

Supporting Information

Imidazole Grafted Dipyridyl Polybenzimidazole for High Temperature Proton Exchange Membrane

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1. Materials and reagents

Poly(2,2' -[p-oxydiphenylene]-5,5' -benzimidazole) (OPBI) powder was purchased from Shanghai Shengjun Polymer Technologies Co., Ltd. 4,4'-Oxybisbenzoic acid, 3,3'-Diaminobenzidine were purchased from TCI (Shanghai) Chemical Industry Development Co., Ltd. [2,2'-Bipyridine]-4,4'-dicarboxylic acid, polyphosphoric acid, NaHCO₃, absolute ethyl alcohol (EtOH) and N,N-Dimethylacetamide were purchased from Energy Chemical Co, Ltd. (China). 85 wt.% phosphoric acids were purchased from Shanghai Macklin Biochemical Co., Ltd. 1-(2-chloroethyl) imidazole were purchased from Ark Pharma Scientific Limited (China).

2. Characterization methods

The chemical structures of the DPPBI and grafted ImDPPBI were analyzed using ¹H NMR spectroscopy, which was conducted on a Bruker Avance-500 (500MHz) using dimethyl sulfoxide-D₆ (DMSO-d₆) as the solvent. Fourier transform infrared (FT-IR) absorption spectra of COPBI-s were measured at 400 to 4000 cm⁻¹ using a Nicolet 6700 spectrometer. A SU-70 SEM was used to examine the surface and cross-section morphologies of the membranes. A TA Q50 thermal gravimetric analyzer was used to determine the weight loss in a dry nitrogen atmosphere with a flow rate of 40 mL min⁻¹ and a heating rate of 10 °C min⁻¹ from 100 °C to 800 °C.

All membranes were immersed in an 85% phosphoric acid (PA) solution at

160 °C for 24 h. Following that, PA-doped membranes were dried overnight in a vacuum oven to a constant weight. The gross PA uptake was calculated using the following formula:

$$\text{Gross PA Uptake} = (W_d - W_0)/W_d \quad (1)$$

where W_0 (g) is the weight of the pristine membrane and W_d (g) is the weight of the membrane after saturated PA doping at 160 °C.

Furthermore, phosphoric acid doped content (ADC) is positively correlated with the proton conductivity to some extent. ADC is determined according to the following formula.

$$\text{ADC} = [W_2 - W_1]/W_1 \quad (2)$$

In this equation, W_1 (g) and W_2 (g) represent the weight of the membrane before and after doping, respectively.

The deformation ratio after doping can be calculated from the following equation:

$$\text{Deformation ratio (\%)} = ([L_2 \times B_2 \times D_2]/[L_1 \times B_1 \times D_1]) \times 100\% \quad (3)$$

where L_1 (cm), B_1 (cm), and D_1 (mm) represent the length, width, and thickness of the pristine membrane, respectively, whereas L_2 (cm), B_2 (cm), and D_2 (mm) represent the length, width, and thickness of the PA-doped membrane, respectively.

Tensile strength and elongation at break of PA-undoped and -doped membranes (dried overnight in a vacuum oven) were cut into dumbbell-shaped samples and measured using a SANS-CMT4204 system with a 5-mm min⁻¹

extension rate.

The resistance of the PA-doped membranes was tested by an electrochemical workstation (Zahner IM6ex, Germany) using the alternating current impedance method. The parameters are as follows: 1–10⁵ Hz frequency, 10 s quiet time, and 0.01 V amplitude. The PA-doped membranes were cut into rectangular samples (1 × 4 cm) and placed on an electrode covered with an airtight mold. The temperature was raised to 120 °C and maintained for 2 h to obtain anhydrous conditions. Then, the mold temperature was raised to 180°C and equilibrated for 15 min. The measurements were taken while the mold was cooled to 120 °C in 10 °C increments, with a 15-min equilibration time for each temperature set point. The proton conductivity was then calculated using the following equation:

$$\sigma = L/RD \quad (4)$$

where σ (S cm⁻¹), L (cm), R (Ω), and D (cm) are the proton conductivity, distance between the two electrodes, resistance of the PA-doped membrane, and thickness of the PA-doped membrane, respectively.

The fuel cell performance was measured using single-cell stacks. The pristine membranes were immersed in 85% PA at 160 °C for 24 h, and their ADL was consistent with the above test. The PA-doped membranes and electrode were cut into square samples (membrane: 3.5 × 3.5 cm; electrode: 2.25 × 2.25 cm). The active area of the membrane-electrode assembly was 5 cm². The loading of Pt in the catalyst layer was ~1 mg/cm². The polarization

curves were obtained without gas humidification at 160 °C using hydrogen (80 mL min⁻¹) and oxygen (160 mL min⁻¹).