J Appl Electrochem (2010) 40:341–344
DOI 10.1007/s10800-009-0002-4

ORIGINAL PAPER

Ag nanowires and its application as electrode materials in electrochemical capacitor

Zhong-Ai Hu · Yao-Xian Wang · Yu-Long Xie · Yu-Ying Yang · Zi-Yu Zhang · Hong-Ying Wu

Received: 1 November 2008 / Accepted: 18 August 2009 / Published online: 3 September 2009

Abstract Silver nanowires were synthesized on a large scale by using anodic aluminum oxide (AAO) film as templates and serving ethylene glycol as reductant. Their morphological and structural characterizations were characterized with field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and selected area electron diffraction (SAED). The electrochemical properties of silver nanowires as electrode materials for electrochemical capacitors were investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge technique in 6 M KOH aqueous electrolyte. The Ag_2O/Ag coaxial nanowires were formed by the incomplete electrochemical oxidation during the charge step. The maximum specific capacitance of 987 F g^{-1} was obtained at a charge–discharge current density of 5 mA cm^{-2}.

Keywords Ag nanowire · Anodic aluminum oxide film · Electrochemical capacitor · Specific capacitance

1 Introduction

Electrochemical capacitors as a novel charge storage device can be used from mobile electronic devices to hybrid electric vehicles because of their high power density, excellent reversibility, and long cyclic life [1], but their applications are still limited due to the low energy density [2, 3]. In electrochemical capacitors, the reactions occur in the nanosize thick region at the electrode–electrolyte interface [4], so a large electrochemical interface is favorable to the enhancement of the power density. The electrode materials and structure have been intensively studied to improve the energy density and power density of electrochemical capacitors. As known to us all, the small crystalline size shows a high proton diffusion coefficient [5], which is benefit to the improvement of the electrochemical performance. However, the resistance between nanoparticles and conductor will remarkably increase making the electrode have an even worse performance [6].

In contrast, some research results have indicated that the modification of morphology and microstructure of electrode materials could become a very feasible approach for capacitance promotion [7]. The high surface area one-dimensional nanostructured materials such as nanotubes [8], nanowires [9], nanorod [10], etc., have been intensively investigated as electrode materials in electrochemical energy storage devices [11], because they can provide short diffusion path lengths to ions and excitons, leading to high charge/discharge rates [12]. Martin's group has demonstrated that high surface area nanowire of SnO_2 and V_2O_5 have significantly improved rate capability compared with thin films of the same material [13–15]. However, their applications are still limited due to the low conductance and high cost.

It is reasonable to believe that the coaxial metal/oxide nanowire not only have high conductivity but also provide the low carrier of electronic transfer for electrochemical reactions. Furthermore, one-dimensional nanostructure can reduce diffusion resistance of electrolytes in the rapid charge/discharge processes. Nano-structured Ag_2O has the potential of high speed charge/discharge additionally [16], so we attempted to use Ag_2O/Ag coaxial nanowires as

---

Z.-A. Hu (✉) · Y.-X. Wang · Y.-L. Xie · Y.-Y. Yang · Z.-Y. Zhang · H.-Y. Wu
Key Laboratory of Polymer, College of Chemistry and Chemical Engineering, Northwest Normal University, 730070 Lanzhou, People's Republic of China
e-mail: zhongai@nwnu.edu.cn

electroactive materials for electrochemical capacitors in the present work. First, the Ag nanowires with long aspect ratio were used directly as the raw materials of electrodes, and then the Ag_2O/Ag coaxial nanowires were formed by the incomplete electrochemical oxidation during the charge step. The charge/discharge process is corresponding to rapid redox transition between the Ag and Ag_2O on the coaxial nanowires. The present method is a new idea for preparing electrode materials of electrochemical capacitors.

2 Experimental

2.1 Preparation of silver nanowires

All of the chemical reagents used in this experiment were analytical grade. Silver nanowires were synthesized according to the procedure reported elsewhere [17]. The anodic aluminum oxide (AAO) template was produced from pieces of high-purity aluminum foil (30 mm × 12 mm, 99.99%) via two-step anodization processes. After the second anodization, the pore size of AAO was widened to about 60 nm by etching treatment in H_3PO_4 solution. In order to fabricate silver nanowires, a solution of $AgNO_3$ (20 g L^{-1}) dissolved in ethylene glycol was placed in a vessel, and then a piece of pretreated template was immersed in the solution. After following ultrasonic treatment for 10 min, the reaction system was heated at 120 °C for given time resulting in the formation of array of sliver nanowires inside the pores of AAO templates. The template filled with silver nanowire was placed in 3 M NaOH solution to dissolve away framework of the template and reveal all the silver nanowires. After purified by repeatedly washing, the products were completely transferred into a vessel filling with ethanol.

2.2 Electrode preparation and electrochemical measurement

The working electrodes were prepared by mixing silver nanowires with 15 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) emulsion to form slurry, which was filled into a foamed nickel with an apparent area of 1 cm^2 and then dried and cold rolled to a sheet. Electrochemical measurements were performed on a CHI660B electrochemical working station (CH Instrument). A typical three-electrode cell was employed. The electrolyte was 6 M KOH solution. An Hg/HgO electrode and a platinum plate were used as the reference electrode and the counter electrode, respectively.

2.3 Characterization of silver nanowires

Field emission scanning electron microscopy (FESEM) images of the silver nanowires were obtained with a JSM-6701F field emission scanning electron microscope. Transmission electron microscopy (TEM) and electron diffraction studies were performed with a JEM-2010 microscope operated at 80 kV. X-ray diffraction (XRD) analysis was performed on a Rigaku D/MAX2400 diffractometer with Cu Kα radiation to investigate the phase and crystal structure.

3 Results and discussion

3.1 Morphology and crystal structure of silver nanowires

Figure 1 shows the surface morphology of the typical silver nanowires. All of them have a uniform diameter of about 60 nm, which is approximately consistent with pore diameter of the used AAO template. The length of the most nanowires is more than 5 μm. However, a small amount of nanorods is also observed in the sample, which may be related to some negative factors such as obstruct of nanochannels in the reaction process, or break of nanowires in the cleaning, separating, and dispersing process.

TEM photographs of silver nanowires are shown in Fig. 2. As seen from Fig. 2, the resultant nanowires are dense, continuous, and uniform in diameter. The diameter is about 60 nm. The results are in good agreement with the nanochannel of AAO template used in the experiment. The inset of Fig. 2 gives the selected area electron diffraction (SAED) pattern on a part of the nanowire. It indicates that the silver nanowire fabricated in our experiment is polycrystalline.

Fig. 1 FESEM images of silver nanowires. Scale bar = 0.2 μm

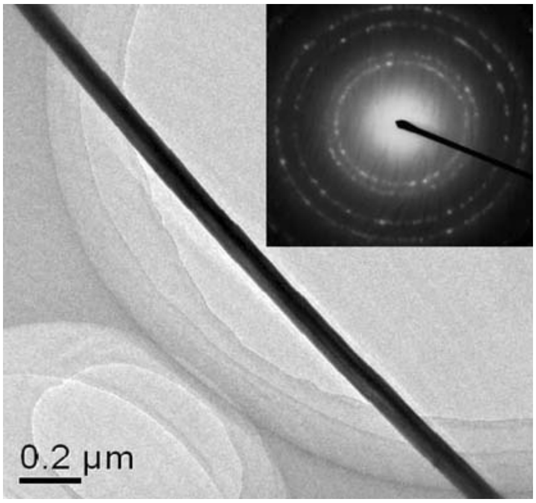


Fig. 2 TEM image of individual nanowire. The inset gives the microdiffraction pattern recorded by focusing the electron beam on this wire. Scale bar = 0.2 µm

Figure 3 shows XRD pattern of the silver nanowires. It shows the diffraction peaks with *d*-spacings of 2.35, 2.04, 1.44, and 1.23 Å, which are consistent with that of face centered cubic (fcc) Ag metal phase. Energy dispersive X-ray (EDX) analysis shows that the wires are made of pure silver suggesting that residuals can be totally removed from the nanowires by a simple washing process.

3.2 Electrochemical properties of silver nanowires

The cyclic voltammetry (CV) of silver nanowire electrodes in 6 M KOH was shown in Fig. 4. Obviously, the shape of curves reveals that the capacitance characteristic of the silver nanowire electrode is distinct from that of the electric double-layer capacitance, which would produce a CV curve with close to an ideal rectangular shape. The present results imply that the measured capacitance is mainly associated with the redox mechanism. On curve, two redox peaks are, respectively, found at approximately 280 and 140 mV on the positive and negative sweeps, which are attributed to the following redox reaction between the Ag and Ag_2O.

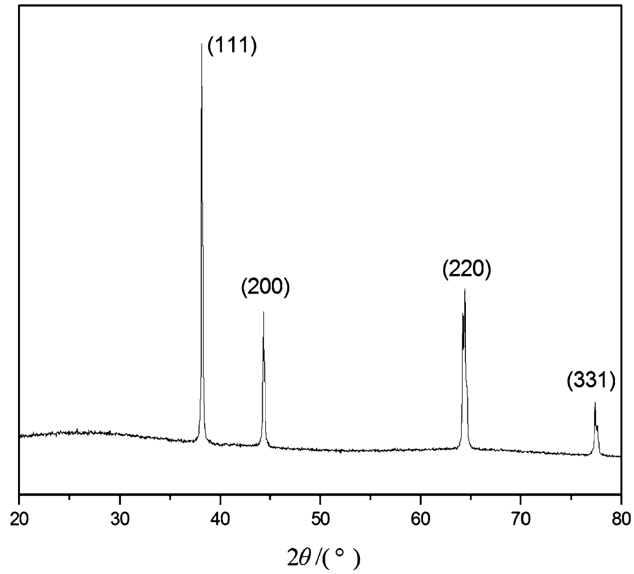


Fig. 3 XRD pattern of freestanding silver nanowires

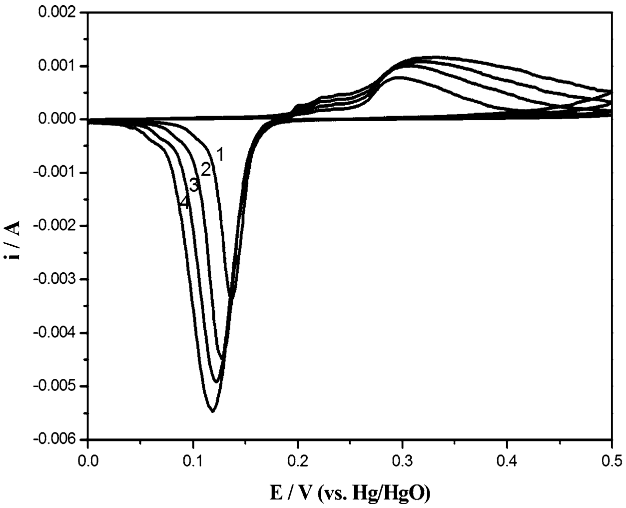


Fig. 4 CV curves of silver nanowire electrode in 6 M KOH at (1) 10 mV s^{-1}, (2) 20 mV s^{-1}, (3) 30 mV s^{-1}, and (4) 40 mV s^{-1}

$$2Ag + 2OH^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Ag_2O + H_2O + 2e^- \qquad (1)$$

Typical CV curves measured at 10, 20, 30, and 40 mV s^{-1} for silver nanowire electrodes were shown in Fig. 4, respectively. It can be noted that the shape of CV curves have no change and the redox-peak position is nearly consistent at different sweep rates. This exhibits that the silver nanowire electrode has an excellent reversibility [18, 19].

The specific capacitance values were evaluated by a charge/discharge cycling measurement, which is considered to be the most reliable. The form of calculation equation is as follows:

$$C_m = I \times t/(\Delta V \times m) \qquad (2)$$

Here, C_m is specific capacitance, I is charge–discharge current, t is the discharge time in seconds corresponding to the voltage difference (ΔV) in volts, and m is the mass of silver nanowires in grams.

The electrochemical capacitive behavior was examined by charge/discharge cycling at various current densities ranging from 5 to 20 mA cm^{-2}. As shown in Fig. 5, the single electrode specific capacitance of 987 F g^{-1} was

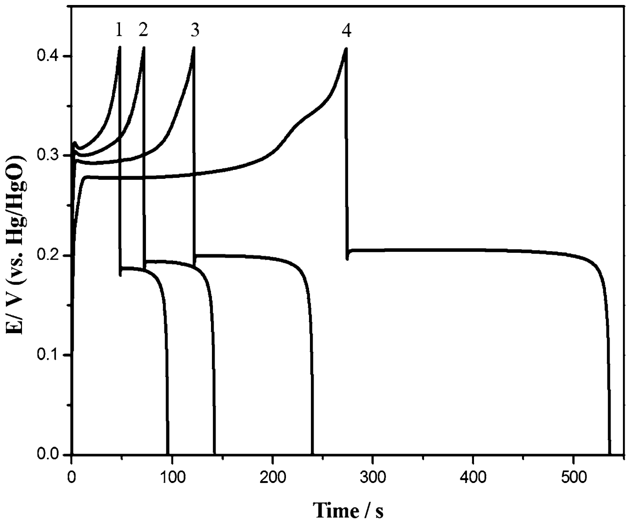
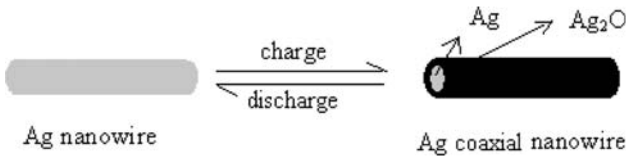


Fig. 5 Charge–discharge curves of silver nanowires in 6 M KOH at (1) 20 mA cm$^{-2,}$ (2) 15 mA cm^{-2}, (3) 10 mA cm^{-2}, and (4) 5 mA cm^{-2}



Scheme 1 Schematic diagram showing transition between the Ag nanowires and the Ag/Ag$_2$O coaxial nanowires

obtained at 5 mA cm^{-2}. Although this specific capacity is not so high comparing with some materials [20, 21], its energy density is actually higher as conductive graphite was absent in the electrode. In addition, it is found that specific capacitance depends on the discharge current density. The effect of current density on specific capacitance may be caused by the transport of the effective ions into active materials. Higher concentration polarization at the large current density make charging process finished in short time [12, 22]. Thus, there is not enough diffusion of ions from electrolyte to interphase.

We also find from Fig. 5 that the efficiency of charge/discharge cycling is more than 0.97, and there is no irreversible drop. This trend is continued even at high current density of 20 mA cm^{-2} indicating that the silver nanowire electrode has excellent electrochemical capacitive characteristics. The high specific capacitance results from the microstructure built by nanowires, which has facile electrolyte penetration, fast proton exchange, and excellent conductivity [12]. Besides the basic reaction can play a vital role in the capacitive behaviors of the silver nanowire electrode. During the charge/discharge steps, transition between the Ag nanowires and the Ag/Ag$_2$O coaxial nanowires can occur. The Ag$_2$O/Ag coaxial nanowires (shown in Scheme 1) were formed during the charge step. According to the ratio of the theoretical capacitance of Ag nanowires to its measured value, the oxide layer thickness was estimated to be about 6.6 nm. In other words, Ag$_2$O/Ag coaxial nanowires consist of the shell of 6.6 nm and mandril of 46.8 nm in diameter.

4 Conclusions

Silver nanowires were synthesized on a large scale by AAO template systems. Ag$_2$O/Ag coaxial nanowires were formed during the charge step and contribute to the electrochemical capacitance. The Ag$_2$O/Ag coaxial nanowires consist of the shell of 6.6 nm and mandril of 46.8 nm in diameter by estimating. The experimental results shown that the capacitance characteristic of the silver nanowire electrode originated from pseudocapacitance behavior associated with the redox mechanism and the maximum specific capacitance was up to 987 F g^{-1} at a charge–discharge current density of 5 mA cm^{-2}. The present method provides a new idea for preparing electrode materials of electrochemical capacitors.

Acknowledgments We gratefully acknowledge the support of this work by Natural Science Funds in Gansu Science and Technology Committee (0803RJ2A005) and postgraduate advisor program of Provincial Education Department of Gansu.

References

1. Arbizzani C, Mastragostino M, Soavi F (2001) J Power Sources 100:164
2. Kim C (2005) J Power Sources 142:382
3. Yuan GH, Jiang ZH, Aramata A et al (2005) Carbon 43:2913
4. Gupta V, Miura N (2005) Electrochem Solid-State Lett 8:630
5. Watanabe K, Kikuoka T, Kumagai N (1995) J Appl Electrochem 25:219
6. Tao F, Guan M, Zhou Y et al (2008) Cryst Growth Des 8:2157
7. Xing W, Li F, Yan ZF et al (2004) J Power Sources 134:324
8. Armstrong G, Armstrong AR, Bruce PG et al (2006) Adv Mater 18:2597
9. Prasad KR, Miura N (2004) J Power Sources 134:354
10. Susanti D, Tsai DS, Huang YS et al (2007) J Phys Chem C 111:9530
11. Arico AS, Bruce P, Scrosati B et al (2005) Nat Mater 4:366
12. Hu CC, Chang KH, Lin MC et al (2006) Nano Lett 6:2690
13. Li N, Martin CR, Scrosati B (2000) Electrochem Solid State Lett 3:316
14. Li N, Martin CR, Scrosati B (2001) J Power Sources 97–98:240
15. Patrissi CJ, Martin CR (1999) J Electrochem Soc 146:3176
16. Pan JQ, Sun YZh, Wang ZH et al (2007) J Mater Chem 17:4820
17. Hu ZhA, Ch Kong, Han YX et al (2007) Mater Lett 61:3931
18. Pang SC, Anderson MA, Chapman TW (2000) J Electrochem Soc 147:444
19. Huang QH, Wang XY, Li J et al (2007) J Power Sources 164:425
20. Cao L, Xu F, Liang YY et al (2004) Adv Mater 16:1853
21. Gupta V, Gupta S, Miura N (2008) J Power Sources 175:680
22. Zhang HX, Zhang ML (2008) Mater Chem Phys 108:184