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Preparation and characterization of electrospun copoly (phthalazinone biphenyl ether ketone) superfine fibrous membrane served as plating template of Pd

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ABSTRACT

Novel copoly (phthalazinone biphenyl ether ketone) (PPBEK) superfine fibrous membrane was successfully fabricated through electrospinning, and characterized by SEM, DSC, TGA and tensile test. The solution concentration of PPBEK suited for electrospinning was 0.10–0.30 g mL^{-1}, and the average diameter of PPBEK fibers increased obviously with the increase of solution concentration. The electrospun PPBEK superfine fibrous membrane had very high glass transition temperature (> 242 °C), excellent tensile strength (4.94–18.66 MPa) and superior chemical resistance, which were critical advantages for the membrane as plating template applied in fuel cells. Pd was deposited on the PPBEK fibrous template by electroless plating with a layer thickness of ~250 nm. TEM shows that Pd nanoparticles dispersed well on PPBEK fibers and the diameter was about 4 nm. The as-prepared Pd/PPBEK superfine fibrous membrane had good conductivity and was successfully applied as free-standing electrocatalytic electrode for methanol oxidation without using any conductive support.

1. Introduction

Poly (phthalazinones) such as poly (phthalazinone ether ketone) (PPEK), poly (phthalazinone ether sulfone) (PPES) and the copolymer poly (phthalazinone ether sulfone ketone) (PPESK) have been proven to exhibit excellent thermal stability, mechanical strength, chemical resistance and membrane-forming ability [1–3]. Preferably, these high-performance polymers can be dissolved in common organic solvents [4] (N-methyl-2-pyrrolidone (NMP) and chloroform [5]) at ambient temperature, due to the aromatic heterocyclic twist non-coplanar structure in their main chain [6]. Therefore, these polymers are promising for fabricating various membranes applied in those requiring high temperature and pressure environments. It was reported that modified PPEK has been used to prepare anion exchange membrane [7] and ultrafiltration membrane [8], but few reports have been made on PPEK membrane prepared by electrospinning. Electrospinning is considered to be a simple and effective method for preparing nanofiber membranes [9], which have many remarkable characteristics such as fine diameters [10], large specific surface area, high porosity and high permeability [11]. Lei et al. [12] prepared Pd/polyamide 6 (PA6) composite membrane using electrospun PA6 nanofiber as template. The membrane was successfully applied as free-standing electrocatalytic electrode for alcohol oxidation. Han et al. [13] deposited gold particles on the electrospun polyacrylonitrile (PAN) fibrous mat, and the composite membrane with high conductivity and electrocatalytic activity can be directly used as electrode towards methanol oxidation. However, in terms of the free-standing support, common polymers may not be the best template in the application of fuel cell, because most of them have low glass transition temperatures and poor chemical resistance. In view of this, PPEK electrospun fibrous membrane is an attractive candidate as plating template due to its outstanding comprehensive properties.

Herein, we report, for the first time, the fabrication of electrospun copoly ((phthalazinone biphenyl ether ketone) (PPBEK) superfine fibrous membrane and its fundamental properties as the possible plating template in the field of fuel cell. PPBEK fibrous membrane was coated with Pd through electroless plating process.

2. Materials and methods

PPBEK was synthesized by the nucleophilic substitution polycondensation [14] of monomers: 1,2-Dihydro-4-(4-

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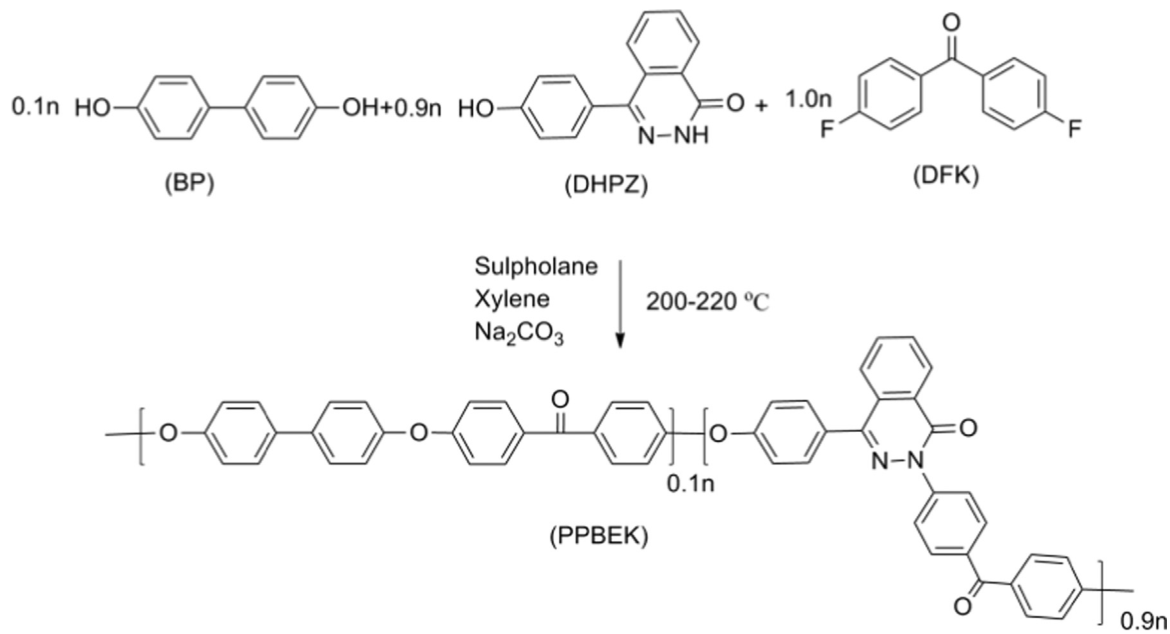

Scheme 1. Polymerization of PPBEK.

hydroxyphenyl)-1-(2H)-phthalazinone (DHPZ), 4,4′-Dihydroxybiphenyl (BP) and 4,4′-difluoro benzophenone (DFK), as shown in Scheme 1. The reaction was conducted under nitrogen. After isolated by precipitating in water, the synthesized PPBEK was purified by dissolving in NMP and precipitating in ethanol. The copolymer was characterized by FT-IR and ^{1}H NMR (Figs. S1 and S2).

Electrospinning solutions were prepared by dissolving PPBEK in NMP and THF (3:2, v/v) with different concentrations, ranging from 0.10 to 0.30 g mL^{-1}. Each solution was stirred until PPBEK completely dissolved at room temperature, and then added to a 5 mL glass syringe with a needle tip (0.5 mm diameter). The flow rate of the solution was 1.0 mL h^{-1}. An applied voltage was 12 kV and the collection distance between the needle tip to aluminum foil was 20 cm. All the samples were fabricated in the relative humidity range of 40–60% and the temperature range of 25–32 °C.

PPBEK fibrous membrane was sensitized by $SnCl_2$ (1 g/L) acidic solution and activated following in $PdCl_2$ (0.25 g/L) solution. After rinsed with deionized water, the activated membrane was immersed into electroless plating solution, which was made of $PdCl_2$ (15 mM), Na_2EDTA (0.11 M) and $NH_3 \cdot H_2O$ (0.79 M). With the addition of hydrazine (11 mM), the reduction of Pd^{2+} was triggered. After hours of electroless deposition, Pd-coated PPBEK fibrous membrane was provided, washed in deionized water, and dried at 40 °C.

$$2Pd(NH_3)_2{}^{+} + N_2H_4 + 4OH^{-} = 2Pd^{0} + 2NH_3 + N_2 + 4H_2O$$

The investigation of methanol oxidation was conducted using a CHI650E electrochemical workstation (Chenhua, Shanghai). The measurements were performed with a three-electrode cell containing free-standing Pd/PPBEK fibrous membrane (2.5 cm × 0.3 cm) as the working electrode, a platinum wire as the counter and a saturated calomel electrode as reference electrode, respectively. All of the electrochemical experiments were performed under nitrogen.

3. Results and discussion

The typical SEM image of electrospun PPBEK fibers obtained from the solution concentration of 0.20 g mL^{-1} (PPBEK-0.20) is presented in Fig. 1. The viscosity of the solution was unsuited to electrospinning when the solution concentration was lower than 0.10 g mL^{-1} or higher than 0.30 g mL^{-1}, which was either too low to form continuous fibers or too high to spray out from the syringe. Beads were deposited on the fibers obviously as the solution concentration was 0.10 g mL^{-1}, indicating that the concentration was still low. The fibers exhibited smooth and uniform surface as the solution concentration increased to 0.15 g mL^{-1}. The average diameters of these randomly oriented fibers were 0.32 ± 0.08, 0.64 ± 0.10, 1.04 ± 0.10, 1.98 ± 0.13 and 5.17 ± 0.54 µm for PPBEK-0.10, PPBEK-0.15, PPBEK-0.20, PPBEK-0.25 and PPBEK-0.30, respectively, which clearly showed that the fiber diameters increased obviously with the increase of solution concentration.

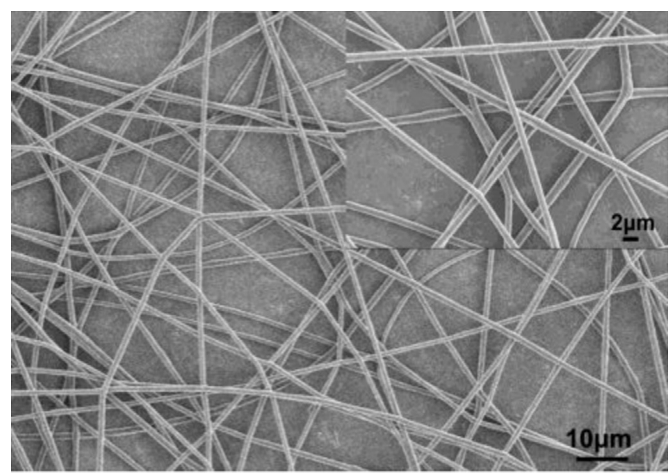

Fig. 1. SEM image of PPBEK-0.20 fibers at low and high magnification (inset).

PPBEK superfine fibrous membranes had very high glass transition temperature (> 242 °C, Fig. S3a), excellent thermal stability (Fig. S3b) and superior tensile strength (4.94–18.66 MPa, Fig. S4). Furthermore, the chemical resistance of PPBEK fibrous membrane was tested. Like PPEK [15], PPBEK can be only dissolved in chloroform, NMP and DMAc. The organic fuels and common electrolyte solutions can not dissolve or corrode PPBEK fibrous membrane. These outstanding properties are critical advantages for PPBEK fibrous membrane as plating template applied in fuel cells.