Support Information

Highly ordered and periodic mesoporous Nafion membranes via silica colloidal mediated self-assembly for fuel cells

Junrui Li[1,2]*, Haolin Tang*[1,*]*, Lutang Chen*[1]*, Rui Chen*[1]*, Mu Pan*[1] *and San Ping Jiang*[3,*]

[1]State Key Laboratory of Advanced Technology for Materials Synthesis and
Processing, Wuhan University of Technology, Wuhan 430070, China

[2]Department of Chemistry, Wuhan University of Technology, Wuhan 430070, China

[3]Fuels and Energy Technology Institute & Department of Chemical Engineering,
Curtin University, Perth, WA 6102, Australia

Experimental Procedures

Materials

All reagents were used as received without further purification. Triblock copolymer surfactants, including poly(ethylene oxide)- b-poly(propylene oxide)- b-poly-(ethylene oxide) copolymer $EO_{20}PO_{70}EO_{20}$ (P123, MW=5800) and $EO_{106}PO_{70}EO_{106}$ (Plutoric F127), tetraethyl orthosilicate (TEOS) and n-butanol (99.4%) were purchased from Sigma-Aldrich. 1,3,5-trimethylbenzene (TMB.99%), concentrated HCl (AR), HF (40%), KCl (AR) and ethanol (AR) were purchased from Shanghai Chemical Company. Nafion 520 ionomers (EW =1000, 5 wt.%) was obtained from Dupont, USA. Nafion 112 (Dupont, USA) was used as pristine Nafion membrane for the purpose of comparison.

Synthesis of mesoporous Nafion with different structural symmetries

Highly ordered Nafion membranes with four different structure symmetries, 2D hexagonal (2D-H), 3D face-centered cubic (3D-FC), 3D body-centered cubic (3D-BC), and 3D cubic-bicontinuous (3D-CB) were prepared and the general synthesizing procedures are as follows in which the Nafion weigh percent in the prepared Nafion/silica composite was controlled at 10 wt%: (a) *2D-H Nafion*. P123

(2.0 g) and 10.3 mL HCl (2M) were dissolved in 62.5 g distilled water. Then Nafion ionomers (5 wt%) was dropwise added under stirring condition to obtain a homogeneous solution. Tetraethoxysilane (TEOS, 4.16 g) was added and stirred for 24 h. After that, the mixture was transferred into an autoclave reactor and reacted at 100 ^{o}C for 24 h. (b) *3D-FC Nafion*. F127 (2.0 g), 2.0 g of TMB and 5.0 g of KCl were dissolved in 120 mL HCl (2M) under stirring for 24h. Then, Nafion ionomers (5 wt%) and 8.3 g of TEOS were dropwise added and stirred for 24 h. The mixture was transferred into an autoclave reactor and reacted at 40 ^{o}C for 72 h. (c)*3D-BC Nafion*. F127 (1.07 g) and 2.12 g HCl was dissolved in 51.44 g distilled water. The solution was heated to 45 ^{o}C before adding 3.21 g of n-BuOH. Nafion and 5.09 g TEOS were then added and stirred for 24 h. Then the mixture was transferred into autoclave reactor at 100 ^{o}C for 24h. (d) *3D-CB Nafion*. P123 (2.0 g) and 3.7 g of HCl were mixed to form a homogeneous solution. The solution was heated to 35 ^{o}C before adding 2.0 g of n-BuOH. Then Nafion and 5.2 g TEOS were added and stirred for 24 h. The mixture was transferred into autoclave reactor at 100 ^{o}C for 24h. Silica was removed from the Nafion/silica precursor by treatment in HF solutions under stirring for 48 h. Then the remained Nafion product was further washed with ultrapure water until the pH reaches about 7. The Nafion product in the solution was isolated and collected by centrifugal treatment at a speed of 4000 r/min for 5 min, followed by drying. Nafion membrane was formed after drying. In this process no other solvents except the water were employed to ensure that the mesoporous structures of Nafion product are maintained in the re-cast process.

Characterization

Small-Angle X-ray Scattering (SAXS) profiles of mesoporous Nafion were recorded on a Rigaku D/MAX-RB diffractometer with a Cu Ka radiation (λ 1.541Ǻ) operating at 40 kV, 50 mA. Nafion suspensions were dispersed in distilled water by ultrasonication, followed by deposition of the suspension on a lacey carbon grid. Transmission electron microscopy (TEM) images were obtained using an electron microscopy (JEOL JEM-2100F). Raman spectra were recorded at room temperature using a micro-Raman spectrometer (Renishaw InVia) in the backscattering geometry with a 514.5 nm Ar^+ laser as an excitation source.

A Perkin-Elmer TGA 7 Thermogravimetric Analyzer was used to study the thermal and water retention properties of the pristine and mesoporous Nafion membrane samples. The as-prepared membranes were heat treated at 80 °C for 4 h before the test. Then the TGA tests were conducted from room temperature to 200 °C with 2 °C min^{-1} ramp rate in air.

Conductivity of pristine and mesoporous Nafion membranes was measured by a four-probe method using a galvanostat/potentiostat (Autolab, PGSTAT30) at room temperature and 80°C at different RH. Electrochemical impedance spectroscopy (EIS) measurements were obtained at frequencies ranging from 100 KHz to 1 Hz with signal amplitude of 10 mV. The relative humidity (RH) was maintained by controlling the humidifier temperature and the humidity of the gas before entering the test chamber.

Nitrogen adsorption isotherms, Brunauer-Emmett-Teller specific surface areas (S_{BET}) and porosity of the samples were measured at -196 °C using Micromeritics ASAP 2020 gas adsorption apparatus (USA). Before adsorption measurement the membranes were cut into small pieces and degassed in flowing nitrogen for 9 h at 100 °C. The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method within the relative pressure range of 0.05—0.20. [Jaroniec, M. and L.A. Solovyov, Langmuir, 2006. 22, 6757-6760] Pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) algorithm. [Kruk, M. and M. Jaroniec, Chemistry of Materials, 2001. 13, 3169-3183]

Hydrogen crossover across the membrane was evaluated at ambient condition by an electrochemical method. Pure hydrogen and nitrogen (99.9999%) were fed without humidifying to the anode and the cathode, respectively, at 300 mL min^{-1}. The potential of the cathode (in nitogen) was swept at 2 mV s^{-1} in a potential range of 0 mV to 700 mV against the anode (H_2/H^+) using a voltammetry system (Autolab, PGSTAT30). Hydrogen crossover was evaluated in diffusion-limited hydrogen oxidation current density obtained in the range of 300 − 350 mV.

BET, porosity and gas crossover

Figure S1a is the N_2 sorption isotherms measured on mesoporous Nafion membranes with different structural symmetries. Mesoporous Nafion with different symmetries have typical type-IV curves and capillary condensation steps. The 2D-H mesoporous Nafion shows capillary condensation at relative pressures of 0.55-0.8, while typical type-IV curves with a clear condensation step at P/P_0= 0.4- 0.7 were observed in 3D-FC, 3D-CB and 3D-BC mesoporous Nafion. The four types of mesoporous Nafion generally give the H_1-type hysteresis loop, suggesting the uniform pore sizes distribution and ordered pore shape of the mesoporous Nafion [Yan Meng et.al, Chem. Mater. 2006, 18, 4447-4464]. The mesoporous Nafion shows rather narrow pore size distributions (Fig.S1b) and the average pore diameter is 5.3, 3.8, 3.8 and 4.7 nm for 2D-H, 3D-FC, 3D-CB and 3D-BC mesoporous Nafion, respectively. BET surface area and pore diameter of the mesoporous Nafion are listed in Table S1. Mesoporous Nafion with structure symmetry 3D-CB exhibits the highest BET surface area of 781 m^2 g^{-1}.

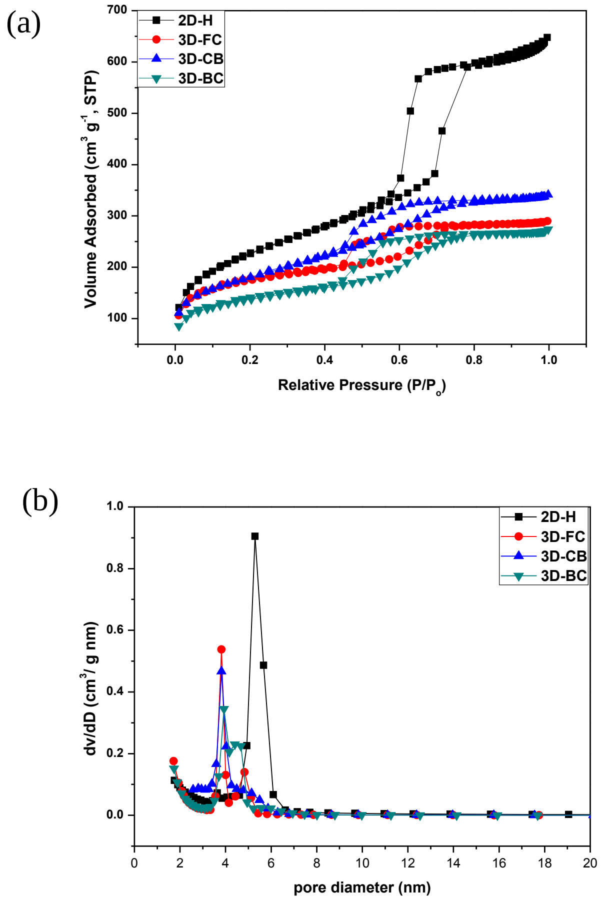

Figure S1. (a) Nitrogen sorption isotherms of mesoporous Nafion membranes with different structure symmetries, and (b) pore size distribution derived from the nitrogen sorption isotherms.

Hydrogen permeability of various mesoporous Nafion membranes was measured by linear sweep voltammograms in H_2/N_2 cell at ambient condition and the results are shown in Fig.S2. For the purpose of comparison, pristine Nafion 112 membrane was also measured. The hydrogen crossover current density values for pristine Nafion 112 membrane and different mesoporous Nafion membranes are summarized and compared in Table S1. Hydrogen crossover currents were in the range of 0.88 to 1.54 mA/cm^2, slightly higher than 0.69 mA/cm^2 measured on pristine Nafion 112. This indicates that mesoporous Nafion membrane has low gas permeability probably due to the synthesis methods of the mesoporous Nafion membranes. The sequence of hydrogen crossover current density values is in good consistent with the BET surface area results: 3D-CB > 2D-H > 3D-BC > 3D-FC. Mesoporous Nafion with 3D-CB shows the largest hydrogen crossover, most likely due to its large surface area. The hydrogen crossover current density values of different mesoporous Nafion membranes are all less than 2 mA, the U.S DOE initial requirement for Nafion membrane in fuel cell (DOE Hydrogen Program: 2005 Annual Progress Report, Page 765).

Table S1. BET surface area and hydrogen crossover current density of pristine Nafion and diverse mesoporous Nafion.

Type of Nafion	S_{BET} (m^2 g^{-1})	*Pore diameter (nm)*	Hydrogen crossover current density (mA cm^{-2})
2D-H mesoporous Nafion	609	5.3	1.15
3D-FC mesoporous Nafion	447	3.8	0.85
3D-CB mesoporous Nafion	781	3.8	1.54
3D-BC mesoporous Nafion	554	4.7	0.88
Pristine Nafion	—		0.69

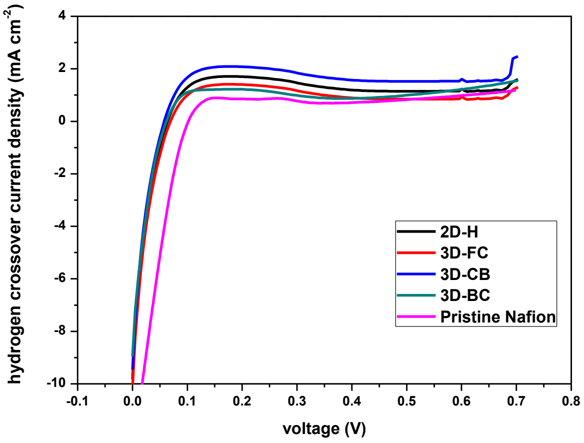

Figure S2. Linear sweep voltammograms for H_2/N_2 cell at ambient condition.

Water uptake:

TGA curves of pristine and mesoporous Nafion membranes with different morphologies are shown in Fig. S3. The initial weight loss for all the membranes is due to the removal of extra free water and physically adsorbed water before 100 ^{o}C. The additional weight loss for pristine membrane before 200 ^{o}C is about 1.2%. In contrast, for mesoporous Nafion membranes with 2D-H, 3D-FC, 3D-CB, 3D-BC structure symmetries, the corresponding weight losses before 200 ^{o}C are 24.3%, 15.5%, 25.8% and 16.2%, respectively. Since all the membranes were pre-heated under 80 ^{o}C for 4h to remove the weakly adsorbed water, the significantly high weight losses around temperatures ranging from 110 to 160 ^{o}C are clearly resulted from the vaporization of the water condensed in the mesopores of mesoporous Nafion membranes. The results clearly demonstrate that highly ordered mesoporous Nafion membranes is capable of retaining significantly higher amount of water than the random nanochannels in the pristine Nafion.

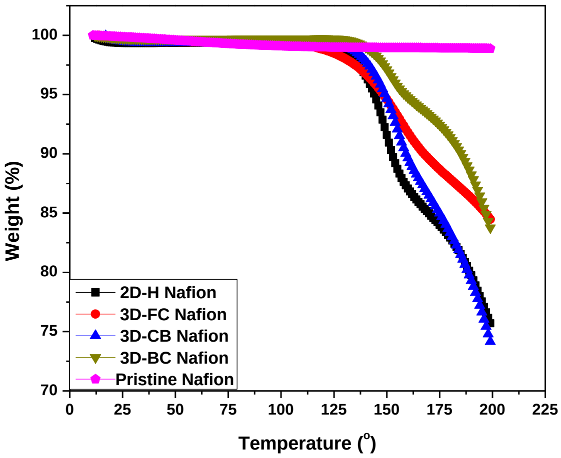

Figure S3. TGA curves of pristine Nafion 115 and mesoporous Nafion membranes with different structure symmetries.

Proton conductivity

Proton conductivities of various mesoporous and pristine Nafion electrolytes were measured by electrochemical impedance spectroscopy. Figure S4 shows the typical impedance curves measured at room temperature under 100%RH. The proton conductivity of Nafion membranes was also measured at 80^{o}C under different RH and the results are summarized in Table S1. Under 100% RH at room temperatures, the proton conductivity of mesoporous Nafion is in the range of 0.030 – 0.064 Scm^{-1}, higher than 0.025 Scm^{-1} measured on pristine Nafion. The most significant benefit of the mesoporous Nafion with different structural symmetries is the substantially enhanced proton conductivity at reduced RH. In the case of pristine Nafion, the proton conductivity decreased from 0.082 Scm^{-1} to 0.013 Scm^{-1} when RH was reduced from 100 to 40% at 80^{o}C, a 84% reduction in conductivity. The proton conductivity of mesoporous Nafion with different structural symmetries is much less sensitive to the change in RH. The best results were observed for Nafion membranes with 2D-H and 3D-BC symmetries. The proton conductivity is 0.101 Scm^{-1} at 100%RH and 80^{o}C and decreases to 0.051 Scm^{-1} when the RH is reduced to 40%, a 50% reduction in conductivity. However, the conductivity of Nafion with 2D-H and 3D-BC structure is 4 times better than that of pristine Nafion membrane under identical conditions.

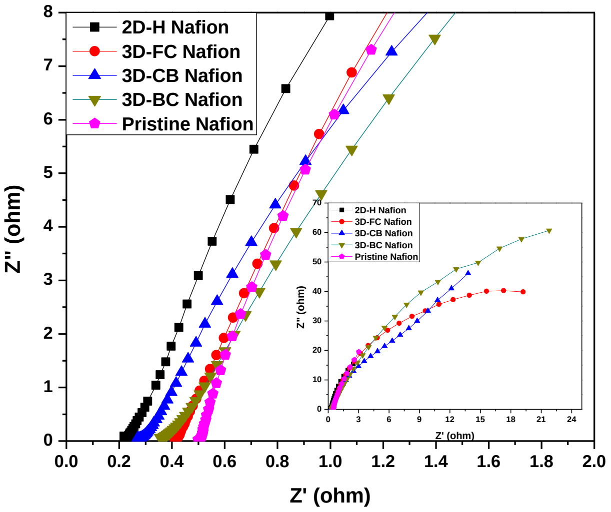

Figure S4. Electrochemical impedance spectra of pristine, 2D-H, 3D-FC, 3D-CB and 3D BC Nafion membranes measured at room temperature (RT) and fully humidified condition; inlet is the full EIS curves of pristine and mesoporous Nafion membranes.

Table S2. Proton conductivities of pristine Nafion and mesoporous Nafion membranes with different structural symmetries measured at different conditions.

Nafion membranes	*Proton conductivities, S cm^{-1}*		
	Room temp, 100%RH	80^{o}C, 100%RH	80^{o}C, 40%RH
Pristine Nafion	0.025	0.082	0.013
2D-H Nafion	0.064	0.101	0.048
3D-FC Nafion	0.030	0.089	0.030
3D-CB Nafion	0.061	0.101	0.051
3D-BC Nafion	0.032	0.089	0.026