Electronic Supplementary Information for

Hydrocarbon blend membranes with suppressed chemical crossover for redox flow batteries

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Experimental details

Materials synthesis and membrane preparation

The details of preparation of SPEEK and PSf-ABIm are available elsewhere.[1] 15 g of PEEK (Victrex) were dissolved in 750 mL of concentrated sulfuric acid (Fisher Scientific), vigorously stirred at room temperature for 55 h, and gradually transferred into a large volume of ice-cold water under mechanical agitation. The polymer precipitate was filtered, washed thoroughly with large amount of deionized water until the pH was neutral, and dried at 100 °C overnight.

The synthesis of PSf-ABIm was carried out by a condensation reaction between carboxylated polysulfone and 2-amino-benzimidazole (ABIm) using triphenylphosphite as a dehydration agent at 100 ºC for 3 h to form the amide unit. Lithium chloride was used to enhance the dissolution of the reactants and product in dimethylformamide. The formation of PSf-ABIm was confirmed by the absorption bands in the FT-IR spectra at 3400 and 1630 cm^{-1}, corresponding, respectively, to isolated N–H stretching and C=N stretching.

The plain SPEEK and SPEEK/PSf-ABIm blend membranes were prepared by casting the N,N-dimethylacetamide solution of SPEEK or SPEEK+PSf-ABIm (5 wt. % PSf-ABIm) polymers on a glass plate and drying at 65 ºC overnight then at 100 °C in a vacuum oven for 24 h.

Ion exchange capacity and water uptake

The ion exchange capacities (IECs) and water uptake of the plain SPEEK and SPEEK/PSf-ABIm blend membranes were determined as below.[2] The ion exchange capacities (IECs) of the plain SPEEK and SPEEK/PSf-ABIm blend membranes were determined by suspending the vacuum-dried membranes (~ 0.2 g) in 1.0 M NaCl solution (50 ml) for 24 h to liberate the H$^+$ ions and then titrating with standardized 0.05 M NaOH solution (Fisher Scientific) using phenolphthalein as an indicator. Finally, the IEC was calculated as

$$IEC = \frac{\Delta V_{NaOH} \cdot C_{NaOH}}{W_{dry}} \qquad (1)$$

where ΔV_{NaOH} is the consumed volume of NaOH solution, C_{NaOH} is the concentration of NaOH solution, and W_{dry} is the dried weight of the membrane.

Equilibrium water uptake of the membranes was determined at room temperature by measuring the weights of the dry membrane (W_{dry}) and the wet membrane (W_{wet}) as

$$W_{uptake} = \frac{(W_{wet} - W_{dry})}{W_{dry}} \times 100\% \qquad (2)$$

Membrane area resistance

The area resistance measurements were conducted on an impedance analyzer (1260 FRA, Solartron Analytical) combined with a potentiostat (1287, Solartron Analytical). The amplitude of the sinusoidal signal for AC impedance was set as 10 mV rms over a frequency range of 7 kHz to 1 Hz. A solution of 1.0 M $VOSO_4$ in 2.0 M H_2SO_4 was fed to both sides of the membrane. The effective membrane area was 5 cm^2.

Mechanical strength

The stress–strain behavior of the membrane was measured with an Instron 5966 tension tester at room temperature. All samples were kept in de-ionized water for 24 h before the test to ensure they were saturated with water.

Chemical stability

The chemical stability of plain SPEEK and SPEEK/PSf-ABIm blend membranes were evaluated by scanning electron microscopy (SEM) after immersing the membranes in a solution of 1.0 M charged vanadium $(VO_2)^+$ electrolyte in 2.0 M H_2SO_4 at room temperature for 2 and 100 days.

Vanadium permeability

The concentration of $(VO)^{2+}$ ions permeated through the membrane was determined according to the literature procedure.[3] The left cell was filled with 1.0 M $VOSO_4$ in 2.0 M H_2SO_4 solution, while the right cell was filled with 1.0 M $MgSO_4$ in 2.0 M H_2SO_4 solution to equalize the ionic strengths and to minimize the osmotic pressure effect. The concentration of $(VO)^{2+}$ in a sample solution collected from the right cell was measured with an UV–vis spectrometer (Cary 5000).

VRB single cell performance

A membrane was sandwiched with two graphitic carbon felt electrodes and was clamped by two graphite polar plates with straight flow channels. 1.0 M V^{2+}/V^{3+} in 2.0 M H_2SO_4 solution and 1.0 M $(VO)^{2+}/(VO_2)^+$ in 2.0 M H_2SO_4 solution, serving as negative and positive electrolytes, respectively, were circulated through the corresponding half-cell. The active area of the single cell was 5 cm^2 and the volume of the electrolyte solution was 20 mL for each half-cell. Charge–discharge cycling tests were conducted with an Arbin BT 2000 battery cycler (Arbin instruments). A maximum voltage of 1.7 V and a minimum voltage of 0.8 V for charge and discharge were employed to avoid the corrosion of carbon felts and graphite plates.

References:
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3. Q. T. Luo, H. M. Zhang, J. Chen, P. Qian, Y. F. Zhai, J. Membr. Sci., 2008, **311**, 98–103.