Supplementary Information

Reducing oxygen transport resistance within catalyst layer for fuel cells by adopting intrinsically microporous ionomer

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1. Material and methods

1.1 Materials

4,4-dihydroxybiphenyl, 2,2,2-trifluoroacetophenone, trifluoromethanesulfonic acid (TFSA) and chlorosulfonic acid were purchased from Shanghai Meryer. Chloroform, dimethyl sulfoxide (DMSO), isopropanol, dichloromethane (DCM) and methyl alcohol were purchased from Kelong Reagent. 60 wt% Pt/C (Johnson Matthey), 75 wt% PtRu/C (Tanaka Kikdfinzoku Kogyo-TKK), Nafion HP and Nafion 212 membrane, and carbon paper (SGL 28BC) were purchased from Suzhou Sinero Technology Co.Ltd.

1.2 Synthesis of poly(xanthene) of intrinsic microporosity (PIM)

4,4-dihydroxybiphenyl (1.79 g, 9.60 mmol), 2,2,2-trifluoroacetophenone (1.674 g, 9.60 mmol) and 14 mL DCM were added into a 50 mL flask and stirred at room temperature for 1 h. 2 mL TFSA was slowly added, and reacted at 0 °C for 2 h to obtain a high-viscosity polymer solution. The polymer solution was poured into methanol/water (1/1), filtered to obtain polymer solid, washed with hot methanol and deionized water three times in turn, and dried to obtain white fibrous polymer.

1.3 Synthesis of sulfonated PIM (SPIM)

PIM (1g) and DCM (20 mL) were added into a 50 mL flask, and stirred at room temperature until dissolved. 0.2 mL chlorosulfonic acid was added to the solution drop by drop at 0 °C and reacted for 0.5 h. The dark brown solid was precipitated, the solid was filtered, and the polymer (SPIM) was obtained by washing with deionized water to neutral. SPIM was dissolved in DMSO/isopropyl alcohol (4/1) to prepared the 5 wt% ionomer solutions.

1.4 Proton nuclear magnetic resonance (¹H NMR) test

The chemical structures of PIM and SPIM were studied by ^1H NMR (Agilent 400MR DD2). $CDCl_3$ and DMSO-d6 was used as solvent. The IEC of SPIM was determined by calculating the integral area ratio of g-H peak to the total aromatic H-peak.

1.5 Morphology test

The catalyst layer was observed by the Scanning Electron Microscopy (SEM, JEOL JSM-5900LV) and Transmission electron microscopy (TEM, Thermo Fisher scientific-Talos F200s).

1.6 BET test

Specific surface and pore structure of PIM, SPIM and catalyst layer was measured

by BET testing device (Kubo-X1000). Before the test, the sample was ground into powder, and the sample with a weight greater than 0.1 g was taken for 12 h degassing treatment at 120 °C

1.7 Conductivity test of SPIM

Conductivity of SPIM and Nafion 212 membrane were tested by alternating current impedance (Solartron 1287&Solatron 1260, 1 to 10^7 Hz). SPIM membrane was quickly tested in ultra-pure water to obtain the impedances (R) at different temperatures. The H$^+$ conductivity (σ) could be calculated from the following equation:

$$\sigma = \frac{L}{R \times A}$$

(2.1)

Where L was the distance between the two electrodes, and A was the cross-sectional area of dry membrane.

1.8 Thermal stability

The thermal stability of PIM and SPIM were measured by the thermogravimetric analyzer (TGA-Q500, TA Instruments) with temperature range from room temperature to 1000 °C, 10 °C min^{-1} heating rate and N$_2$ atmosphere.

1.9 Electrochemical performance test

Oxygen reduction reaction (ORR) activity and electrochemical active surface area (ECSA) were performed by a standard three-electrode system in electrochemical workstation (VersaSTAT 3F) at room temperature (298 K). The system consisted of a glassy carbon working electrode, an Ag/AgCl reference electrode, and a graphite rod counter electrode. All potentials in this study were given relative to a reversible hydrogen electrode (RHE). The working electrodes were prepared by applying catalyst ink onto glassy carbon (GC) disk electrodes. In order to obtain a catalyst ink, 2 mg of 60 wt% Pt/C catalysts and 5 μL of 5 wt% Nafion or SPIM ionomer solution were

dispersed in 400 μL of isopropyl alcohol by sonication of 30 min to form a homogeneous ink. For the preparation of the working electrode, the glassy carbon (GC) electrode was pre-polished with 300 and 50 nm alumina slurries for several minutes, then 10 μL of the catalyst ink was drop-coated on the rotation disk electrode (RDE), giving a mass loading of 0.153 mg cm^{-2}. All the electrodes were pre-treated by cycling the potential between 0 and 1.2 V at a sweep rate of 50 mV s^{-1} for 30 cycles in order to remove any surface contamination prior to ORR activity test. The activity of catalysts was performed by recording linear sweep voltammetry (LSV) curves in the oxygen-saturated 0.1 M $HClO_4$ solution. The LSV curves for ORR were recorded at potential scan rate of 10 mV s^{-1}. The rotation speed was controlled at 500, 1000, 1600rpm. ECSA was measured by the CO-stripping test that was conducted in N_2-saturated 0.1 M $HClO_4$ electrolyte at a sweep speed of 10 mV s^{-1} between 0.0 and 1.2 V after potential holding for 10 min at 0.1 V in CO-saturated 0.1 M $HClO_4$ electrolyte.

1.10 Fuel cell test

Nafion HP membrane, and SPIM and Nafion ionomer solution were selected to conduct fuel cells test. 75 wt% PtRu/C and 60 wt% Pt/C were used as anode and cathode catalysts with 0.06 mg cm^{-2} Pt loading. After catalyst and ionomer with different ratio were dispersed in mixture of isopropanol via sonicated for 1 h at room temperature, the catalyst ink was prepared successfully. Gas diffusion electrode (GDE) technology was applied to prepare the membrane electrode assembly (MEA) with 5 cm^2 effective area, and was equipped on fuel cells test system (850e Multi Range, Scribner Associates Co.) to test single-cells performance after hot pressed at 135 °C for 2.5 minutes.

1.11 Oxygen transmission resistance test

Oxygen transmission resistance of MEA was measured by limiting current density (i_{lim}) on Fuel cells test system (850e Multi Range, Scribner Associates Co.). The

specific principle was as follows. The process of gas from the inlet to the Pt catalyst

site in the fuel cells was controlled by gas diffusion, which was called steady state

diffusion, and its diffusion flux (J) can be determined by Fick law:

$$J = - D\frac{\partial C}{\partial X}$$

(2.2)

Where J represented the amount of gas passing through the unit area in unit time,

D was the diffusion coefficient, C was the concentration of gas diffusion, and X was

the distance of gas diffusion.

In the actual process, assuming that the diffusion coefficient D was independent of

concentration, equation (2.2) can be expressed as:

$$J = D\frac{\Delta C}{X}$$

(2.3)

Where ΔC represented concentration difference of diffused gas. In addition, D/X

was related to the diffusion coefficient k, so equation (2.3) also can be expressed as:

$$J = k\Delta C = \frac{\Delta C}{R_{total}}$$

(2.4)

Where R_{total} represented the total transmission resistance of oxygen during the fuel

cells test ($k = 1/R_{total}$). Faraday's law showed that the molar flux (J) of oxygen molecules

was related to the current density (i).

$$R_{total} = \frac{\Delta C_{O_2}}{J_{O_2}} = \frac{4F}{i}\Delta C_{O_2}$$

(2.5)

Where the concentration difference (ΔC_{O_2}) was the difference between the oxygen

concentration (C_{inlet}) of cells inlet and the oxygen concentration ($C_{Pt\ surf}$) of the

catalyst surface.

$$\Delta C_{O_2} = C_{inlet} - C_{Pt\ surf}$$

(2.6)

When the cell reached the limit current density (i_{lim}), $C_{Pt\,surf}$ can be regarded as zero, and $\Delta C_{O_2} = C_{inlet}$. C_{inlet} was related to the mole fraction ($X^{inlet}_{O_2}$) of oxygen during testing. For ideal gas, equation (2.5) can be expressed as:

$$\Delta C_{O_2} = C_{inlet} = \frac{P}{RT}X^{inlet}_{O_2}$$

(2.7)

Where T was kelvin temperature of cells, P was total gas pressure, and R was gas constant. R_{total} was obtained by combing equations (2.5) and (2.7):

$$R_{total} = \frac{4F}{i_{lim}} \frac{P}{RT} X^{inlet}_{O_2}$$

(2.8)

After i_{lim} under different pressures were measured by changing the test pressure, R_{total} was calculated from equation (2.8). It was reported that R_{total} was composed of bulk phase transport resistance (R_{bulk}) and local oxygen transport resistance (R_{local}).

$$R_{total} = R_{bulk} + R_{local}$$

(2.9)

Combining equation (2.5) and (2.9):

$$R_{total} = \frac{4F}{i_{lim}}\Delta C_{O_2} = R_{bulk}\frac{P}{P_0} + R_{local}$$

(2.10)

Where P_0 was standard atmosphere.

The prepared MEA was assembled and the fuel cell was activated at a voltage of 0.6 V for 2-3 h before the i_{lim} test. The test conditions were as followed, the cell temperature of 80 °C, the anode and cathode gas humidity of 100% RH, and the test voltage of 0.5 V. Low concentration oxygen (1% O_2) was selected to reduce the i_{lim} and ensure that no excess product water was produced. Three different back pressure conditions of >100 KPa were selected and the corresponding i_{lim} was obtained by testing under different back pressures. The corresponding total transmission resistance (R_{total}) was calculated by substituting i_{lim} into the equation (2.8). According to the equation

(2.10), the slope and intercept were obtained by fitting different R_{total} and oxygen pressure P_{O_2}, which were R_{bulk} and R_{local} respectively. When the catalyst Pt load was low, R_{local} was approximated equivalent to the transmission resistance of oxygen through the ionomer layer.

2. Results and Discussion

a   b

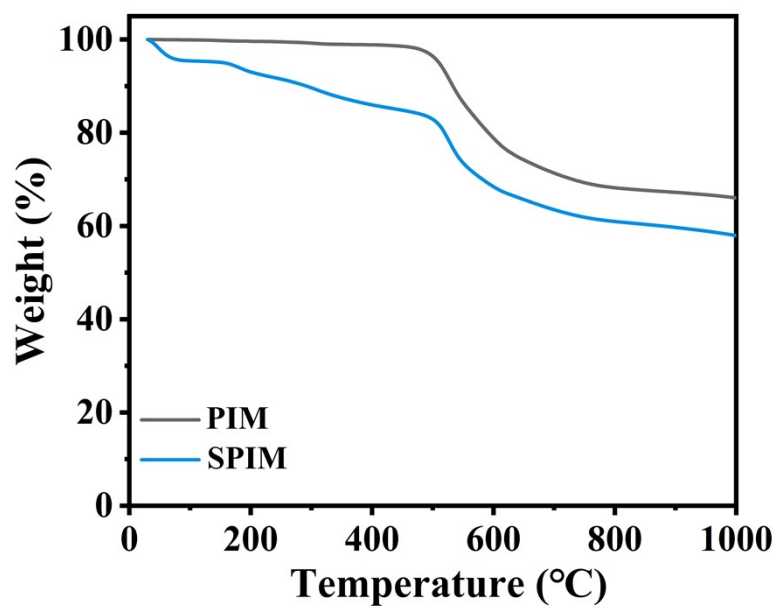**Fig. S1.** The picture of (a) SPIM solid and (b) ionomer solution with 5 wt%. SPIM dissolved in DMSO/isopropanol (4/1).

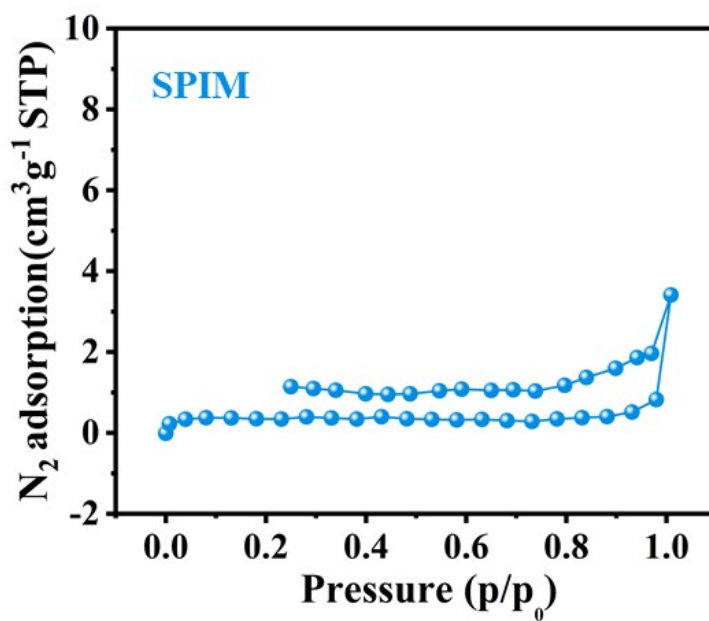**Fig. S2.** TG curves of PIM and SPIM. The mass loss before 100 °C was belong to water.

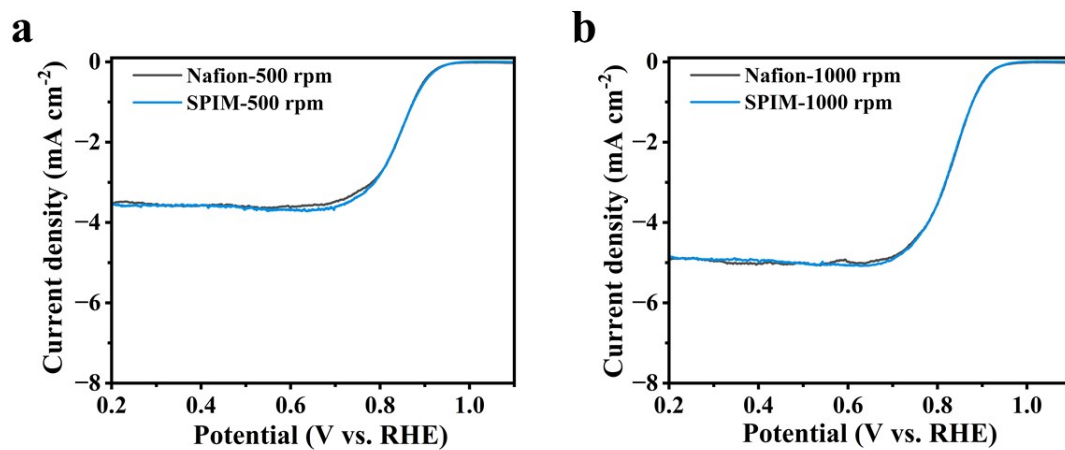**Fig. S3.** BET of SPIM polymer after enlarging for Fig. 1(g).

Fig. S4. LSV curves of catalyst layer with Nafion and SPIM ionomers and 60 wt% Pt/C catalyst in (a) 500 rpm and (b) 1000 rpm.