

Dry modification of electrode materials by roller vibration milling at room temperature

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Abstract

For the first time dry roller vibration milling at room temperature was used to prepare active carbon (AC) nano-particles and to modify MnO₂ powder as electrode materials. In 30 min AC was milled to a mean particle size of 30–50 nm with increased crystallinity and higher specific surface area, predominantly mesoporous and with improved pore diameter distribution. Then, AC nano-particles were incorporated with MnO₂ or bismuth-doped MnO₂ nano-particles synthesized by sol–gel methods to prepare nano-composite electrode materials for studying their electrochemical performance. The AC nano-particles combined with 10 wt.% bismuth-doped MnO₂ nano-particles were found to possess excellent electrochemical property with specific capacitance up to 308 F/g and without obvious attenuation with increasing current. Our method seems to open a new way to improve AC based electrode materials used for clean energy such as super capacitors.

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Keywords: Active carbon; Roller vibration milling; Electrode materials; Nano-materials; Super-capacitors

1. Introduction

For producing clean energy, electrode materials for electrochemical capacitors (EC), and super-capacitors, have been a subject of extensive exploration and development (Liu, Deng, & Wan, 2002; Su, Wu, Zhao, Chen, & Bao, 2004; Tanahashi, Yoshida, & Nishino, 1990; Zheng & Jow, 1995). Among the candidates of electrode materials including carbon nano-tubes and active carbon (AC), and transition metal oxides such as MnO₂ and RuO₂ (Bach, Henry, Baffier, & Livage, 1990; Hu & Wang, 2002; Vukovic & Cukman, 1999; Zheng, Cygan, & Jow, 1995), AC is preferred because it is non-polluting to environment, free from toxicity, cheap, capable of fast loading and unloading and its long lifetime. However, most commercial AC has poor crystallinity, poor conductivity, and low specific electronic capacity especially with increasing current.

To improve AC, much effort has been made to modify its structure by chemical treatment, such as gas-phase or liquid-phase oxidation, and repeated activation (Meng, Zhang, Li, Lu, & Ling, 2002; Tian & Zhang, 2004; Wang, Wang, & Liang, 2003), at the cost, however, of unavoidable pollution of envi-

ronment and increased cost of production. For the first time this work used dry roller vibration milling (RVM) at room temperature (Wang, 2002; Wang et al., 2006) to prepare AC nano-particles and to modify MnO₂ and bismuth-doped MnO₂ nano-particles synthesized by sol–gel methods. Composite electrode materials consisting of AC and MnO₂ nano-particles were then prepared by various methods, for studying their electrochemical performance.

2. Experimental

Modification experiments were conducted in a dry roller vibration mill (RVM) (Wang, 2003) at room temperature equipped with a 2.5-L grinding chamber and a 0.12-kW motor. To provide proper atmosphere and prevent dust explosion, the entire operation was performed in a glove box filled with nitrogen. In a typical experiment, 150 g raw AC powder (provided by Aowei Technology Development Co. Ltd., Shanghai, China) were placed in the mill container without any dispersant, using stainless steel rods as grinding medium (Wang, 2003; Wang et al., 2006) and keeping a weight ratio of the medium to powder as 60:1. The milling test lasted 3 h, 4 samples were collected in succession at 0.5, 1, 2 and 3 h. Similarly, MnO₂ particles were modified by 30 min milling in RVM (sample 3 RVM modified MnO₂). As shown in Fig. 1, MnO₂ nano-particles (sample 2)

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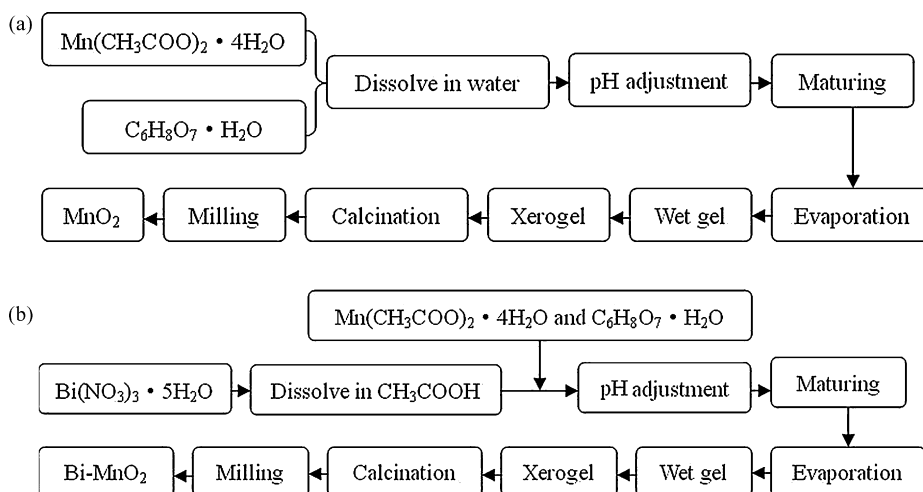


Fig. 1. Preparation of MnO_2 by sol-gel method: (a) preparation of MnO_2 nano-particles; (b) preparation of bismuth-doped nano- MnO_2 .

and bismuth-doped nano- MnO_2 (sample 1) were synthesized by sol-gel methods as follows (Men & Xia, 1997; Xia & Men, 1998). First dissolve fully citric acid and manganese triacetate dehydrate in deionized water or dissolve bismuth nitrate in acetic acid, to obtain a transparent solution, by adjusting pH. After 24-h maturing, the aqueous solutions were let to experience polycondensation and form a gel at 60°C , then the wet-gels were dried at 100°C and calcined for 12 h at 280°C , then the calcined material were milled into powder in an agate mortar.

Particles size and morphology were characterized by X-ray diffraction (XRD, D/max-rB 12 kW, Rigaku Corporation, Japan), scanning electron microscopy (SEM, XL30-S-FEG, Philips, Netherland), and atomic force microscopy (AFM, SPM9500-J3, SHIMADZU, Japan) was used to obtain accurate three-dimensional information. The specific surface area of the active carbon was determined by physical adsorption using N_2 at 77 K in an automatic adsorption system (Autosorb-1, Quantachrome, USA).

The electrodes were prepared by mixing the active materials (AC and MnO_2), conductive agent (acetylene black), and binder (polytetrafluoroethylene, 30 wt.%) in isopropanol in a ratio of 20:5:0.15 in wt.%. The slurry was pressed on a nickel screen ($1 \times 2 \text{ cm}^2$) current collector and punched to a disc of 1 cm in diameter at 12 MPa for 2 min. The typical active material mass load of electrode material is 20 mg/cm^2 . Then the electrodes were dried in vacuum at 100°C for 12 h to remove the solvent totally. Using a platinum counter electrode and a standard calomel reference electrode (SCE), we tested the electrode performance in a beaker-type electrochemical cell configuration with KOH (5 mol/L) as aqueous electrolyte. Both voltage-current characteristics (CHI600B electro-chemical workstation, scan rate 5 mV/s) and charge/discharge properties (BK-6016 battery test system) were measured.

3. Results and discussion

Fig. 2(a) and (b) show respectively the SEM image of the AC raw material and the AFM image of the AC

nano-particles after 30 min milling. The AC nano-particle size distribution is shown in Fig. 2(c), averaging to about 30–50 nm. And AFM shows that AC nano-particles were less than 15 nm in thickness, spherical and uniformly dispersed. As the AFM used the tapping mode, the nano-particles look somewhat round due to the influence of the scanning probe.

Fig. 3 summarizes the variation of the specific surface area of AC against milling time, showing the dominance of micropore (<2 nm) surface in the starting material. After 30 min milling the mesopore (2–50 nm) surface area increases to $1811 \text{ m}^2/\text{g}$, which represents 57% of the total. However, when the milling time is prolonged to 3 h, micropore area regains its prevalence as in the starting material, suggesting degradation of the structure of the material. Apparently 30 min milling not only reduces particle size adequately and increases crystalline effectively, but also improves pore diameter distribution of the AC particles. While reducing particle size, vibration milling helps to increase specific surface area by breaking some macropores (>50 nm) or closed pores to smaller or open pores. The significance of increasing mesopores lies in the enhancement of the specific capacitance of porous AC materials because the electrolyte ions are more likely to access mesopores than micropores (Frackowiak & Beguin, 2001; Lee & Pyun, 2006; Meng, Liu, Song, & Ling, 2004; Tamai, Kakii, Hirota, Kumamoto, & Yasuda, 1996).

Fig. 4 shows the XRD patterns of the raw material and the AC nano-particles. From curve 2, one can see that sample after 30 min milling retained its hexagonal graphite structure, but the diffraction peaks, especially the peak (003) at 26.3° and (101) at 43.1° , became higher and sharper, suggesting an improvement of the crystallinity of the material. However, when milling was prolonged to 3 h, the XRD (curve 3) seems to turn back to that of the original materials (curve 1), indicating that the material performance degraded with excessive milling, which is consistent with the pore structure analysis of Fig. 3. Under compressing, shearing and rubbing during the milling process, when the instantaneous energy was above the activation energy of phase change, the crystallization transformation occurred. Especially under the influence of mechanochemistry,

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