

A hierarchical porous carbon membrane from polyacrylonitrile/polyvinylpyrrolidone blending membranes: Preparation, characterization and electrochemical capacitive performance

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Abstract

Novel hierarchical porous carbon membranes were fabricated through a simple carbonization procedure of well-defined blending polymer membrane precursors containing the source of carbon polyacrylonitrile (PAN) and an additive of polyvinylpyrrolidone (PVP), which was prepared using phase inversion method. The as-fabricated materials were further used as the active electrode materials for supercapacitors. The effects of PVP concentration in the casting solution on structure feature and electrochemical capacitive performance of the as-prepared carbon membranes were also studied in detail. As the electrode material for supercapacitor, a high specific capacitance of 278.0 F/g could be attained at a current of 5 mA/cm² and about 92.90% capacity retention could be maintained after 2000 charge/discharge cycles in 2 mol/L KOH solution with a PVP concentration of 0.3 wt% in the casting solution. The facile hierarchical pore structure preparation method and the good electrochemical capacitive performance make the prepared carbon membrane particularly promising for use in supercapacitor.

Key words

porous carbon; supercapacitors; phase separation; electrode materials; additive

1. Introduction

Energy consumption is forecasted to have severe problems in future for economic development and ecology protection of the world. Thus, the development of new inexpensive, flexible, light-weight and environmentally friendly energy storage devices is currently a strong demand [1–5]. Supercapacitors are under serious consideration as an alternative energy/power source, because this kind of energy consumption is designed to be more sustainable and more environmentally friendly. The electrode material plays a key role in supercapacitors. Hence for the capacitive performance of supercapacitors, the nature of electrode material is very important [6]. Normally, the electrode materials of supercapacitors can be categorized into three types as follows [7]: carbon materials, conducting polymers and metal oxides [8–10].

It is well known that a high specific surface area is the ba-

sic requirement for the carbon-based electrode materials since supercapacitor stores energy physically using reversible adsorption and desorption of the electrolyte ions onto the surface of active materials [11]. Among these carbon materials, activated carbons with a surface area of 3000 m²/g have been successfully prepared as electrodes for commercial supercapacitor devices. However, a poor rate performance has been observed for such a kind of high specific surface area porous carbon materials, mainly due to the high ion-transport resistance and insufficient ionic diffusion within the micropores, which in turn limit the pore accessibility of the electrolyte ions at high scanning rates [12]. In order to develop high-performance energy-storage carbon-based electrode materials, the challenge is how to achieve the desirable properties such as large specific surface area, high conductivity and efficient porosities. Obviously, the microstructure and synthesis method of carbon materials are particularly crucial.

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The phase-inversion process is induced by immersion precipitation, which is a well-known technique for preparing asymmetric polymeric membranes [13,14]. The porous polymer scaffolds can be fabricated into an asymmetric membrane by the phase separation process. The fast exchange between solvent and non-solvent leads to the generation of porous tunnels within the matrix during the phase separation process, forming a continuous and interconnected porous structure. Furthermore, the as-prepared composite can be heat-treated to carbonize the carbon precursor. During the carbonization procedure, both the molecular reaction as well as volume shrinking can happen. Thus, 3D nanoscale architecture porous structure is produced. The desirable morphology and good performance of the resulting membrane can be easily controlled by changing the compositions of constituents and/or additives, being set off by exchange between solvent and non-solvent, and heat transfer through temperature variation [15–19]. Recently, introduction of various additives as a third component, such as NaCl, LiCl, ethanol, ethylene glycol, PVP, poly(ethylene glycol) (PEG), etc., to a casting solution to enhance the desired properties of the membranes has been received more and more attention. As mentioned in the reported study [20], using additives as a pore-forming agent will enhance the permeation properties of membranes. We combine these processes as a simple and economical method for synthesizing porous carbon materials.

In this work, we attempted to construct a porous carbon with interconnected and hierarchical 3D nano-architecture by phase inversion with PVP-added in casting solutions. The effects of PVP added in casting solutions on structure feature and electrochemical performance of the as-prepared carbon membranes were also studied. High capacitance, excellent rate performance and long-term stability of the prepared electrochemical materials were achieved in 2 mol/L KOH aqueous solution.

2. Experimental

2.1. Materials

Analytical grade 2,2-azobisisobutyronitrile (AIBN), polyvinylpyrrolidone (PVP-30), N,N-dimethylformamide (DMF) and absolute alcohol were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received without any further purification. Vinylcyanide (AN) purchased from Sinopharm Chemical Reagent Co. Ltd. was purified via distillation before use.

2.2. Synthesis of polyacrylonitrile (PAN) precursor

PAN was synthesized as follows: AN (9.6 g) and AIBN (0.028 g) were dissolved in 30 mL DMF with magnetic stirring at 70 °C for 6 h, and then the sample was precipitated by ethanol. And the resulting PAN precipitate was washed thoroughly with distilled water several times. Finally, the product was dried under vacuum at 30 °C.

2.3. Preparation of PAN membranes (PM)

PAN membranes were prepared by a phase-inversion technique. The percents of components in solutions were calculated as follows

$$P (\%) = \frac{M_P}{M_P + M_S + M_A} \times 100\% \quad (1)$$

$$S (\%) = \frac{M_S}{M_P + M_S + M_A} \times 100\% \quad (2)$$

$$A (\%) = \frac{M_A}{M_P + M_S + M_A} \times 100\% \quad (3)$$

where, $P (\%)$ and $S (\%)$ are the concentrations of PAN (15 wt%) and solvent (DMF) in solutions, respectively. Meanwhile, $A (\%)$ means the concentration of the additive (PVP) in solutions. First, these prepared solutions were stirring at 70 °C until a clear homogeneous solution was obtained. The bubbles in solutions were removed by vacuum degassing. Then, the membranes were prepared with the casting solutions by spin coating coupled with a liquid-liquid phase separation technique at room temperature. And subsequently the solution films were immediately immersed in a deionized water bath for 24 h. After complete coagulation, the membranes were peeled off and then dried for 24 h at room temperature before characterization. The morphology and nanostructure of PM can be tuned by adjusting the additive concentrations in the casting solutions of 0, 0.1 wt%, 0.3 wt%, 0.7 wt%, 1.0 wt% and 5 wt%, which were named as PM-0, PM-1, PM-2, PM-3, PM-4 and PM-5, respectively.

2.4. Preparation and modification of hierarchical porous carbon membrane

Hierarchical porous carbon membranes (HPCMs) were further prepared through a simple polymer carbonization method involving two steps as follows: (1) preoxidization, the synthesized PAN membranes were heated and preoxidized at 200 °C in air for 5 h; (2) carbonation, the members were pyrolyzed at 800 °C under a flowing nitrogen for 2 h and then the samples were cooled down to room temperature. To introduce oxygen-containing functional groups on carbon surface, the carbon membranes were oxidized by nitric acid. 0.1 g of dried carbon membrane was treated with 10 mL HNO₃ solution at 80 °C for 6 h through refluxing process. After being treated with acid, the samples were recovered and washed thoroughly with distilled water until the pH value was close to 7, and the resulting products were further dried at 60 °C for 16 h. The HPCMs fabricated by PM-0, PM-1, PM-2, PM-3, PM-4 and PM-5, were named as HPCM-0, HPCM-1, HPCM-2, HPCM-3, HPCM-4 and HPCM-5, respectively.

2.5. Structure characterization

The microstructure and morphology of the as-prepared HPCMs were characterized by field emission scanning elec-

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