 1. SEM photographs of (a) unmanaged carbon foam substrate, (b) PbO_2 particles and (c) activated carbon with carbon nanotubes and PVDF additives.