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Effect of fine layer structure on electrochemistry properties

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ABSTRACT

In this work, we have mainly investigated the electrochemical properties of Bi_2SiO_5 and $Bi_2O_2CO_3$. They have the different layer structures and the areal capacitance (10.1 mF cm^{-2}) of $Bi_2O_2CO_3$ electrode is 2.9 times higher than that (2.6 mF cm^{-2}) of Bi_2SiO_5 one at 0.1 mA cm^{-2}. After 4000 cycles, 84% and 81% capacitances are retained for $Bi_2O_2CO_3$ and Bi_2SiO_5 electrodes, respectively. Because $Bi_2O_2CO_3$ has a lower BET area (3.634 m^2 g^{-1}) and a higher electrical resistance (5.231 Ω cm^2) than Bi_2SiO_5 (35.13 m^2 g^{-1}, 2.022 Ω cm^2), their different electrochemical properties have been mainly attributed to the different fine layer structures. For $Bi_2O_2CO_3$, the anion layers and cation layers are completely separated and the unobstructed passageways form, which would favour to get in and out for ions and improve the capacitance. For Bi_2SiO_5, the newly-formed Bi−O−Si bonds can improve conductivity, but there is no passageway between the anion layers and cation layers, which does not favour for the getting in and out of ions. This study demonstrates that fine layer structure has a significant influence on the electrochemical properties.

1. Introduction

Electrochemical energy storage devices have attracted increasing attention for the promising applications in solving the severe problems of energy shortages [1–3]. Among, supercapacitors are ones of the most promising energy storage devices, due to the high power density, long cycle lifetime and fast charge and discharge rates [4–7]. Among various electrode materials, RuO_2 has a high capacitance, but its high cost limits the wide applications [8,9]. The cheap transition metals oxides only have the lower capacitance [10–14]. It is desirable to develop new, inexpensive electrode materials.

Among various materials, layer structures, such as V_2O_5 [15], graphite [16], MoS_2 [17], *etc.* have been intensively studied as the excellent electrode materials. Recently, we have found that although with the similar layer structure, Bi_2SiO_5 and $Bi_2O_2CO_3$ exhibit obviously different electrochemical properties. To the best of our knowledge, however, little work has been done to investigate the effect of layer structure on the electrochemical properties. It is desirable to reveal the structure-property relationship.

In this work, two layer structures (Bi_2SiO_5 and $Bi_2O_2CO_3$) are synthesized by a simple hydrothermal method, and their electrochemical properties are mainly investigated by cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS). Further, the Bi_2SiO_5- and $Bi_2O_2CO_3$-based asymmetric micro-supercapacitors have been fabricated and their electrochemical

performances have been measured. This study demonstrates that the unobstructed passageways of $Bi_2O_2CO_3$ favour to improve the electrochemical performances.
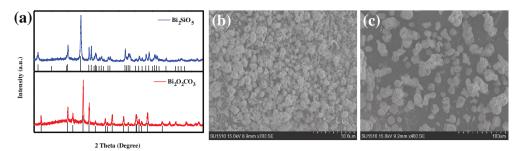
2. Experimental

2.1. Sample preparation

All reagents were of analytical grade, purchased from Beijing Chemical Reagents Industrial Company of China, and were used without further purification.

2.1.1. Bi$_2$SiO$_5$

Typically, 0.5 mmol Na_2SiO_3 (0.142 g) was dissolved in 30 mL distilled water under magnetically stirring. Then, 0.305 g BiOBr was added to the above solution. Herein, the BiOBr precursor was synthesized using a hydrothermal method [18]. After 30 min, the mixture was transferred into a Teflon-lined autoclave, then maintained at 160 °C for 24 h. The resultant precipitate was washed with distilled water and absolute ethanol several times, respectively. Finally the sample was dried at 60 °C for 6 h.

2.1.2. Bi$_2$O$_2$CO$_3$

Typically, 0.5 g urea (8.33 mmol) was dissolved in 40 mL ethanol. Then, 2.45 g Bi(NO$_3$)$_3$·5H$_2$O (5.05 mmol) was added to the above

solution under magnetically stirring. After being stirred for 0.5 h, the resulting suspension was transferred into a Teflon-lined autoclave and maintained at 180 °C for 12 h. The product was obtained using the similar procedures as above.

2.2. Characterization

The crystal structures of the samples were determined by X-ray powder polycrystalline diffract meter (Rigaku D/max-2550VB), using graphite monochromatized Cu K α radiation (λ = 0.154 nm), operating at 40 kV and 50 mA. The XRD patterns were obtained in the range of 20–80° (2θ) at a scanning rate of 7° min^{-1}. The samples were characterized on a scanning electron microscope (SEM, Hitachi SU-1510) with an acceleration voltage of 15 keV. Nitrogen sorption isotherms were performed at 77 K and < 10^{-4} bar on a Micromeritics ASAP2010 gas adsorption analyzer. Before measurements, each sample was degassed at 150 °C for 5 h. Surface area was calculated by the Brunauer-Emmett-Teller (BET) method.

2.3. Electrochemical measurements

All the electrochemical measurements were carried out on a CHI 660D electrochemical working station at room temperature. In the three-electrode system, carbon fibers coated with Bi_2SiO_5 or $Bi_2O_2CO_3$, Pt wire (diameter: 0.1 cm, length: 4 cm) and standard saturated calomel electrode (SCE) were used as the working electrodes, counter electrode and reference electrode, respectively. Herein, carbon fibers were used as the current collector of working electrode, and 1 M KOH aqueous solution was used as the electrolyte.

To fabricate the working electrode (with an area of 0.25 cm^2), 80 wt % of active materials (Bi_2SiO_5 or $Bi_2O_2CO_3$), 10 wt% of acetylene black (conductivity agent) and 10 wt% of polyvinylidene fluoride (binder) were dispersed in 1-methyl-2-pyrrolidinone to form a homogeneous slurry. Then the slurry was dotted on the carbon fibers and dried for 24 h at room temperature. The mass of active material (Bi_2SiO_5 or $Bi_2O_2CO_3$) on the carbon fibers is 2 mg. Cyclic voltammetry (CV) and chronopotentiometry (CP) were conducted in a potential range of 0–0.8 V and 0–0.6 V, respectively. Electrochemical impedance spectroscopy (EIS) was performed from 0.1 Hz to 100 kHz at an open circuit potential with an alternating current (AC) voltage of 5 mV.

To fabricate the asymmetric micro-supercapacitor, the flexible, conductive carbon fibers were also used as the current collector [19,20]. The working electrodes for micro-supercapacitors were fabricated by the similar procedures to those for three-electrode test. For the micro-supercapacitors, the mass of active material (Bi_2SiO_5 or $Bi_2O_2CO_3$) on the carbon fibers is 5 mg. The negative electrode of micro-supercapacitors is fabricated as follows: 2 mg of activated carbon was dispersed in 1 mL ethanol to form a homogeneous ink under sonicating; then, 50 μL ink was coated onto the carbon fibers, in which 0.1 mg of activated carbon was contained. Typically, Bi_2SiO_5 (or $Bi_2O_2CO_3$)/carbon fiber was employed as the positive electrode, the activated carbon/carbon fiber was employed as the negative electrode, and 1 M KOH aqueous solution was used as the electrolyte. First, the activated material (Bi_2SiO_5 or $Bi_2O_2CO_3$) and activated carbon were

coated on the carbon fibers, respectively; then one piece of cellulose paper (as separator) was used to package the activated carbon coated electrode (negative); finally, the micro-supercapacitor was assembled by encircling the negative electrode with the positive electrode. In order to prevent the leakage of electrolyte, one piece of plastic film was used to package the micro-supercapacitor, then 1 M KOH aqueous solution was injected. The volume of our asymmetric micro-supercapacitors is 0.023 cm^3. The mass ratio of positive and negative electrodes is based on the charge balance theory (q$^+$ = q$^-$), which depends on specific capacitance (C), potential range (ΔV), and the mass of active materials on electrodes (m), namely, q = mCΔV. In order to ensure q$^+$ = q$^-$, the mass balance follows the Equation of $\frac{m^-}{m^+} = \frac{C^+\Delta V^+}{C^-\Delta V^-}$.

3. Results and discussion

3.1. Crystal structure and morphology

Fig. 1a shows that all the diffraction peaks of the samples are well in agreement with standard JCPDS-ICDD Card No. 36-0287 and 41-1488, demonstrating the formation of phase-pure Bi_2SiO_5 and $Bi_2O_2CO_3$, respectively. We did the particle size analysis by scanning electron microscope (SEM) and estimated that the particle sizes of Bi_2SiO_5 and $Bi_2O_2CO_3$ are about 10 μm and 20 μm, respectively Fig. 1(b, c). Bi_2SiO_5 has the monoclinic space group *CMC21*, with the unit cell parameters of a = 15.097(5) Å, b = 5.436(7) Å and c = 5.350(8) Å [21]. Fig. 2a illustrates that Bi_2SiO_5 is built by the alternated $(SiO_3)^{2-}$ anion layers and $(Bi_2O_2)^{2+}$ cation layers. Moreover, the featured Bi−O−Si bonds (2.417 Å) formed between cation and anion layers [21]. $Bi_2O_2CO_3$ has the monoclinic space group *IMM2*, with the lattice parameters of a = 3.865 Å, b = 3.865 Å and c = 13.675 Å [22]. On base of the unit cell parameters of a, b and c of $Bi_2O_2CO_3$, we can find the unit cell in the "Findit" software, which establishes the completely separated $(Bi_2O_2)^{2+}$ layers and $(CO_3)^{2-}$ layers. Fig. 2b shows that no Bi−O−C bonds form between cation and anion layers [23], similar to $Bi_2O_2(OH)$ (NO_3) [24]. It is observed that their layer structures are different obviously.

3.2. Electrochemical properties of electrodes

We have investigated the electrochemical properties of both Bi_2SiO_5 and $Bi_2O_2CO_3$ electrodes by cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS). Fig. 3a and c show the CV curves at different scanning rates between 0 and 0.8 V (*vs.* SCE). The rectangle CV curves indicate an ideal electric double-layer capacitive behavior and a fast charge/discharge rate [25]. Fig. 3b and d show the charge/discharge curves at different current densities. For the non-linear galvanostatic charge/discharge curves, the energy accumulated (E$_{int/C}$), energy released (E$_{int/D}$), energy densities (E$_{s,int/C}$, E$_{s,int/D}$) and energy efficiency (η$_E$) can be calculated using Eqs. (1)–(5) as follows [26].

$$E_{int/D} = I \int_{t(Umax)}^{t(Umin)} U(t)dt \tag{1}$$