



New comprehensions on structure superiority of asymmetric carbon membrane and controlled construction of advanced hierarchical inner-structure for high performance supercapacitors

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ABSTRACT

In this study, both asymmetric and symmetric carbon membranes are designed and fabricated through liquid-liquid phase separation and solvent evaporation, respectively. In contrast, asymmetric carbon membrane exhibits asymmetric porous structure with 3 D nanoscaled architecture, which facilitates ion transportation by shortening diffusion pathways for charging and discharging process. Meanwhile, PEG is introduced into the casting solution to mediate the pore size to a rational range and enhance the surface area. When the ratio of PEG is 10 wt%, the carbon membrane shows the highest specific surface area and hierarchical porous size. A maximum specific capacitance of 247 F g^{-1} is achieved at the current density of 0.5 A g^{-1} with good rate capability in an aqueous electrolyte of 6 mol L^{-1} KOH within the potential range of -1 to 0 V . Moreover, symmetric supercapacitors device assembled with the prepared carbon membrane achieved high energy density (9 Wh kg^{-1}) and power density (400 W kg^{-1}) in $1 \text{ M Na}_2\text{SO}_4$ solution. The high electrochemical performance reveals the advantage of the rational micropore structure, and the asymmetric membrane architecture rose by fast solvents exchanging during phase-separation.

1. Introduction

Supercapacitors, also known as electrochemical capacitors or supercapacitors, have high power density and long service life. It has attracted much attention as a new energy storage device that can fill the chasm between traditional dielectric capacitors and battery [1–7]. Based on the energy storage mechanism, supercapacitors can be divided into two categories: electrochemical double-layer capacitors (EDLCs) and pseudocapacitors [8–12]. As is known to us, electrode material is one of the most important issues in determining the ability of energy storage for supercapacitors [13,14]. Typically, carbon-based materials are made for EDLCs, and conducting polymers and transition metal oxides are made for pseudocapacitors as electrode materials [6]. In the past few years, carbon electrode materials for supercapacitors have been widely investigated, because of its high conductivity, lower resistance, and good stability [15,16]. A great quantity of carbon materials, such as activated carbon [17], carbon black [18], carbon onions [18,19], carbon nanotubes [20,21], and graphene have been the most

commonly employed for electrode materials EDLCs to improve the capacity [22,23]. Liu et al. reported that using a crab shell as the template for mesoporous carbon and the specific capacitance is estimated to 152 F g^{-1} [24]. Huang et al. demonstrated a strategy that used the mesoporous carbon spheres to graft carbon nanofibers to prepare electrode materials, which showed a high specific capacitance of 190 F g^{-1} [25]. However, the real specific capacitance of activated carbon hardly achieved to 20% of its theoretical value. The reason for this is that the slow ion transportation in the pores limits the effective utilization of high specific area [26,27]. Hence, a good matching between the electrode material pore size and the dimensions of ionic species are necessary for an optimal performance of electrode materials [28].

The research results indicate that the carbon materials with a hierarchical pore structure really exhibit excellent performance in supercapacitors [29–32]. The contributions of the various pores with different pore size distribution to EDLCs can be summed up as follows [3,33–35]. i) A partial desolation of ions allowed access to matched

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pores (< 2 nm) to storage energy in the interface. ii) In the mesopores of 2–50 nm, the electrolyte ions are free to migrate via a short ions diffusion path, where a double layer can quickly formed. Also, a pore size distribution in the range of 2–5 nm, which is larger than the size of two solvated ions, was then identified as a way to improve the energy density and the power capability of supercapacitors. iii) Macropores (> 50 nm) are equivalent to an ion buffer library in the electrolyte, which has the function of storing electrolyte and facilitating ions transfer. At present, many studies have proven that a wide distribution from micropore to macropore in the material structure results in good electrochemical properties [23,36–44]. Nevertheless, there is no work focusing on preparation of asymmetric carbon membrane and study the effect of the specific pore size distribution in membrane on electrochemical storage performance in the absence of the other types of pores.

In this paper, we compared the structure and performance of symmetric and asymmetric carbon membranes, and found some new comprehensions on the effect of various pore distributions on the electrochemical process. We used symmetric and asymmetric carbon membranes as the research subjects, which had the same kind of small pores (< 10 nm). The difference of them was that the asymmetric carbon membrane contained large pores (> 10 nm) acquired by liquid-liquid phase separation technology while preparing the precursor. The effect of these large pores on the electrochemical performance was investigated. It is demonstrated that asymmetric carbon membrane possessed a pore structure more suitable for electrochemical reaction. Moreover, to further enrich the pore structure and improve the electrochemical performance of these carbon membranes, the additive of polymer like PEG was employed as pore-forming agent to seek the more rational pore size distribution of the “small pores”. The effects of the mass ratio of PEG in casting solution on the structure and electrochemical performance of the carbon membrane were also discussed in detail. In addition, it worth mentioning that the novel and facile synthetic method to prepare hierarchical pore structure materials exhibited great potential for the fabrication electrode materials for supercapacitors or other energy storage devices.

2. Experimental

2.1. Chemicals

Acrylonitrile (AN) was purchased from *Sinopharm Chemical Reagent Co. Ltd.*, and purified by distilled prior to use. Analytical grade 2, 2-Azobisisobutyronitrile (AIBN), *N, N*-dimethylformamide (DMF), and absolute alcohol were purchased from *Sinopharm Chemical Reagent Co. Ltd.*, and used as received without any further purification. Polyethylene glycol (PEG) with average molecular weight of 400 was commercially obtained from *Aladdin*.

2.2. Preparation of polyacrylonitrile (PAN) precursor

PAN was synthesized by solution polymerization according to the previous work [29,30]. Typically, AN (19.2 g), and AIBN (0.056 g) were dissolved in 60 mL of DMF with magnetic stirring at 70 °C for 6 h. 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 40 °C for 24 h.

2.3. Fabrication of PAN membranes

PAN membrane was prepared by traditional solvent evaporation (no phase-separation), and liquid-liquid phase-separation technique, respectively. i) Asymmetric polymer membrane (APM). In typical, PAN (10 wt%), and PEG (0–15 wt%) were added into DMF, which was heated at 120 °C to obtain a homogeneous solution. The casting solution was subsequently degassed for 10 min to remove any air bubbles

present, and prepared as membrane by spin coating coupled with a liquid-liquid phase separation technique at room temperature while being added into a coagulation bath of distilled water. After that, the resulting membrane was immersed in distilled water at 20 °C for another 24 h to remove solvent. Finally, the membranes were dried at 30 °C under vacuum for 24 h ii) Symmetric polymer membrane (SPM). The casting solution was prepared as membrane by spin coating as mentioned-above, which was heat-treated at 60 °C under vacuum for 48 h to remove the solvent.

2.4. Preparation porous carbon membrane

Porous carbon membrane was prepared through a simple carbonization method involving two steps. Firstly, the fabricated PAN membrane was pre-oxidized at 250 °C in air for 2 h. Then, it was subsequently pyrolyzed at 800 °C under a flowing nitrogen atmosphere for 2 h. The carbon membranes fabricated by APM and SPM were named ACM and SCM, respectively.

2.5. Structure characterization

The microstructure and morphology of the PAN membranes and carbon membranes were characterized by field emission scanning electron microscope (SEM, JSM-6701 F, JEOL, Japan) and transmission electron microscopy (TEM, JEOL, JEM-2010, Japan). The N₂ adsorption-desorption isotherms of samples were measured at 77 K using ASAP 2460 (Micromeritics, USA) to measure the specific surface area. The specific surface area was calculated by the Brunauer-Emmett Teller plot of the nitrogen adsorption isotherm. Non Local Density Functional Theory (NLDFT) model was adopted to analyze the pore size distribution of samples (calculation model: slit/cylindrical pore, NLDFT equilibrium model). The t-plot method was adopted to analyze the micropore surface areas. The total pore volume was calculated based on the N₂ adsorbed amount at a relative pressure around 0.995. The porosity and macropore size distribution of membranes were characterized using mercury porosimeter (AutoPore IV 9500, Micromeritics co., America). Before the test, the sample was fully dried and vacuumized. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Perkin-Elmer PHI ESCA System with Al Ka (1486.6 eV) as the X-ray source.

2.6. Electrochemical measurements

All the electrochemical measurements including cyclic voltammetry (CV), galvanostatic charging/discharging (GCD) and electrochemical impedance spectroscopy (EIS) were performed using an electrochemical working station (CHI660E, Shanghai, China) in the 6 M KOH aqueous electrolyte. Conventionally, three-electrode system including the as-prepared active material as work electrode, a platinum foil electrode as counter electrode, and a saturated calomel electrode (SCE) as reference electrode were employed to evaluate electrochemical performance. As a usual, the work electrode was prepared by mixing active material, conducting graphite, acetylene black, and poly (tetrafluoroethylene) emulsion at the weight ratio of 80: 7.5: 7.5: 5 to make a homogeneous black paste. The resulting slurry was spread onto a 1 cm² nickel foam current collector. After drying in a vacuum oven at 60 °C for 8 h, the nickel foam that has been coated with active materials was pressed under a pressure of 10 MPa with tablet machine for 30 s in order to enhance the adhesion between the active materials and the current collector. Mass loading of active material is 4 mg cm⁻². The specific mass capacitance of an electrode based on galvanostatic cycle test was calculated by

$$C = \frac{I \times \Delta t}{\Delta V \times m} \quad (1)$$

where I (A), Δt (s), ΔV (V), and m (mg) were the discharging current, the discharging time, the voltage range during the discharging process,

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