



A novel synthesis of hierarchical porous carbons from resol by potassium acetate activation for high performance supercapacitor electrodes

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ABSTRACT

A novel strategy for the synthesis of hierarchical porous carbons (HPCs) from resol by potassium acetate activation for advanced supercapacitor electrodes was reported.

The resultant HPCs with a high specific surface area up to 1201 m² g⁻¹ as a supercapacitor electrode exhibits a high specific capacitance of 226 F g⁻¹ at 0.05 A g⁻¹. Besides, the electrode shows high rate capability with 62.4% retention from 0.05 to 20 A g⁻¹. Moreover, it demonstrates good cyclic stability, showing a high capacitance retention of 97.1% over 5000 charge-discharge cycles at 2.0 A g⁻¹. The facile, efficient and template-free synthesis strategy for novel 3D-HPCs may promote commercial application of HPCs in the fields of supercapacitors.

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1. Introduction

Over decades of the growing interests towards nanotechnology, various materials have been used as electrodes for supercapacitors, including porous carbon materials, transition metal oxides and conducting polymers. Though conductive polymers and transition metal oxides have been extensively studied, those materials still have their drawback for their low conductivity, poor stability and cycle property, which limit their practical applications [1,2]. Carbon based materials are the most important electrode materials for supercapacitors due to their high surface area, desirable electric conductivity, well-developed pore-size distribution, good chemical stability and relatively low price, etc [3–6]. Amongst them, HPCs materials are very popular as electrode materials for supercapacitors [7–9]. Over the past years, activating methods used KOH, NaOH, ZnCl₂ as activating agents are commonly way to prepare HPCs for electrode materials of supercapacitors [10]. However, those activating agents are highly

corrosive to manufacturing devices, and will pollute the environment during the producing process. Given this, searching for appropriate precursors and optimizing activating agent would be of importance for improving the electric double-layer capacitors' performance.

In the latest years, different alkali salts are used as activating agents to prepare HPCs. Those alkali salts are low in corrosion to the manufacturing facilities, and could be removed easily in the subsequent treatment process. By using K₂CO₃ activating, activated carbon from peanut shell with a surface area of 1236 m² g⁻¹ was fabricated [11]. Yuan Gao et al. synthesized HPCs with high surface area as well as highly developed mesoporous structure employing different alkali salts, including K₂CO₃, K₂SiO₃, Na₂SiO₃, K₂B₄O₇ and Na₂Al₂O₄ as activating agents [12].

Inspired by the above mentioned work of the other researchers, herein, we prepare HPCs from resol by adding potassium acetate for the first time. Phenolic compounds are good carbon precursor of carbon materials, due to their high-purity, high carbon yields and good electric conductivity [13,14]. Potassium acetate is weakly corrosive, and commercially available. The structural characterization results show that the annealing temperature is important for constructing 3D hierarchical porous nanostructure. When used as

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supercapacitor electrode, the as prepared sample exhibits low equivalent resistance, high specific capacitance, and excellent rate-capability in a two-electrode system due to the three-dimensional interconnected porous framework and rich porosities.

2. Experimental

2.1. Preparation of HPCs

In a typical synthesis process, potassium acetate was added into resol with a mass ratio of 3:1 (potassium acetate: resol) and stirred for 30 min at 50 °C in a beaker. Then the hybrid was held at 120 °C for 8 h to cure. The cured sample was heated to the desired temperatures and heat treated for 1 h under N₂ protection, followed by cooling naturally to room temperature. At last, the obtained product was washed with deionized water for 3 times followed drying at 120 °C for 12 h. After cooled to room temperature, HPCs-x was obtained (x is annealing treating temperature (°C)). For comparison, the resol precursor was annealed under the same conditions as that of HPCs-800. After washing and drying, the resulting material was named RC-800.

2.2. Characterizations

The scanning electron microscopy (SEM, Hitachi BCPCAS-4800, Tokyo, Japan), and X-ray diffraction (XRD, Bruker/D8 advance) were used to characterize the structure and the morphologies of the samples. Nitrogen adsorption-desorption isotherm were measured using a Micromeritics ASAP 2020 instrument for samples. The total surface area of the HPCs samples was calculated from the Brunauer-Emmett-Teller (BET) equation. The pore size distribution was estimated based on density function theory (DFT) model [15,16]. The micropores and mesopore volume were determined by the density functional theory (DFT) for samples based on the N₂ isotherm adsorption data.

2.3. Electrochemical measurement

The electrochemical measurements were tested using a two-electrode testing device in 7 M KOH aqueous electrolyte at room temperature. The test electrode was prepared by mixing as-prepared carbon samples, acetylene black and polytetrafluorene polytetrafluoreneethylene (PTFE) binder with a weight ratio of 80:10:10. The galvanostatic charge/discharge performance and cyclic voltammetry (CV) were evaluated by Arbin cell tester (BT2000) and electrochemical workstation (Solartry 1280 Z), respectively. Electrochemical impedance spectroscopy (EIS, frequency) tests were conducted over the frequency ranging from 0.01 Hz to 100,000 Hz with potential amplitude of 5 mV at an open circuit potential on a CHI 760E electrochemical workstation. The electrochemical stability test was performed by repeating the charge/discharge test at current density of 2 A g⁻¹ for 5000 cycles. The specific capacitance of a single carbon electrode was evaluated from the discharge curve over a potential range of 0–1 V according to the eqn (1).

$$C = 2 I \Delta t / (m \Delta V) \quad (1)$$

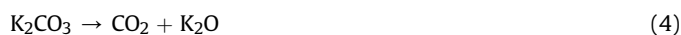
here, C is the specific capacitance (F g⁻¹), I is the discharge current (A), ΔV is the potential change in discharge (V), t is the discharge time for the voltage change (s), and m is the mass of the active material (in the single electrode, g). The factor of 2 comes from the fact that the total capacitance measured from the test cells is the sum of two equivalent single electrode capacitors in series.

3. Results and discussion

3.1. Microstructure characterization

Fig. 1 shows the N₂ adsorption-desorption isotherms and the corresponding pore-size distributions of the as prepared samples. Obviously differences of HPCs present combined type I and IV adsorption/desorption isotherms as shown in Fig. 1a. With the annealing temperature increasing, the much elevated N₂ adsorption at low relative pressure implies the developed micropores [17]. The hysteresis loops are widened from P/P₀ = 0.8–0.99 to 0.4–0.99, which means the wider mesopores distribution and some small mesopores and macropores are created. The maximum adsorption volume at P/P₀ = 0.99 increases for several times, implying dramatically increased pore volume. As shown in Table 1, the S_{BET}, V_{total} and V_{mes} of HPCs-800 can reach 1201 m² g⁻¹, 1.09 cm³ g⁻¹ and 0.24 cm³ g⁻¹, respectively, which are much higher than those of HPCs-600 (S_{BET}: 897 m² g⁻¹; V_{total}: 0.43 cm³ g⁻¹; V_{mes}: 0.04 cm³ g⁻¹), proving the powerful activation ability of the resulting potassium alkaline substances (KOH, K₂CO₃, K₂O or K) at high annealing temperature [18]. Both mesopores volume and macropores volume increase dramatically with the annealing temperature, implying pore creation and pore widen mechanisms are all involved in activation process. As shown in Fig. 1b, HPCs-800 shows different pore size distribution from those of HPCs-600 and HPCs-700. Besides of a large amount of micropores around 1–2 nm and mesopores of 2–7 nm, large mesopores of 15–50 nm and macropores of 50–80 nm appear. Moreover, the peak intensity of all relating pores increases dramatically with the temperature, demonstrating that the potassium alkaline substances can produce micropores and mesopores and enlarge the space that they occupy to form macropores.

There were many chemical reactions during the potassium alkaline substances activation (from equations (2)–(6)). Potassium acetate decomposed into K₂CO₃ at about 303 °C and resol completely decomposed at about 600 °C. The as-formed K₂CO₃ reacted with carbon to produce CO and K (equation (3)), and many micropores (0.29 cm³ g⁻¹, Table 1) were generated, while a small amount of mesopores (0.04 cm³ g⁻¹, Table 1) formed simultaneously at 600 °C for HPCs-600. The as-formed K₂CO₃ can also decompose into CO₂ and K₂O at temperatures higher than 700 °C (equation (4)). As temperature rising, micropores began to decrease. HPCs-700 obtained 0.28 cm³ g⁻¹ micropores. Meanwhile, some more mesopores (0.13 cm³ g⁻¹, Table 1) were created by stronger etching and expanding of K₂CO₃. When the temperature increased to 800 °C, the resulting CO₂, K₂O and undecomposed K₂CO₃ can be further reduced by carbon to form CO and metallic K at higher temperature. It is believed that the as-prepared K can efficiently intercalate into the carbon lattices of the carbon matrix to enlarge the carbon lattices [19]. Pores were still developing with the temperature increasing. However, the micropores decreased due to intensive erosion and much more mesopores and macropores appeared. The HPCs-800 gained the least micropore (0.27 cm³ g⁻¹) and largest mesopore (0.24 cm³ g⁻¹) volumes and an apparently amount of macropores ranged from 50 to 80 nm.



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