



Crystallizable diluent-templated polyacrylonitrile foams for macroporous carbon monoliths

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ABSTRACT

Polyacrylonitrile (PAN) foams with different pore structures were prepared for the fabrication of macroporous carbon monoliths. The foams were prepared through thermally induced phase separation (TIPS) method using dimethyl sulfone (DMSO₂) as a crystallizable diluent. Honeycomb-like porous foam is obtained from PAN/DMSO₂ mixture containing about 5 wt.% PAN, and those with channel-like pores are resulted from the mixtures with 10–40 wt.% PAN. However, they only have few mesopores and the porosity is as low as 30–47% for the foams prepared from those mixtures containing 50–60 wt.% PAN. Real-time observation with polarized optical microscopy reveals that the channel-like structure stems from the spherulitic orientation of DMSO₂ crystals in the polymer matrix. Taking into account this morphology, DMSO₂ crystals are capable of acting as *in situ* formed templates, which subsequently enable to shape the final pore structure of PAN foams. Macroporous carbon monoliths with honeycomb- or channel-like pores were constructed from PAN foams by oxidative stabilization and carbonization. Their graphitic structure and specific surface areas were analyzed by wide-angle X-ray diffraction and Brunauer–Emmett–Teller measurement. This TIPS method using crystallizable diluent provides a new route to control the porous structure of PAN foams for carbon materials.

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1. Introduction

Carbon materials with unique mechanical properties and chemical inertness have attracted considerable attention for electrochemical double-layer capacitors [1–3], catalyst supports [4], electrode materials in Li-ion batteries [5,6], water purification filters [7], and chemical adsorbents [8,9]. Despite various precursors, polyacrylonitrile (PAN) is the most suitable one for carbon fibers with excellent performance because of its high melting point, considerable carbon yield, and relatively cheap price [10–13]. It is accepted that fast pyrolysis of PAN generates a graphitic structure by thermal stabilization and subsequent carbonization. Recently, intensive studies have focused on the design and construction of porous structures for carbon materials with controllable pore number, pore size and functional surface in an effective fashion [6,14].

Various methods have been adopted to prepare porous carbon materials. Physical and chemical activation enables to create pores by subjecting the carbon to steam at high temperature, but is

complex, time-consuming, and difficult to control the pore structure. Templating method is capable of constructing ordered porous carbons with well-defined structures depending on the framework of the used templates [15–19]. Inorganic materials (e.g., silica or silica particles, zeolites, and anodic alumina oxide (AAO) membrane) are often used as hard-templates. For example, mesoporous carbons were prepared with silica as the template [18,19]. However, for a polymer precursor with high viscosity, it is difficult to completely diffuse and fill into the space of templates [20]. Unexpected defects will be left in the resulted porous carbon materials. Therefore the templating method is more suitable for thin films or fibers than bulky materials. Given these, another method has been developed based on phase separation and then carbonization from block copolymer or polymer blend with a sacrificial component [21–24]. This component serves as soft-template, allowing for replication of the phase separated structure into carbon materials. Microdomains of the sacrificial component can be selectively removed during pyrolysis. Accordingly, the morphology and scale of the microdomains must be bound to confine the pore structures. Thomassin et al. [25] developed a templating compression molding process using a polyacrylonitrile-poly(vinyl acetate) block copolymer to prepare mesoporous carbon fibers. As the sacrificial block, poly(vinyl

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acetate) favored the penetration of the copolymer into AAO template and created nanopores in the final carbon fibers by pyrolysis at 600 °C. This technique combined the advantage of the templating method and the microphase separation of block copolymer. Nevertheless, PAN-based block copolymers are limited and their phase separation is not well understood.

It should be promising to design the pore structures of carbon monoliths *a priori* through the preparation of porous polymer precursors [26–29]. Thermally induced phase separation (TIPS) is useful to fabricate polymer foams and separation membranes [30–36]. Several phase separation processes can be thermodynamically driven by temperature in polymer–diluent systems. After removing the diluent, cellular, lacy, bi-continuous, spherulitic, or metallic structures are usually obtained by varying the preparation conditions such as polymer concentration and/or by modulating the polymer–diluent interactions (quantified as interaction parameter). Generally, if a system possesses strong polymer–diluent interaction (small interaction parameter), solid–liquid phase separation takes place via polymer crystallization; otherwise, the polymer/diluent mixture undergoes liquid–liquid phase separation and shows an upper-critical temperature behavior upon cooling [30,31]. For a specific polymer, the polymer–diluent interaction can also be modulated by adding a non-solvent [37]. Olivier et al. [38] reported PAN foams for carbon materials using maleic anhydride as the diluent. This study proposed an ingenious way to design the porous framework. However, it was pointed out that maleic anhydride is only suitable for PAN with a very low concentration because of the low dissolubility [39].

We report here a method to control the pore structures of PAN foams using crystallizable dimethyl sulfone (DMSO2) as the diluent. As a polar solvent with high melting point, DMSO2 can dissolve PAN in a wide range up to 70 wt.%. PAN foams with honeycomb- or channel-like pores were prepared by varying the polymer concentration, the background of which was particularly studied from the perspective of DMSO2 crystallization in the polymer matrix. These PAN foams were then used as precursors for macroporous carbon monoliths by the oxidative stabilization and carbonization processes.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, $M_n = 115,000$, $M_w = 251,000$, $MWD = 2.19$) was kindly supplied by Anqing Petroleum Chemical Corporation of China. It is a copolymer of acrylonitrile (AN) and vinyl acetate (VA), and the molar ratio of AN:VA is 24:1. The polymer was crushed finely and dried at 60 °C in an oven before use. Dimethyl sulfone (DMSO2, 99% purity) was purchased from Dakang Chemicals Co., Ltd of China. De-ionized water was chosen as the extractant. Ethanol and hexane (AR grade) were commercially obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification.

2.2. Preparation of PAN foams

PAN and DMSO2 were premixed with various compositions and sealed in glass tubes (8 mm in diameter and 1 mm thick). PAN concentration ranged from 5 to 60 wt.%. These tubes were immersed into an oil bath at 160 °C until the mixtures transformed into homogeneous solutions. After quenching the solutions into an oil bath at 30 °C, the obtained solid mixtures were immersed into de-ionized water with gentle vibration for 4 days at 30 °C to extract DMSO2 completely. To prevent collapse of pores during drying, water in the pores was exchanged by ethanol and hexane for 1 day

in consequence. The resulted foams were dried in vacuum oven at 30 °C overnight.

2.3. Preparation of porous carbon monoliths

Porous carbon monoliths from PAN precursors are usually prepared through two steps: (a) oxidative stabilization in air at a temperature between 200 and 300 °C, and (b) final carbonization in an inert atmosphere at temperatures between 600 and 1000 °C. In this work, the pristine PAN foams were placed in a quartz tube housed within an electric tube furnace, and heated to 250 °C at a rate of 1 °C/min and maintained at 250 °C for 1 h. Subsequently, the oxidized samples were conducted under the protection of nitrogen, heated to 800 °C at a rate of 2 °C/min and then held for 1 h at 800 °C for carbonization.

2.4. Determination of phase diagram

Differential scanning calorimeter (DSC, Pyris-1, Perkin–Elmer, USA) was used to determine the melting and crystallization temperatures of PAN/DMSO2 mixtures. After hermetically sealed in an aluminum DSC pan, a sample of 5–8 mg was heated from 0 °C to 160 °C at 20 °C/min, maintained at 160 °C for 3 min to eliminate thermal history, cooled to 10 °C at 5 °C/min, and then reheated to 160 °C at 5 °C/min.

2.5. Wide-angle X-ray diffraction (WAXD)

WAXD was carried out on a Rigaku D/Max-2550PC X-ray diffractometer (Panalytical, Netherlands). The radial scans at a voltage of 40 kV and a current of 40 mA using a Cu:K α radiation were employed on PAN/DMSO2 mixtures, PAN foams, and porous carbon monoliths. Data were collected at 0.0167° interval with counting for 10 s at each step.

2.6. Scanning electron microscopy (SEM)

FESEM (Sirion-100, FEI, USA) was used to observe the morphologies of the porous materials. Samples were frozen and fractured in liquid nitrogen to obtain tidy cross-section. After sputtered with gold using an ion sputter JFC-1100, samples were imaged by FESEM at an acceleration voltage of 25 kV.

2.7. Polarized optical microscopy (POM)

Polarized optical micrographs were recorded on an Olympus BX-5 POM equipped with a Linkam hot stage (CSS450, Linkam, UK) and a temperature controller (Linksys32, Linkam, UK). PAN/DMSO2 mixtures used here and the experimental parameters were as same as those in DSC measurements. Each sample was sliced into small pieces and placed between a pair of glasses, the edges of which were sealed with Teflon tape to prevent losses caused by evaporation. Photographs were taken by a CCD camera or a digital camera.

2.8. Pore size and porosity measurements

Dilatometer was employed to measure the apparent volume (V_a) of the porous samples, which was used to calculate the apparent density (d_a) and the porosity (ρ). A dilatometer filled with mercury was immersed in a water bath at 30 °C and recorded the height (h_0) of the mercury in the capillary with a diameter (D). Thereafter, a piece of porous materials with weight (m_0) was put into the conical beaker and record the height (h_1). The apparent volume, the apparent density, and the porosity can be defined as equations (1)–(3), respectively. Table 1 lists the density of PAN bulk (d_{PAN}).

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