Journal of Power Sources 365 (2017) 362–371

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Ultrahigh surface area meso/microporous carbon formed with self-template for high-voltage aqueous supercapacitors

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HIGHLIGHTS

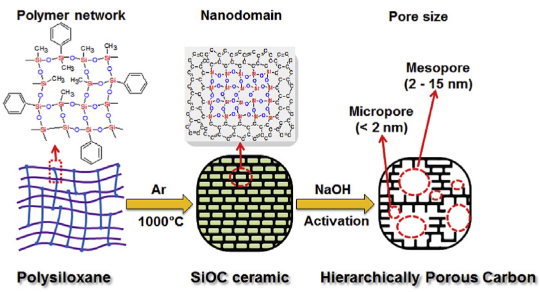
- The meso/microporous carbon (MC) is synthesized by a simple self-template method.
- The MC electrode exhibits excellent performance in capacitance and rate capability.
- Three neutral electrolytes are studied to enhance the energy density of capacitors.
- The maximum operating voltage is essentially restricted by the positive potential.
- The symmetric supercapacitors exhibit high energy densities in aqueous solutions.

ARTICLE INFO

Article history:
Received 30 March 2017
Received in revised form
21 August 2017
Accepted 31 August 2017

Keywords:
Meso/microporous carbon
Aqueous supercapacitors
High-voltage
High energy density

GRAPHICAL ABSTRACT



ABSTRACT

A new hierarchically porous carbon has been synthesized with self-template of silica phase from a commercial silicone resin by pyrolysis and subsequent NaOH activation. The obtained carbon materials achieve an ultrahigh specific surface area (2896 $m^2\ g^{-1}$) with abundant mesopores. The C800 sample demonstrates excellent performance in supercapacitors, with a high capacitance of 322 F g^{-1} at 0.5 A g^{-1} and outstanding rate capability (182 F g^{-1} at 100 A g^{-1}) in a three-electrode system using 6.0 mol L^{-1} KOH electrolyte. The energy density is improved by widening the voltage window using 1.0 mol L^{-1} alkali metal nitrate solutions ($LiNO_3$, $NaNO_3$, KNO_3) in which the strong solvation of alkali metal cations and nitrate anions effectively reduce the activity of water. In a symmetric supercapacitor, the maximum operating voltage is essentially restricted by the potential of positive electrode and the total capacitance is dominated by the capacitance of the anion at the positive electrode. The symmetric supercapacitors based on C800 deliver a high energy density of 22.4 Wh kg^{-1} at a power density of 0.23 kW kg^{-1} in 1.0 mol L^{-1} $LiNO_3$ with a voltage of 1.8 V and long-term stability with a retention of 89.87% after 10000 cycles.

1. Introduction

To meet the increasing demand for portable electronic devices and hybrid electric vehicles, supercapacitors based on porous carbons (electrical double-layer capacitors, or EDLCs) have received extensive attention owing to their advantages of high power

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http://dx.doi.org/10.1016/j.jpowsour.2017.08.114
0378-7753/

density and long cycle life compared with rechargeable batteries [1–3]. However, the wide application of supercapacitors has been hampered by their relatively low energy densities. The energy density of commercial supercapacitors based on traditional activated carbon is about 5 Wh kg^{-1}, which is much lower than that of lithium-ion batteries (about 100 Wh kg^{-1}) [4–6]. Therefore, considerable efforts have been devoted to increasing the energy density of supercapacitors without losing the high specific power and cycling stability.

It is well-known that the energy density of supercapacitors is proportional to the specific capacitance of the material and the square of the operating voltage ($E = 0.5\ CV^2$) [7,8]. To effectively increase the energy density of supercapacitors, extensive research has been carried out to increase the operating voltage. Generally, the electrochemical window is limited by the stability of the electrolytes. The operating voltage range is usually limited to 1.0 V in acidic and alkaline aqueous media, while the stability window of organic electrolytes is wider than 2.5 V [9]. However, organic electrolytes usually have low conductivity and high viscosity. Additionally, organic electrolytes are unfriendly to the environment and complicated to use due to their sensitivity to moisture. Hence, neutral aqueous media are considered as promising electrolytes from the viewpoint of application since they are cheap, environmentally friendly, non-corrosive and suitable for various current collectors. In recent years, neutral aqueous solutions such as sulfate and nitrate have attracted much interest due to relatively wider electrochemical window, which can be as wide as 1.6 V–2.0 V [9,10]. Widening of the electrochemical window in neutral aqueous solutions may be attributed to the strong solvation of ions and low concentration of protons or hydroxyl groups. However, large solvated ions migrate slower, especially in narrow pores, leading to declined rate capability.

Another important way to increase the energy density of supercapacitors is to develop new high performance materials with ultra-high effective surface area. Nowadays, new types of porous carbon materials with high specific surface area, excellent conductivity, low cost and environmental friendliness have been widely researched for energy storage and conversion applications especially for EDLCs [11,12]. Considering that the energy storage mechanism in EDLCs is based on ion adsorption at the electrode/electrolyte interface, the performance of EDLCs is largely determined by the specific surface area, pore structure of the carbon material and ion dimension [13–15]. In addition, introducing specific types of functional groups to the carbon surface would be beneficial for the electrolyte to access the carbon surface easily and may contribute some pseudo-capacitance [16]. Usually, porous carbon materials with a high specific surface area contain mostly micropores, and suffer from a poor rate performance due to sluggish ionic diffusion within the micropores [17,18]. Thus, it is important to develop hierarchically porous materials combining micropores with mesopores and macropores to improve the performance in terms of both capacitance and rate capability. Preparing hierarchically porous materials with different carbon sources by different method has been widely reported [5,19–21]. Macropores can play a role as reservoir to supply electrolyte ions from the bulk to the electrode/electrolyte interface, while mesopores can provide larger accessible surface area and serve as channels for fast ion transport, which will be beneficial for the accessibility of micropores [15,22]. Obtaining both a high specific surface area and a large proportion of mesopores in porous carbon materials often resorts to addition and subsequent removal of sacrificial templates, which complicates the synthesis process and raises the materials cost.

Recently, we developed a facile method to produce meso/microporous carbon material from a polysiloxane precursor using a traditional activation process. The new carbon material achieved an ultrahigh surface area and a large mesopore volume without using any additional templates. The polysiloxane precursor was prepared by addition polymerization under a platinum based catalyst [23]. In this work, we used commercial silicone resin as a precursor to produce nonporous SiOC ceramic followed by NaOH activation. The silica distributed in the framework of SiOC ceramic can function as a self-template to modulate hierarchically porous carbon formation with optimized pore structure. Different from our previous work, the silicone resin is a commercial product and it polymerizes through condensation without a platinum catalyst. Using commercial silicone resin further simplified the process and reduced the cost, and can potentially facilitate large scale production. The hierarchically porous carbon prepared from the commercial silicone resin achieved a specific surface area as high as 2896 $m^2\ g^{-1}$ and it contained micropores and mesopores. The porous carbon material showed high specific capacitance and outstanding rate capability (322 F g^{-1} at 0.5 A g^{-1} and 182 F g^{-1} at 100 A g^{-1}) in a three-electrode system. Moreover, the corresponding symmetric supercapacitor operated in 1.8 V exhibited an excellent stability (89.87% capacitance retention after 10000 cycles) and a high energy density of 22.4 Wh kg^{-1} in 1.0 M $LiNO_3$, which is much higher than most previously reported carbon-based symmetric supercapacitors in aqueous electrolytes.

2. Experimental

Synthesis of silicone resin derived carbon: The process for synthesizing the hierarchically porous carbon is shown in Scheme 1. A commercial silicone resin (Wacker SILRES 604) was heated to 1000 °C at a 5 °C min^{-1} ramp rate and held for 4 h under argon atmosphere, followed by cooling down to room temperature naturally. After pyrolysis the silicone resin was converted into a carbon-rich SiOC ceramic, which was then pulverized and ground to fine powders. Then the obtained powder was mixed with NaOH with a mass ratio of 1:4 in a nickel crucible. The mixture was heated to 700 °C, 800 °C and 900 °C at a 5 °C min^{-1} ramp rate and held for 1 h under argon atmosphere. The obtained product was washed with de-ionized water until the filtrate was neutral. The sample was finally dried at 120 °C in an oven. The dried samples were designated as C700, C800 and C900 according to the NaOH activation temperature.

Materials characterization: The crystal structure of the materials was characterized by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with Cu-Kα radiation. Raman spectra were obtained using a Horiba modular Raman system with a diode laser with wavelength of 532 nm. Nitrogen absorption/desorption measurement was performed to characterize the pore structure on a Micromeritics ASAP 2020 analyzer. The specific surface area was derived by the Brunauer-Emmett-Teller (BET) model and the pore size distribution (PSD) was derived from a density functional theory (DFT) model. The morphology analysis of the samples was performed by scanning electron microscopy (SEM, ZEISS Supra 55) and transmission electron microscopy (TEM, FEI Tecnai G2 F30). An X-ray photoelectron spectrometer (ESCALAB 250XL) was used to investigate the surface chemical properties of the samples.

Electrochemical measurements: The working electrode consisted of active material, acetylene black, and PTFE binder with a mass ratio of 8:1:1. The mixture was rolled into sheets with a uniform thickness of 100–150 μm and cut into slices of 1 cm in diameter. Then the slices were dried in a vacuum oven at 110 °C overnight and pressed onto a piece of titanium mesh as the working electrode. The mass of the active material in each working electrode was about 1.2–1.5 mg. The three-electrode tests were carried out in an aqueous solution (6.0 M KOH) with Pt electrode as the counter electrode and Hg/HgO electrode as the reference