One-step synthesis of hierarchically porous carbons for high-performance electric double layer supercapacitors

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HIGHLIGHTS

- HPCs with mass production are prepared by a one-step template-free method.
- Lower synthesis and manufacturing costs.
- HPCs based supercapacitors show superior electrochemical performances.
- Effect of pore structure on the electrochemical performances of HPCs is studied.

GRAPHICAL ABSTRACT
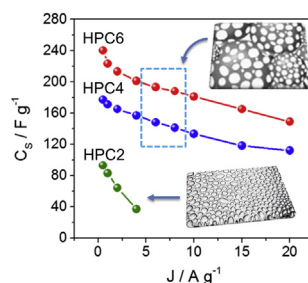
ABSTRACT

With plenty of unique porous structure at micro-/nano scale, hierarchically porous carbons (HPCs) are promising for usage in advanced electric double layer supercapacitors (EDLCs) as the electrode materials. However, wide-range adoption of HPC for practical application is largely shadowed by its extremely complex synthesis process with considerably low production efficiency. Herein we reported a simple template-free, one-step sintering method, to massively produce the HPCs for high-performance EDLCs. Resorting to the 3D structure modification of the wide pore size distribution, high surface area of HPCs (up to 3000 m^2 g^{-1}) was achieved. By using 1 M Na_2SO_4 as electrolyte, the as-fabricated HPCs based EDLCs can be operated reversibly over a wide voltage window of 1.6 V with superior specific capacitance of 240 F g^{-1} under a current density of 0.5 A g^{-1}. In the meanwhile, the EDLCs exhibit excellent rate capability (high power density of 16 kW kg^{-1} at 10.2 Wh kg^{-1}) and long-term cycling stability with 9% loss of its initial capacitance after 2000 cycles. This output performance distinguished itself among most of the carbon-based EDLCs with neutral aqueous electrolyte. Thus, the template-free one-step sintering method produced HPCs for EDLCs represents a new approach for high-performance energy storage.

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1. Introduction

Based on the non-Faradaic processes, the electric double layer capacitors (EDLCs) have emerged an important type of device for next generation energy storage due to their fast charge/discharge rate and excellent cycling stability [1–3]. However, the EDLCs are suffering from far lower energy densities than that of the secondary

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batteries, such as lead-acid batteries and lithium-ion batteries.

Theoretically, according to $E = C_S V^2/2$, the enhancement of energy density (E) of EDLCs can be achieved by maximizing both the specific capacitance (C_S) and the voltage window (V). Experimentally, a variety of strategies were attempted in the past ten years, including intrinsic structure design to increase the specific capacitance [4,5], assembling asymmetric and hybrid structured devices [6,7]; developing the electrolytes with high voltage window [8,9]; The EDLCs with strong acid/alkali aqueous electrolytes indeed exhibit much higher C_S, however, they suffer from narrow voltage window, which can only operate in a voltage of 1.0 V due to the limitation of the water decomposition. And this design was also challenged due to its potential environmental pollution. A promising direction is to design environmentally friendly materials that have outstanding electrochemical properties in salt aqueous electrolytes like Na_2SO_4 and Li_2SO_4 with the merits of high ionic conductivity, high voltage window (up to 1.5–2.0 V), safety, non−corrosiveness and convenient assembly in air [10–12].

Hierarchically porous carbons (HPCs) are such a good candidate and electrochemically stable within a wide range of operating voltage [13–17]. However, most of HPCs were generally fabricated by using hard or soft template-based methods, which required very much complex synthesis procedures with considerably low mass production [18–22]. In hard templating, infiltration of the carbon precursors into the pores of $Ni(OH)_2$ [20] the silica [21], or zeolite templates [22] was carried out, followed by a carbonization treatment and finally the removal of the template to get the template-free porous carbon replica. Thus, to solve this, developing template-free method for the preparation of HPCs materials are critical [23,24], however, it still exists a big challenge.

Here in this work, we reported a simple and effectively template-free method to prepare HPCs based on one-step carbonization and activation of Polyvinylidene Fluoride (PVDF) with molten KOH. By extracting the fluorine element from PVDF and reassembling the C−C bond, the obtained HPCs possess high ratio of micropores, mesopores, and high mass of KOH generated macropores with a high SSA of 3003 m^2 g^{-1}, large pore volume of 2.27 cm^3 g^{-1}, as well as a wide pore size distribution. And these superior features well serve as the EDLC electrode materials and a maximum specific capacitance of 60 F g^{-1} (240 F g^{-1} for a single electrode) with an energy density of 21.2 Wh kg^{-1} has been obtained. In 1 M Na_2SO_4 aqueous electrolyte, the as-developed EDLCs can also be operated reversibly over a wide voltage window of 1.6 V. To date, this output performance is the highest value reported for the hierarchically porous carbons as well as mesoporous carbons based EDLCs with neutral aqueous electrolytes [10,25,26]. Moreover, the HPC-based EDLCs exhibited good rate-capability and also possessed long-term cycling stability with 91% retention after 2000 cycles. These observations unambiguously demonstrate the capability of the template-free one-step processed HPCs as high-performance electrode materials for EDLCs with neutral aqueous electrolytes, which opens up a new approach for high-performance energy storage and is suited for mass production.

2. Experimental

2.1. Synthesis of HPC samples

HPCs were synthesized by directly sintering process. Both the PVDF and KOH were used as precursors to prepare HPCs. The PVDF powder was purchased from Arkema (HSV900, French), and its molecular weight is 800,000–1,000,000 g mol^{-1}. The weight ratio of KOH to PVDF was controlled in a range from 2:1 to 6:1. The samples were prepared from carbonization and activation of PVDF using different amounts of KOH, namely, HPC2, HPC4, and HPC6.

Take the synthesis of HPC6 as an example, 2.5 g PVDF and 15.0 g KOH were added into a Ni crucible. And then put them into a horizontal tube furnace (Φ 60 × 1200 mm, SGSL-1600×, Hefei Kejing Materials Technology CO., LTD, China). The furnace was heated to 380 °C and retained this temperature for 2 h to melt the KOH. Followed by a sequentially heating to 800 °C and stayed for 2 h. The resultants were cooled down to room temperature naturally. All the chemical reactions were preceded under a 160 sccm flowing Ar gas. After the reaction, the products were sonicated in 6 M HCl for 20 min, and then they were washed ordinarily with deionized water and alcohol to remove impurities. The obtained yields for HPC2, HPC4, and HPC6 were about 0.15, 0.45, and 0.68 g, respectively.

2.2. Sample characterization

Scanning electron microscopy (SEM) was carried out on Zeiss Sigma scanning electron microscopes. Energy dispersive X-ray spectroscopy (EDX) was carried out on an EDAX TEAM EDS. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) characterizations were performed with a JEOL JSM-2010 operating at an accelerating voltage of 200 kV. X-ray diffraction (XRD) of the samples was performed with D8 Advance diffractometer with Cu radiation between 5 and 70°. Room-temperature Raman spectra were obtained with a RM2000 microscopic confocal Raman spectrometer with a 514 nm laser beam. X-ray photoemission microscopy (XPS) analysis was carried out with a PHI Quantear SXM (ULVAC-PHINC). Brunaue−Emmertt−Teller (BET) surface areas and density functional theory (DFT) pore size distribution measurements of HPCs were performed with Micromeritics ASAP 2020 surface area and pore size analyzer using nitrogen gas adsorption-desorption isotherm at −196 °C.

2.3. Electrochemical measurements

For assembling EDLCs, 2032 type coin cells were used. 85 wt% of the HPCs, 8 wt% conductive agent (Super C45, Timcal) and 7 wt% Polytetrafluoroethylene (PTFE, Sigma Aldrich) binder were mixed in isopropyl alcohol, and blended for 30 min before using. The obtained slurry was heated at 80 °C to remove excess isopropanol and then kneaded thoroughly and rolled down to shape it into 100−120 μm thick films. After drying for 24 h at 120 °C, the films punched into 1.1 cm diameter electrodes and the mass of a single electrode for HPC2, HPC4, and HPC6 are about 9, 6.5 and 4 mg, respectively. The as-rolled tape densities of HPC2, HPC4, and HPC6 electrodes are 0.79 ± 0.02, 0.60 ± 0.03, 0.42 ± 0.02 g cm^{-3}, respectively. Then the HPC disks were pressed onto nickel foam and the electrode plates were further mechanically compacted. A cellulose separator (F4050, NKK) was sandwiched between two electrodes to fabricated symmetrical supercapacitors and 1 M Na_2SO_4 and 6 M KOH were employed as the electrolytes.

The cyclic voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) were carried out by using the electrochemical workstation (CHI660E). And EIS was obtained in the frequency range from 100 kHz to 10 mHz. The galvanostatic charge-discharge (GCD) process and cycle-life test of EDLCs were measured on an Arbin MSTAT4 multi-channel galvanostat/potentiostat instrument. The specific capacitance of EDLC electrodes can be calculated as:

$$C_S = I\Delta t \Big/ \Delta U m \left(F\, g^{-1} \right) \tag{1}$$

where I, Δt, ΔU and m are respectively the applied current, the discharge time, the potential window after IR drop and the total