

## Support Information:

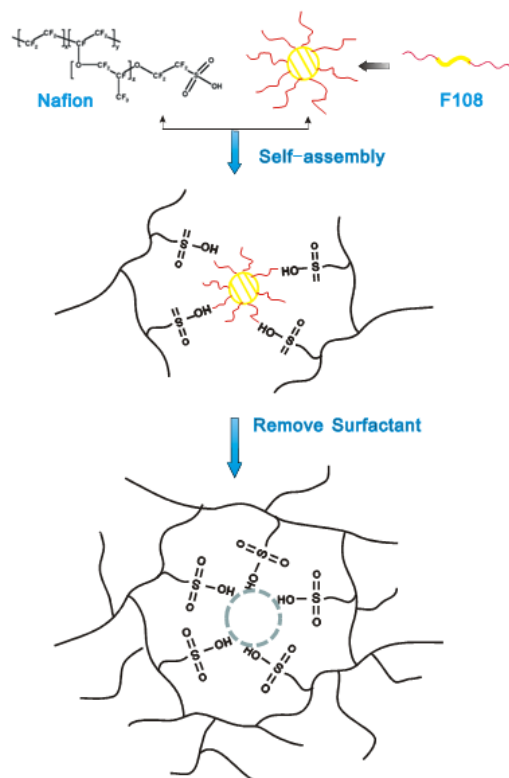
### Highly Ordered Mesoporous Nafion Membranes for Fuel Cells

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#### 1. Synthesis of mesoporous Nafion and cell preparation

The mesoporous Nafion membranes were synthesized as follows. Firstly, 20 wt% non-ionic block copolymer, Pluronic<sup>TM</sup> F108 (PEO<sub>127</sub>-PPO<sub>48</sub>-PEO<sub>127</sub>,  $M_w = 14600$ , BASF Corp.) surfactant solution was mixed with 2-propanol (99.9%, Sigma-Aldrich) and deionized water (2-propanol : H<sub>2</sub>O = 90 wt.% : 10 wt.%) at room temperature under stirring. Then as prepared F108 solution was put into a beaker and the pH of the solution was adjusted to pH=1 by addition of 2 M H<sub>2</sub>SO<sub>4</sub>, stirring for 2 h. Nafion 520 ionomers (EW =1000, 5 wt.% Nafion, DuPont, USA) were dropwise added into the beaker containing F108 solution and stirred for another 2 h. In the present study, 40 g of Nafion 520 and 4 g of F108 surfactant were used. Then, the mixtures were poured into Petri dishes and were placed into a vacuum oven for heat treatment at 50°C for 5 h, 90°C for 2 h and finally at 120°C for 1 h. The microscopic phase separation on a nanometer scale was developed through self-assembly due to the interaction between hydrophilic parts of Nafion ionomer and the hydrophilic PEO groups of Pluronic F108 surfactant, which lead to the ordered arrangement of the micelle templatings with self-assembled surfactant. After the heating treatment, the membranes were immersed in de-ionized water, boiled and refreshed several times to remove the F108 surfactant template until the transparent membranes were obtained. The thickness of the casted mesoporous Nafin (meso-Nafion) was in the range of 125±5 μm.

The synthesis of mesoporous Nafion membranes via a micelle templating method with self-assembled Pluronic F108 surfactant is schematically shown in Figure S1.



**Figure S1.** Synthesis of mesoporous structure in Nafion via a surfactant-directed self-assembly process. The dotted circle refers to the ordered mesopores formed after the removal of F108 surfactant.

Conventional Nafion 115 (thickness:  $\sim 125\ \mu\text{m}$ , DuPont, USA) was used as the comparison for evaluating the properties and performance of meso-Nafion membranes. Both meso-Nafion and Nafion 115 membranes were treated according to the standard procedure of 1 h in a 5 wt%  $\text{H}_2\text{O}_2$  solution at  $80^\circ\text{C}$ , 1 h in Milli-Q water at  $80^\circ\text{C}$ , and 1 h in an 8 wt.%  $\text{H}_2\text{SO}_4$  solution at  $80^\circ\text{C}$ . After each treatment, the membranes were rinsed in Milli-Q water three times to remove traces of  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$ . The membrane was stored in Milli-Q water before use.

Membrane-electrode-assembly (MEA) was fabricated using Nafion 115 and meso-Nafion membranes. E-TEK 20wt%Pt/C catalysts and 5% Nafion solution were used to make the catalyst layer for anode and cathode. Pt and Nafion loadings of the catalyst layer were  $0.5\ \text{mgcm}^{-2}$  and  $1\ \text{mgcm}^{-2}$ , respectively. PTFE-treated carbon paper (TGP-H-030) was used as the gas diffusion electrodes. The MEAs were hot-pressed at  $125^\circ\text{C}$  under 10 MPa for 90 s. Single cells were assembled with the

hot-pressed MEAs and graphite flow field plates. The active area of the cell was 2.5cm x 2.5cm. Hydrogen flow rate was 200 SCCM and oxygen flow rate was 300 SCCM. Both hydrogen and oxygen gases were passed through a molecular sieve. No back pressure was applied. The cell test was done using a fuel cell test station (Greenlight G50 with HyWARE II software, Greenlight innovation corp., Canada).

## 2. Characterization

The small-angle X-ray scattering (SAXS) measurements were performed using the SAXSess high-flux instrument to investigate the mesoporous structure of the Nafion membranes with different F108 contents. The PW 3830 X-ray generator was used as X-ray sources. The data from SAXS experiments were analyzed using the program SAXSquant<sup>TM</sup> (by Anton Paar GmbH.), which produces one-dimensional scattering curves by averaging two-dimensional scattering patterns over linear or circular paths. The input data are TIFF images that are acquired and produced by the program OptiQuant<sup>TM</sup> (by Packard Bioscience) or IMG/PCB images that are produced by the reader software of the BAS-1800<sup>TM</sup> (by Fuji).

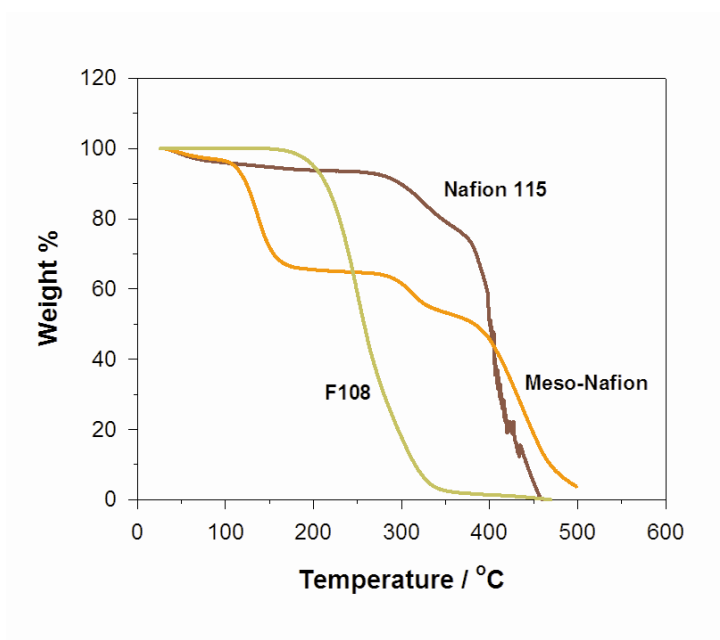
Perkin-Elmer TGA 7 Thermogravimetric Analyzer was used to study the thermal and water retention properties of the Nafion 115 and meso-Nafion membranes. The as-prepared membranes were saturated under 80% RH environments and room temperature for 48 h to reach equilibrium. Then the TGA tests were conducted from 25 °C to 500°C with 5°C/min ramp rate in air.

The proton conductivities of the meso-Nafion and Nafion 115 membranes were measured by using an impedance analyzer (Autolab PG30/GRA, Eco Chemie, Netherlands). Samples were sandwiched between two Pt sheets (2cm×2cm) in contact with graphite plate under constant pressure. The temperature and relative humidity were controlled by a fuel cell test station (Greenlight G50 with HyWARE II software, Greenlight innovation corp., Canada). One Pt sheet was used as the working electrode and the other as the reference and counter electrodes. The electrochemical impedance spectroscopy (EIS) was conducted in the frequency range of 1 MHz to 1 Hz under the

signal amplitude of 10 mV. The proton conductivity measured represents the cross-plane conductivity.

### 3. TGA and water uptake

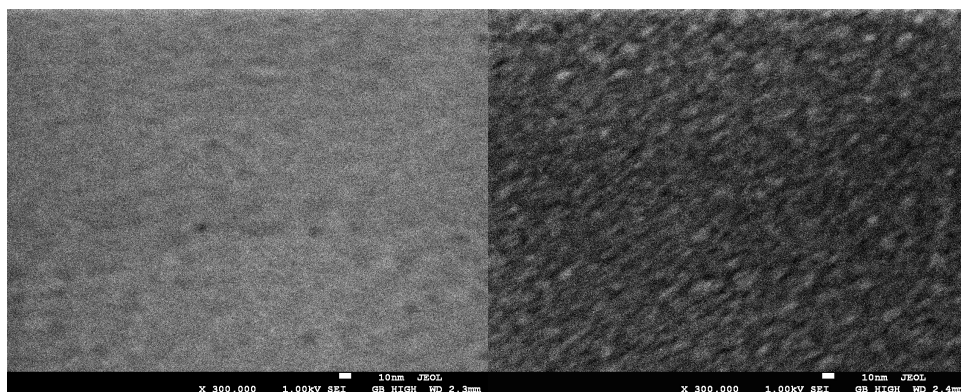
Figure S2 is the TGA curves of F108, Nafion 115 and meso-Nafion membranes. The as-prepared membranes were equilibrated under 80% RH at room temperature for 48 h before the measurement. The initial weight loss of ~5 wt% for the membranes measured from room temperature to 100°C can be attributed to the loss of free water or physically adsorbed water. For Nafion 115 membrane, the additional weight loss before 280°C is ~1%. However, for the meso-Nafion synthesized with 10wt% F108 surfactants, the weight loss is ~30%. Such significantly high weight losses are clearly due to the loss of the water trapped or condensed in the mesopores of the meso-Nafion. On the other hand, F108 surfactant residues, if there is any, would decompose at a much lower temperature of ~200°C (Fig.2b). The mesoporous structure introduced by the micelle templating method with self-assembled surfactants is capable to retain significantly higher water content than the random packed water channels in conventional Nafion. Both membranes start to degrade at a temperature ~350-400°C due to the decomposition of SO<sub>3</sub>H groups followed by pyrolysis of the CF<sub>2</sub>-backbone of the PFSA membranes.



**Figure S2.** TGA curves of Nafion 115, F108 surfactant and meso-Nafion membranes. F108 surfactant was removed before the measurement.

#### 4. FE-SEM results

Figure S3 is the FE-SEM micrographs of the surface of Nafion 115 and meso-Nafion membranes. Though the size of pores cannot be adequately measured, the meso-Nafion clearly shows porous microstructure formation as compared to that of Nafion 115.



**Figure S3.** SEM micrographs of Nafion 115 (left) and meso-Nafion membrane (right) surface.