Porous Acetylene-black Spheres as the Cathode Materials of Dye-sensitized Solar Cells

Fengshi Cai,[1] Jun Chen,*[1] and Ruisong Xu[2]
[1]Institute of New Energy Material Chemistry, Nankai University, Tianjin 300071, P. R. China
[2]Guangzhou Institute of Geochemistry, Chinese Academy of Science, Guangzhou 510640, P. R. China

(Received September 5, 2006; CL-061018; E-mail: chenabc@nankai.edu.cn)

Porous acetylene-black (AB) spheres were used as the cathode materials of dye-sensitized solar cells (DSC), showing low-cost, high electrochemical activity and energy-conversion efficiency (5.76%), indicating the potential replacement of noble-metal Pt in the cathode of DSC.

Dye-sensitized solar cells (DSC) have attracted much attention as the low-cost, high-efficiency, environmentally friendly solar-energy transfer devices since the discovery in 1991.[1] Up to now, much of the research in DSC has been focused on the components of photoelectrode,[2] dye sensitizer,[3] and electrolyte.[4] However, limited work has been carried out on the cathode (counter electrode, CE), which is usually made of noble-metal platinum on conducting glasses and plays an important role for the catalytic I_3^- reduction and electron transfer in DSC to keep high photovoltaic performances.[5,6] It was recently found that the carbon film with 80% graphite powder and 20% carbon black as the CE of DSC could obtain a conversion efficiency of 6.67%.[7] Meanwhile, carbon nanotubes were also used as the CE of DSC, showing a conversion efficiency of 4.5%.[8] In addition, applying activated carbon[9] and C_{60} thin films[10] to CE of DSC has already been reported. Therefore, the performance of carbon CE is dramatically affected by the microstructure and conductivity of the carbon materials that make up the cathode. Here, we reported on the promising properties of porous acetylene-black (AB) spheres as the CE of DSC.

Porous AB spheres were prepared by the pyrolysis of acetylene in a tubular reactor, in which undiluted C_2H_2 (99.99% purity) was introduced into a furnace for heating treatment at 650 °C in Ar (99.99%, 5 mL per min) for 2 h. After cooling to room temperature, the porous AB spheres (20 mg) were ultrasonically suspended in ethanol (20 mL) for 30 min. The AB counter electrode was prepared by spin-coating (1000 rpm for 1 min) the solution on a F-doped SnO_2 glass (FTO) (sheet resistance of 10 Ω per square, Nippon Sheet Glass). After the AB film was dried at 60 °C for 5 min, the spin-coating and drying procedures were repeated five times. The thickness of AB films can be controlled by altering the concentration or the spinning speed. The as-prepared AB films were characterized by a Philips XL-30 scanning electron microscope (SEM). Figure 1a shows the SEM image of a typical AB film by a spin-coating technique. The image clearly displays that the AB particles were well dispersed on the FTO glass and formed a uniform film with the thickness of about 125 nm. The SEM images in Figures 1b and 1c show the porous-structure character of the film, which benefits the electron transfer by the sufficient contact between AB and electrolyte. Further evidence for the AB particles can be found from the transmission electron microscopy (TEM) image (Figure 1d), illustrating that the diameters of the AB spheres are 50–100 nm. The BET specific surface areas of the porous AB spheres were very high with about 280 m^2/g.

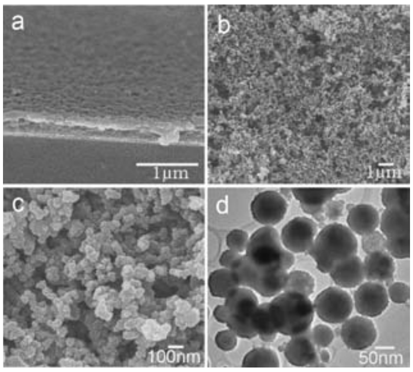

Figure 1. SEM (a), (b), (c) micrographs of AB thin films deposited on FTO glass and TEM (d) image of the porous AB spheres.

In order to examine the catalytic activity of the AB spheres, the efficiencies of DSC using the AB films deposited on FTO electrode were measured. The photoanodes of the DSC employed in the experiments were composed of nanocrystalline TiO_2 film with 10-μm thickness, prepared according to the previous method.[11] The electrode was immersed into 3×10^{-4} M N3 dye ethanol solution at room temperature for overnight to afford sensitization, and the resulting film was clipped with acetylene black CEs. The composition of the electrolyte is 0.6 M of 1,2-dimethyl-3-propylimidazolium iodide (DMPImI), 0.1 M of LiI, 0.05 M of I_2 and 0.5 M of *t*-butylpyridine (*t*BP) in a mixture of acetonitrile/methoxypropionitrile (volume ratio, 1:1). The area of the dye-absorbed TiO_2 electrode was 0.16 cm^2. Photoelectrochemical data were measured using a 500-W xenon light source that was focused to give 100 mW/cm^2, the equivalent of one sun at AM 1.5, at the surface of the test cell. The spectral output of the lamp was matched in the region of 400–800 nm with the aid of a sunlight filter so as to reduce the mismatch between the simulated and the true solar spectrum. The applied potential and cell current were measured using a Keithley model 2400 digital source meter (Keithley, U.S.A.).

Figure 2 illustrates the *I–V* curves (photocurrent density to voltage) of the cell with AB film, Pt and only FTO as counter electrodes. The short-circuit photocurrent density (*J*sc), open-circuit photovoltage (*V*oc), and filling factor (*FF*) of the AB electrode are 13.92 mA cm^{-2}, 724 mV, and 0.57, respectively, yielding a photovoltaic conversion efficiency (η) of 5.76%. As a comparison, with Pt and only FTO as the counter electrode, the corresponding efficiencies (η) are 7.18 and 0.25%, respectively. This result clearly indicates that the AB film with porous spheres serves as electrochemical catalyst for DSC.

To elucidate the catalytic activity of AB counter electrode, electrochemical impedance spectroscopy (EIS) was further used to analyze the interfacial charge-transfer resistance (R_{CT}) be-

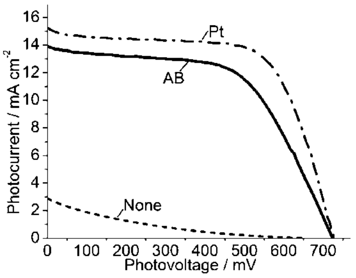

Figure 2. *I–V* curves of DSCs with 20-μm AB films, Pt and only FTO as counter electrodes under AM1.5–100-mW/cm^2 light irradiation.

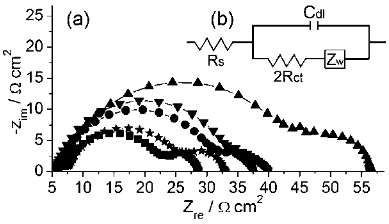

Figure 3. (a) Nyquist plots for the DSC with different AB film thickness on the counter electrode (thickness: 700 nm (▲), 5 μm (▼), 10 μm (●), 20 μm (■), 25 μm (★)) taken at zero bias potential and 10 mV amplitude. The cell was filled with the electrolyte: 0.6 M of DMPImI, 0.1 M of LiI, 0.05 M of I_2, and 0.5 M of *t*-butylpyridine (*t*BP) in a mixture of acetonitrile/methoxypropionitrile (volume ratio, 1:1). (b) Equivalent circuit for the impedance spectrum. R_S: serial resistance; R_{CT}: charge-transfer resistance of one electrode; C_{dl}: double layer capacity of one electrode; Z_W: Warburg impedance (diffusion impedance).

tween the electrolyte and the CE. The electrochemical performance was investigated by means of a PARSTAT 2273 instrument. The electrical impedance spectra were characterized using Zsimpwin software. Procedure of the impedance measurement was followed previous literature.[6,12] Figure 3a shows the Nyquist plots of the sandwich type cells with two identical AB-film electrodes. Two semicircles were observed in the measured frequency range of 0.01–10^6 Hz (Figure 3a). The semicircle in the high-frequency region of 10^3–10^5 Hz is attributed to the impedance related to charge-transfer process occurring at the counter electrode/electrolyte interface; While the semicircle in the low-frequency region of 1–10^3 Hz is attributed to the Nernstian diffusion within the electrolyte.

Figure 3b shows the equivalent circuit of the impedance analysis for the AB counter electrode of the DSC. The fitting results are summarized in Table 1. As the thickness of the AB film on the CE increases, the charge-transfer resistance (R_{CT}) decreases. The reduction of R_{CT} is attributed to the increase of surface area with the thick AB film. It is reported that R_{CT} should be $\leq 10\,\Omega\,cm^2$ for a good performance of the DSC.[12] When the thickness of AB films are 20 μm, R_{CT} at the counter electrode/electrolyte interface achieves 7.9 Ω cm^2, and a high conversion efficiency of 5.76% is obtained for the DSC. This indicates that electrochemical activity with porous AB spheres as the cathode of DSC is enhanced by the large surface area of the porous character.

Table 1. Charge transfer resistance (R_{CT}) of cell with different thickness of counter electrodes

Thickness/μm	R_{CT}/Ω cm^2	R_s/Ω cm^2
0.7	20.0	5.39
5	14.3	5.46
10	12.6	6.08
20	7.9	6.78
25	9.1	7.46

In summary, porous AB spheres with a high specific surface area of 280 m^2/g were used as the cathode materials of DSC and furthermore, a thin AB film with 20-μm thickness shows an energy-conversion efficiency of 5.76% due to the high electrochemical activity in iodide/triiodide redox reaction. This work is promising in the area of replacing noble-metal Pt in the cathode of DSC.

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