Supporting Information

One-step synthesized HPW/silica Inorganic Electrolyte Membrane for PEM Fuel Cell

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1. Synthesis of HPW/meso-silica electrolyte and fabrication of HOW/meso-silica electrolyte membranes

The ordered HPW/silica mesoporous nanocomposites were prepared as follows. First, 12-phosphotungstic acid, $H_3PW_{12}O_{40} \cdot nH_2O$ (HPW, Sigma-Aldrich), Tetraethoxysilane (TEOS, Sigma-Aldrich), ethanol and water with molar ratio of 0.007:1:11:2.5 were thoroughly mixed and vigorously stirred for 30 min to form a silica gel solution. P123 surfactant solution was separately prepared by dissolving P123 in ethanol and water with weight ratio of 0.012:9:2.5. After stirred for 30 min, the surfactant solution was slowly added to the previously prepared silica gel solution and then stirred for another 1h. P123 surfactant added to the silica gel solution was controlled as 1.2 mol% of TEOS. The resulted gel was poured into indium tin oxide (ITO) glass sheet and slowly dried at 40 °C for 7 days. The dried solids were grinded and heat treated at 400°C with a temperature rate of 1 °C/min for 1 h in nitrogen and then in air at the same temperature for another 24 hrs. The final content of HPW in the self-assembled HPW/meso-silica was kept as 25 wt%. Pure mesoporous silica powders were also prepared according the procedure above without the addition of HPW. Mixed HPW/meso-silica was prepared by throughout mixed 25 *wt.*% HPW power with 75 *wt.*% pure meso-silica powder in a solution of 50 *wt.*% ethanol and 50 *wt.*% water, then dried in 80°C with stirring for 30min and in 100 °C for another 30 min.

The HPW/meso-silica electrolyte membranes were prepared from the HPW/meso-silica powder using polyimide (PI) as binder. The electrolyte powders are self-assembled 25wt% HPW/meso-silica, pure mesoporous silica and mixed 25wt% HPW/meso-silica. Polyimide powder (~5 *wt.*%) mixed with n-methyl pyrrolidone was mixed thoroughly with the electrolyte powder in an agate pestle mortar for 1 h. The mixture was dried at 180 °C for 2 h. And the dried powder was then hot-pressed in a single-ended compaction stainless-steel die (5 cm diameter) under conditions of 380 °C and 30 MPa for 30 min. The thickness of the HPW/meso-silica electrolyte disc was 600 μm.

The Pt/c catalyst slurry (60 *wt.*% Pt/C, Johnson Matthey, 5 *wt.*% Nafion DE 520 and water) was sprayed to both sides of the self-assembled or mixed 25wt% HPW/meso-silica electrolyte membrane to form the catalyst layer. Pt catalyst loading of the anode and the cathode was 0.4 mg Pt/cm^2 and the dry loading of Nafion was 0.4 mg/cm^2. Coated Toray TGPH-060 carbon paper was used as the gas diffusion layer to form the membrane-electrode-assembly (MEA) for the electrochemical tests. The effective surface area of the MEA was 4 cm^2.

2 Characterization

Transmission electron microscopy (TEM) images were taken using JEM-2010FEF at 200kV. Small-angle X-ray diffraction (XRD) patterns of HPW/meso-silica composite were recorded on a Rigaku D/MAX-RB diffractometer with a CuKα radiation operating at 40 kV, 50mA. Nitrogen adsorption-desorption isotherms were measured with a Quantachrome Autosorb-1 analyzer at 77K. Prior to the measure, the samples were degassed at 200°C for at least 3h. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The pore-size distribution was derived from the adsorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method.

Single fuel cell test was set-up by mounting the MEA in a fuel cell clamp. The gas permeability or crossover of the PEM was assessed by measuring the limiting oxidation currents of the crossovered H$_2$ at 80°C, using the Autolab PG30/FRA. H$_2$ gas (300 normal cm^3/min) was fed to the anode side of the cell while N$_2$ was fed to the cathode. By applying a dynamic potential from 0 to 0.6 V vs. the anode (i.e., DHE) at 0.5 mV/s, the limiting H$_2$ oxidation current was measured. The anode side, where hydrogen evolution took place, served as the counter electrode as well as the DHE reference electrode.

The performance of the cell was measured using H$_2$ as fuel gas and oxygen as oxidant without back pressure. H$_2$ and oxygen flow rates were both 200 mL/min. The gas was humidified at 80°C and 100%RH. Eelectrochemical impedance spectroscopy (EIS) of the single cells was investigated by an Autolab with amplitude of 5mV over a frequency range from 10mHz to 10 KHz under a dc bias of 100 and 600 mA/cm^2. Due to the much faster reaction kinetics of the H$_2$ oxidation reaction on the Pt/C electrocatalysts as compared to that of the O$_2$ reduction reaction, the cell impedance would be mainly dominated by the electrode reaction at the cathode.

3. Stability and durability of the self-assembled HPW/meso-silica

The stability of the self-assembled HPW/meso-silica was investigated by the ionic exchange capacity (IEC) tested in water. **Figure S1** is the ionic exchange capacity (IEC) loss of self-assembled 25 *wt.*% HPW/meso-SiO_2 inorganic membranes, measured in water. As a comparison, a mixed 25wt% HPW/meso-SiO_2 membrane was also tested. The decrease in IEC value indicates the bleeding or leaching of HPW in the composite. The result shows a rapid HPW loss of the mixed HPW/meso-SiO_2 membrane, indicating the existence of individual HPW clusters outside the mesopores of mesoporous silica in the mixed HPW/meso-SiO_2 composite. However, the self-assembled HPW/silica mesoporous inorganic electrolyte membrane is relatively stable and the loss in IEC is much slower during the test in water. This shows that the HPW molecule in the self-assembled HPW/meso-silica composite is very stable, indicating that the majority of the HPW molecules are trapped or anchored inside the mesopores of the silica mesostructure.
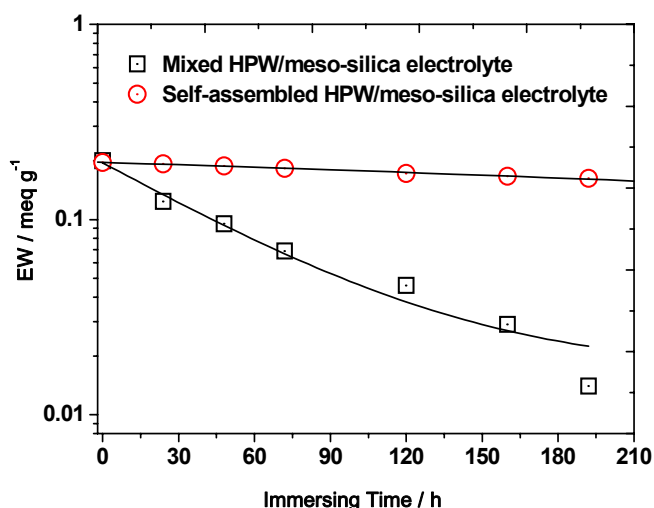

Figure S1. Ionic exchange capacity (IEC) degradation of the self-assembled HPW/meso-silica inorganic electrolyte membrane and the conventional mixed HPW/meso-SiO_2 composite electrolyte.

Figure S2 is the plots of H_2 crossover through the self-assembled HPW/meso-silica inorganic electrolyte membrane and a Nafion 112 polymer membrane in an acceleration chemical test. The tests were performed by immersing the samples in the H_2O_2-metallic impurities solution for various periods, and then the H_2 crossover through the membrane was measured. The composition of the H_2O_2-metallic impurities solution was 30 wt% H_2O_2, 12.3ppm Fe, 6.1ppm Cr, and 5.4ppm Ni. The metal ions solution was obtained by treating

SS316L stainless steel (commonly used as the bipolar plates in PEM fuel cells) in 0.5 mol/L nitric acid. The results show that the hydrogen crossover through the perfluocarbon Nafion 112 polymer membrane increased dramatically during the long-term reaction with H_2O_2-metallic impurities solution. The H_2 crossover reached to 36 mA/cm^2 after 72 h, implying the decomposition of the polymer and much of pinholes emerged in the polymer membrane. In contrast, the self-assembled 25wt% HPW/meso-silica inorganic electrolyte membrane is very stable in the H_2O_2-metallic impurities solution because the silica and HPW are inert to the chemical oxidation reaction of the solution.
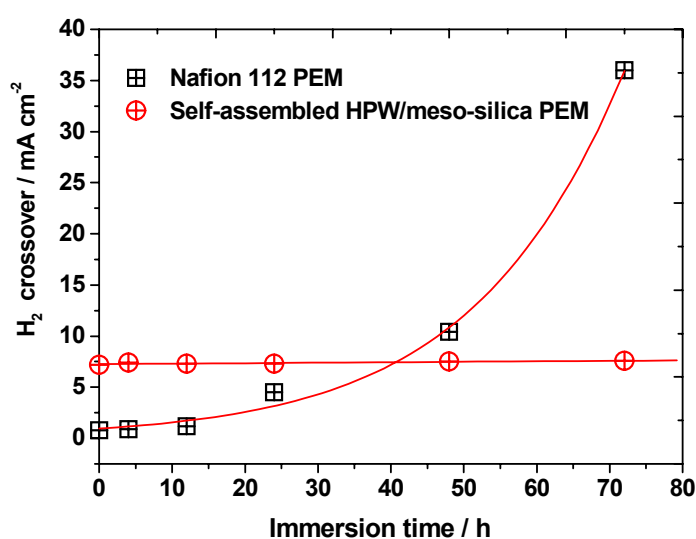

Figure S2. H_2 crossover through the self-assembled 25wt% HPW/meso-silica inorganic electrolyte membrane and the Nafion 112 polymer membrane as a function of immersing time in H_2O_2-metallic impurities solution.