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Highly porous carbon spheres prepared by boron-templating and reactive H_3PO_4 activation as electrode of supercapacitors

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ABSTRACT

Porous carbon spheres with high specific surface area (2955 $m^2 g^{-1}$) and large pore volume (1.65 $cm^3 g^{-1}$) were prepared by incorporating boron in spherical polymeric precursors followed by reactive H_3PO_4 activation. In such a process H_3PO_4 acted as both an activating agent to activate the polymeric precursors and a reactant to extract out the pre-embedded boron from the carbonized spheres through formation of base dissolvable BPO_4, hence generated additional pores in the carbon spheres and also widened the pore diameters. With these improved texture properties, the porous carbon spheres exhibited much enhanced energy storage capacities as electrode of symmetrical electrochemical capacitor in 1 M $TEABF_4$/PC electrolyte. Energy densities of 31.3 and 20.3 Wh kg^{-1} were obtained at power densities of 259 and 11,000 W kg^{-1} (based on the active mass of both electrodes), respectively, which were much higher than those of the porous carbon spheres prepared without boron template and commercial activated carbons (YP-50F, Kuraray). This study provided a versatile strategy to tune the texture properties of porous carbons by combining element incorporation and reactive chemical activations, thus could be potentially used to fabricate high performance carbonaceous electrode materials for electrochemical energy storage devices.

1. Introduction

Supercapacitors, also known as electrical double layer capacitors (EDLCs), are of a class of energy storage devices possessing excellent high power density and ultralong cycle stability, which makes them good power sources for portable electronic devices, emergency power backup, cold-starting assistants, and electric vehicles [1,2]. In EDLCs, charges are mainly stored at the interface of electrode/electrolyte by formation of an electrical double layer. As a consequence, electrode materials with high accessible surface area to the electrolyte ions are generally desired for improving the energy storage property [3,4]. Activated carbons (ACs) are so far the most successfully commercialized electrode materials of EDLCs because of their high specific surface area, enriched microporous structure, wide availability, non-toxic nature, and high stability [5]. Unfortunately, the high inner resistance and large portion of surface area inaccessible to the electrolyte ions impede their charge storage performance, resulting in limited capacitance and powder densities. In addition, the packing density of commercial ACs is usually smaller than 0.6 g cm^{-3} [5], which is not beneficial for achieving a high volumetric energy density in EDLCs. Owing to these reasons, fabrication of carbon electrode materials with both high gravimetric and volumetric densities has been the continuous research focus of many researches in order to optimize the overall performance of EDLCs [6,7].

Besides a high porosity, the irregular morphology of activated carbon particles is believed to be partly responsible for their low packing density because of the existence of a large amount of inter-particle voids. A common way to overcome this problem is to fabricate uniform spherical carbons spheres as in comparison to granular activated carbons, the spherical activated carbons (SACs) can not only attain a high packing density up to 74% of its density but ensure a good electrolyte accessibility through the ordered inter-particle voids, both of which can help to improve the volumetric energy density and powder density of EDLCs [8–12].

To date, various methodologies have been developed to prepare high surface area SACs [13–15]. Among them, incorporation of salt template in precursors followed by post-activation treatment has been adopted to improve the texture properties [16–23]. For example, by using molten zinc dichloride as an activating agent and catalyst for the polymerization reaction, Antonietti et al. prepared porous triazine-

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based materials with a high surface area of 3300 $m^2 g^{-1}$ [21,22]. Ludwinowicz and Jaroniec embedded potassium oxalate into organic spheres derived from resorcinol and formaldehyde polymerization and used it as both the template and activation agent [23]. Removing the inorganic residual by acid washing resulted in SACs with a high surface area of 2130 $m^2 g^{-1}$ and a total pore volume of 1.10 $cm^3 g^{-1}$ [23]. In our previous work [24], incorporation of boron template in polymeric spheres was coupled with phosphoric acid activation to prepare highly porous SACs. A high surface area of 2729 $m^2 g^{-1}$ and a large total pore volume of 1.529 $cm^3 g^{-1}$ were achieved. In this work, the texture properties of SACs were further improved by optimizing the material preparation parameters. It will be shown in this manuscript that, as electrodes of EDLCs, the energy storage properties of the highly porous SACs were much higher than those prepared without boron template and a widely used commercial activated carbon (YP-50F, Kuraray).

2. Experimental details

2.1. Preparation and characterizations of SACs

The detailed preparation process for the SACs with boron template and H_3PO_4 activation can be found in our previous publication [24]. In this work, a reference sample without adding boric acid was prepared to examine the effect of boron template. To further improve the texture properties of SACs, the polymeric precursors with or without boron incorporation were mixed with H_3PO_4 (85 wt%) in a mass ratio of 1:5 and heated at 600 °C for 1 h under flowing argon (99.99%) after drying at 140 °C. The activated powders were washed by 1 M HCl solution first and then 3 M NaOH solution with intermediate filtration and drying steps. To simplify the description, the samples with or without boron incorporation were named as B-templated and nontemplated, respectively. The microstructures and phase of the obtained SACs were examined by scanning electron microscopy (SEM, FEI F50), transmission electronic microscopy (TEM, FEI Talos™ F200S) and X-ray diffraction (D/Max-2500PC) methods. Nitrogen adsorption/desorption isotherms were measured with a surface area and porosimetry analyzer V-sorb 2800P (Gold APP) at 77 K. The specific surface areas were calculated according to the Brunauer–Emmert–Teller (BET) method. The total pore volumes (V_t) were calculated from the amount of adsorbed nitrogen at a relative pressure, P/P_0, of 0.99. The micropore volumes (V_{micro}) were calculated using *t*-plot method. Pore size distributions were determined from the adsorption branches of the isotherms using the quenched solid density functional theory (QSDFT) provided by Quantachrome software.

2.2. Electrochemical measurements

The electrodes were prepared by mixing 80 wt% of active materials, 10 wt% of conductive additive Super C65 (Timcal), and 10 wt% of polytetrafluoroethylene (PTFE) binder (Dakin, 5 wt% suspension in water) in ethanol under hand grinding. After the ethanol and water were completely evaporated, the obtained slurries were rolled into thin sheets, which were then pressed onto an aluminum foil of 18 μm thickness under a pressure of 30 MPa. After drying at 120 °C for 12 h in vacuum, disk-type electrodes of 12 mm in diameter were punctured out from the composite foils. The mass loadings of the active materials in each disk electrode were about 3–5 mg cm^{-2}. 2025 coin-type half-cells were assembled first in Ar-filled glove box by using $LiPF_6$ electrolyte dissolved in EC and DMC (EC:DMC = 1:1), Li metal anode and Celgard 2400 separator. 2025 coin-type symmetric supercapacitors were also assembled using two carbon electrodes of similar mass of active material isolated by a cellulose fibrous separator (NKKTF4030, Japan). The electrolyte was 1 M tetraethyl ammonium tetrafluoroborate ($TEABF_4$) dissolved in propylene carbonate (PC). Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements were performed on a CHI660e electrochemical workstation (Chenhua Instruments, Shanghai) within a voltage range of 3–4.5 V (vs. Li^+/Li) for the half cells and 0–2.6 V for the full cells, respectively. The cycling life measurements were performed on a Land battery tester (CT2001A, Land, Wuhan). The electrochemical impedance spectroscopy (EIS) was measured on a multichannel electrochemical workstation (PARSTAT™ MC, AMETEK, USA) in the frequency range of 100 kHz to 10 mHz at the open circuit voltage (about 0 V) by applying a bias of 5 mV. The Nyquist plots and the plots of capacitance as a function of frequency of three samples were recorded. The relaxation time constant, τ_0, which defines the boundary between the regions of capacitive and resistive behaviors of the supercapacitor, was deduced from the frequency f_0 as follows: $\tau_0 = 1/f_0$, where f_0 can be obtained from the real capacitance plot at $C'/C'_{max} = 0.5$ [25]. The cell capacitances (C_{cell}) and specific electrode capacitances (C_{sp}) of the symmetric supercapacitors were calculated from the GCD curves as follows

$$C_{cell} = (I\Delta t)/(mV)$$

$$C_{sp} = 4 * C_{cell}$$

where I was the discharge current, V was the voltage window after deduction of the IR drop, Δt was the discharged time, and m was the total mass of active materials in both electrodes.

The specific energy density (E_s) and power density (P_s) of the symmetric supercapacitors were calculated as follows:

$$E_s = 0.5 \times C_{cell} V^2$$

$$P_s = E_s/\Delta t$$

where V was the voltage window after deduction of the IR drop, and Δt was the discharge time in hour. For comparison, supercapacitors using the commercial activated carbons YP-50F (Kuraray, Japan) as the active materials were also assembled and tested under the same conditions.

3. Results and discussion

3.1. Structural characteristics of SACs

As was reported in our previous paper [24], boron can be incorporated into polymeric spheres during the hydrothermal polycondensation of resorcinol and hexamethylenetetramine by adding boric acid. During the subsequent H_3PO_4 activation step, the embedded boron can be extracted out from the spheres through formation of BPO_4, which can be further removed by base leaching, resulting in highly porous SACs. In this work, the mass ratio of H_3PO_4 to the polymeric precursor was increased to 5 to further improve the texture properties of SACs. A reference sample without boron incorporation was also treated in the same way to examine the effect of boron template. Fig. 1 shows the SEM images of (a) the activated SACs without boron addition, (b) the as-activated SACs with boron addition, (c) the based washed SACs shown in (b), and (d) the XRD patterns of the corresponding samples. As shown in Fig. 1a, without addition of boron acid, the carbon particles do not all appear as regular spheres. This might be due to the rapid polycondensation of the resorcinol and hexamethylenetetramine at high initial concentrations used in present study. In fact, lowering the starting concentration of resorcinol and hexamethylenetetramine was able to produce uniform polymeric spheres [26]. By contrast, even at the same high resorcinol and hexamethylenetetramine concentrations, incorporation of boron acid promoted the formation of regular polymeric spheres (see Fig. 1b and c). After H_3PO_4 activation, the incorporated boron was extracted out form the spheres through formation of BPO_4 particles (Fig. 1b). After base leaching, almost all of the BPO_4 particles were removed, leaving smooth micron-size porous carbon spheres with diameters of 5–10 μm (Fig. 1c). The XRD patterns of the corresponding samples shown in Fig. 1d supported well the phase change of the SACs before and after base leaching, i.e. washing the H_3PO_4 activated SACs by hot base