



Electrophoretic fabrication of proton exchange membranes in fuel cells

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ABSTRACT

For the first time, the fabrication of proton exchange membranes in fuel cells via an electrophoretic deposition (EPD) method is demonstrated, taking extensively researched sulfonated poly(ether ether ketone) (SPEEK) membranes as a paradigm. The membranes are obtained via depositing SPEEK ionomers, dispersed in a mixed solvent consisting dimethylsulfoxide (DMSO) and water, onto the anodic electrode under different applied voltages ranging from 15 to 25 V. The electrodeposited membranes show a number of differences from cast SPEEK membranes, e.g. smaller ionic clusters, higher surface roughness, higher water uptake and higher dry density. Particularly, the SPEEK membrane electrodeposited at 25 V reaches a proton conductivity of 0.11 S cm^{-1} at 70°C and 100% RH, remarkably surpassing its cast counterpart.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) are a very promising power source for a wide range of applications, from portable electronics, electric vehicles to distributed stationary power stations, because of their merits including high conversion efficiency, high power density, low/zero emission and rapid startup [1]. The proton exchange membrane (PEM), as an electrolyte for proton transport and a barrier to the mixing of fuel and oxidant, is a crucial component in PEMFC because of its sizable effects on the fuel cell's performance and cost. Therefore, many researchers have been exploring different materials and various fabrication methods to obtain PEMs that are more satisfactory technically and economically [2–10].

The method and condition of membrane preparation, as well as the membrane composition, can noticeably affect the microstructure and performance of PEMs. The earliest commercialized and extensively used PEMs in fuel cells, i.e. perfluorinated sulfonic acid membranes under the trademark Nafion, are manufactured via melt extrusion [7,11,12]. While most PEMs reported are prepared through solution/dispersion casting, though under a vast variety of conditions [13–15]. More recently, researchers twisted the solution casting method by adding surfactant [16], non-solvent [17] and using external electric field [18–20] to achieve better connected proton channels in PEMs, and noticeably improved proton conductivities of the membranes were attained.

Among various membrane forming techniques, electrophoretic

deposition (EPD) is ever increasingly used and researched in recent years. A number of advantages can be drawn from EPD, which include high speed and uniform coating, highly efficient utilization of coating materials, applicability to a wide range of materials, easy control of the coating composition and so on. EPD has been used to fabricate homogeneous [21,22], composite [23,24], laminated [25] and functionally graded [26–28] films and coatings that consist of polymers [29,30], ceramics [31,32] or metals [33,34]. In particular, the fabrication of solid oxide fuel cells also widely employs EPD techniques [35–39]. However, the fabrication of PEM by EPD has not been reported in previous literatures to the best of our knowledge.

In this paper, we report our primary trial on the preparation of sulfonated poly(ether ether ketone) (SPEEK) membranes via EPD. The negatively charged SPEEK polymers migrate through a mixed solvent of DMSO and water toward the anodic electrode and then deposit on it to form a membrane, which is then dried and peeled off from the electrode for later testing. The structure and performance of the electrodeposited membranes will be presented and compared with that of the solution cast membrane.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (PEEK) pellets (Vicatex, Grade 450 P, MW = 38,300) were obtained from Nanjing Yuanbang Engineering

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Plastics. Dimethylsulfoxide (DMSO) and concentrated sulfuric acid (95–98%) were purchased from Tianjin Kemiou Chemical Reagent Company and used as received. Pt-Ru/C (60 wt% Pt, 30 wt% Ru) and Pt/C (60 wt% Pt) catalysts were purchased from Johnson Matthey. Also, carbon paper (TGP-H-060) from Toray, carbon black (Vulcan XC 72 R) from Cabot, polytetrafluoroethylene (PTFE) emulsion (60 wt%) from Sigma Aldrich and Nafion solution (5 wt%) from DuPont were purchased. Double-distilled water ($\geq 1 \text{ M}\Omega \text{ cm}$) was supplied by Tianjin Yongqingyuan Environmental Science and Technology Company and was used throughout the experiment.

2.2. SPEEK membrane preparation

The sulfonation of PEEK was carried out following the method described in Ref. [4]. Briefly, 28.6 g dried PEEK was dissolved into 200 mL concentrated sulfuric acid at 35 °C via stirring for 5 h. Then the dissolved PEEK was allowed to react with sulfuric acid at 70 °C for 30 min under stirring to achieve a desired degree of sulfonation. Subsequently, the mixture was decanted into ice-cold water to terminate the reaction and collect precipitated SPEEK, which was then rinsed thoroughly with water and dried at 60 °C to constant weight. The SPEEK thus obtained showed a sulfonation degree of 59.5%, as determined by back titration [4].

The EPD cell accommodates a pair of 316L stainless steel parallel plate electrodes, which are immersed in a membrane solution comprising 2.5 wt% SPEEK, 5 wt% water and 92.5 wt% DMSO (see Fig. 1). The anode plate, 10 mm beneath the cathode plate, is slightly inclined so as to facilitate gas bubbles' sliding off and yet prevent the deposit from deforming under gravity. The anodic electrode has a working area of 50 mm \times 50 mm, while the cathodic electrode is 65 mm \times 65 mm in area to ensure even current profile across the anode surface. All anodic EPD operations were carried out at a constant temperature of 25 °C for a given period of time, but under different voltages, i.e. 15 V, 20 V and 25 V, respectively. The freshly deposited membrane, together with the anodic electrode, was removed from the EPD cell, dried at 100 °C overnight and peeled off from the electrode plate in water. Afterwards, the membranes thus obtained were immersed in 1 M H₂SO₄ at room temperature for 48 h, washed thoroughly and kept in water for later testing. For the purposes of comparison, the solution cast SPEEK membrane under identical conditions was also prepared on a glass plate. Care was taken to ensure that the thickness of cast membranes approaches to that of electrodeposited membranes as far as possible. Hereafter, the cast membrane will be denoted as C membrane. Electrodeposited membranes will be denoted as EX membrane, where X indicates the applied voltage.

2.3. Membrane characterization

The membrane morphology was imaged via field emission scanning

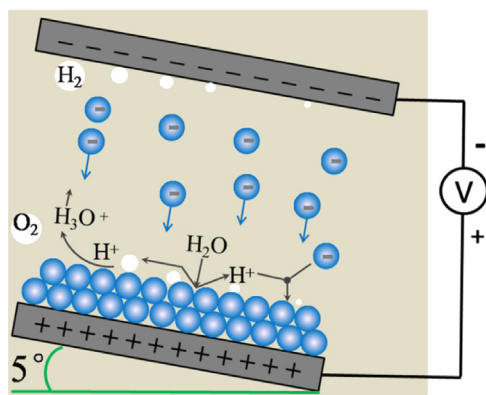


Fig. 1. A schematic of EPD cell for PEM preparation.

electron microscopy (FESEM, Hitachi S4800, Japan). The samples were cryo-fractured in liquid nitrogen to obtain fresh cross-sections, which were sputtered with gold prior to examination. The surface roughness of membrane was measured by tapping mode atomic force microscopy (AFM, Agilent 5500, USA) at room temperature in air. The AFM samples were allowed to equilibrate in air for 24 h before testing. Transmission electron microscopy (TEM, JEOL JEM 2100F, Japan) was carried out to detect the microstructure of membranes. The TEM samples were prepared by immersing in 1 M AgNO₃ solution for 24 h to stain the ionic domains, followed by drying, embedding in epoxy resin, and slicing into $\sim 60 \text{ nm}$ thickness via an ultramicrotome (Leica EM UC7) at room temperature. Small angle X-ray scattering (SAXS) measurements were also carried out using a D/max-2500 powder X-ray diffractometer with the Cu K α radiation ($\lambda = 0.15406 \text{ nm}$). SAXS samples were immersed in distilled water for 24 h at room temperature before testing. The scattering vector (q) was given by the following formula:

$$q = \frac{4\pi \sin \theta}{\lambda} \quad (1)$$

where 2θ is the scattering angle and λ is the wave length.

The density of SPEEK membranes at dry state was determined by hydrostatic weighing according to Archimedes' principle. The sample of dry membrane was weighed in air and water separately. The sample's weight in water was measured with the help of a density kit (Density Kit MS-DNY-54, Switzerland). The sample's density ρ was calculated via the equation:

$$\rho = \frac{m_a \rho_w - m_w \rho_a}{m_a - m_w} \quad (2)$$

where m_w and m_a are the sample's weight in water and air, respectively. ρ_w and ρ_a are the specific weight of water ($9.913 \times 10^{-1} \text{ g cm}^{-3}$) and air ($1.2253 \times 10^{-3} \text{ g cm}^{-3}$), respectively.

Water uptake of membrane was obtained by the calculation according to:

$$\text{Water Uptake} = \frac{w_{\text{wet}} - w_{\text{dry}}}{w_{\text{dry}}} \times 100 \quad (3)$$

where w_{wet} and w_{dry} are the weights of the membrane in wet and dry states, respectively. Dry samples of 2 cm \times 2 cm in size were soaked in water at a specified temperature for at least 24 h to reach swelling equilibrium.

The tensile strength of membranes at ambient temperature was measured via an electronic tensile machine (WDW-2, Zhongke Measuring Apparatus Co., China) with a stretching rate of 10 mm min⁻¹. Samples of both dry and wet membranes were cut into rectangles of 10 mm \times 35 mm for measurement.

The methanol permeability was measured using a diaphragm diffusion cell, as described in Ref. [4,40]. Two chambers of the glass cell were filled with 1 M methanol and pure water, respectively, and separated by the membrane to be tested. As methanol permeated across the membrane and entered into the chamber initially filled with pure water, its concentration in the chamber increased linearly with the permeation time, which was monitored using a differential refractometer (LCD201, WINOPAL). The methanol permeability was then calculated from the slope of the concentration-time linear curve.

The trans-plane proton conductivity of membrane at 100% relative humidity (RH) was measured using a membrane test system (MTS-740, Scribner, USA) [41] connected to an electrochemical workstation (Parstat2273, Princeton Applied Research, USA). The impedance spectrum of membrane was obtained under an oscillating voltage of 10 mV with frequency sweeping from 2 MHz to 1 Hz. The proton conductivity σ was calculated using the equation:

$$\sigma = \frac{L}{RS} \quad (4)$$

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