Supporting Information

Experimental

Membrane modification. Prior to the membrane modification, the Nafion 212 membrane was boiled in 1 M sulfuric acid solution and ultrapure water for 1 h, respectively. Afterward, 14.4 mL ultrapure water, 22.3 mL TEOS and 63.3 mL methanol were mixed in the beaker and stirred magnetically for 5 minutes under ice water bath. With the reaction system controlled at 0 ^oC, TEOS hydrolysis can be ignored without the catalysis of $–SO_3H$ in Nafion. As result, the chemical step can occur controllably in Nafion channels, denoted as "*in*-situ sol-gel" process. Then, the pretreated Nafion membrane was soaked in the mixture for 5/10/30/60 minutes and denoted as *in*-s-Nafion-5, *in*-s-Nafion-10, *in*-s-Nafion-30 and *in*-s-Nafion-60 membranes, respectively. After the membrane was taken out from the mixture, the surface residue was immediately rinsed with deionized water and subsquently soaked in the deionized water/methanol solution for 10 min to remove the excess TEOS. Finally the modified Nafion membrane was aged in the vacuum oven at 100 ^oC for 24 h.

Characterizations. Electrochemical Workstation (Interface 1000, Gamry) was used to evaluate proton conducting performance of the membrane. First, the prepared membrane was cut into strips (1 cm × 3 cm) and immersed in hydrochloride solution (1 M) for 24 h. The hydrochloride in the membrane was then removed by rinsing the membrane with ultrapure water for several times. With the help of a self-made test mold, all proton conduction measurements were performed in-plane in the membranes. The full humidity and low humidity proton conductivity were measured by a four-probe and a two-probe method, respectively. The high temperature proton conductivity of all membrane was measured from low humidity to high humidity and the time interval between the different humidity was 1 h. The values of the proton conductivity were calculated from the electro-chemical impedance spectroscopy (EIS) data as follow:

$$\sigma = \frac{\mathrm{d}}{Rtw}\ (\mathrm{S/cm}) \qquad (1)$$

σ in Eq. 1 represents proton conductivity of either the modified Nafion membrane or the pristine and d represents the value of the distance between the two probes we used during the EIS measurement. w and t represent width and thickness of the membrane samples with the unit of cm, respectively. R represents the resistance (Ω) for conductivity calculation, which was calculated from the EIS result.

The ion exchange capacity (IEC) test was as follow, the HCl treated membrane was firstly kept in the vacuum oven at 100 ℃ for 24 h for the accurate weight testing. The membrane was then immersed in sodium chloride solution (1 M) at 30 ℃ for 24 h. The exchanged protons within the sodium chloride solutions were subsequently titrated with sodium hydroxide aqueous solution (0.05 M). The IEC value was finally measured *via* the following equation:

$$IEC = \frac{V(mL)\times C(M)}{W(g)}\,(\mathrm{mmol/g}) \qquad (2)$$

In Eq. 2, V (mL) and C (M) stand for the volume and concentration of sodium hydroxide solution consumed during the titration, respectively. W (g) in the equation represents the weight of modified membrane sample.

Scanning electron microscopy (SME, SU8010, Japan) with an energy dispersive X-ray spectrometer (EDS) was used to study the cross-sectional morphology of the modified Nafion membrane and high resolution transmission electron microscopy (HR-TEM) images were recorded using FEI Tecnai G2 F30. Prior to the TEM determination, the membranes were stained with 1 M aqueous lead acetate for 48 h and dried under vacuum oven at 100 ^{o}C for 24 h. Small angle X-ray scattering (SAXS) experiments were carried out on NanoSTAR with the q range from 0.007 to 0.228 Å^{-1}. A NetzschSTA 409 PC TG-DTA instrument was applied for the thermal stability study for the modified membrane from 30 ^{o}C to 800 ^{o}C under nitrogen atmosphere. Mechanical properties of all the modified Nafion membranes were evaluated by a universal tensile machine (Labthink XLW) at 25 ^{o}C. The membrane sample was cut into rectangles (0.5 cm × 3 cm) and soaked in water before testing.

Chemical stability measurement was as follow: The membrane was dried in a vacuum oven at 100 ^{o}C for 24 h and the dry weigh (W_{dry}) of was immediately accurately weighted; The dry membrane was placed into a beaker with 200 ml Fenton's reagent (3 ppm $FeSO_4$ dissolve in 3% H_2O_2) at 80 ^{o}C; The membrane was taken out after 24 h and dried under vacuum oven at 100 ^{o}C for 24 h, the retained weights (RW-24) was recorded; The oxidative stability performance was finally evaluated by the percentage of retained weights. Proton conductivity and Mechanical property after the Fenton test were measured and compared with those of the freshly prepared one. In order to confirm the chemical stability of silica in acidic condition, the membrane was soaked in 2 M H_2SO_4 solution for 100 h and the proton conductivity was measured and comapred with the freshly prepared composite membrane.

Water uptake and volume swelling ratios of the modified Nafion membranes were measured at 30 °C. The membrane was cut into regular rectangles and dried under vacuum oven at 100 °C for 24h for the dry weight (W_{dry}) and dry volume (V_{dry}) recording on the membrane sample. The membrane sample was then equilibrated in deionized water for 24 h before the weight (W_{wet}) and wet volume (*wet*) recording. W_{wet} and V_{wet} of the membrane sample were recorded after being taken out from water. The water uptake (WU) and volume swelling (VS) ratios of the membrane were calculated as follow Eqs. 3-4.

$$\mathrm{WU} = (W_{wet} - W_{dry})/W_{dry} \qquad (3)$$

$$\mathrm{VS} = (V_{wet} - V_{dry})/V_{dry} \qquad (4)$$

High Temperature PEMFC Test. The modified Nafion membrane with geographic area of 2.5 cm × 2.5 cm was uniformly coated with 40 wt% Pt/C catalyst on both sides by electrostatic spraying . Catalyst loading on both the anode and the cathode were controlled to be 0.5 mg/cm^2 (Pt loading: 0.2 mg/cm^2). The catalyst coated membrane (active area: 2 cm × 2 cm) was then sandwiched between two sheet of carbon papers (TGP-H-030, Toray), acting as diffusion layers, after activated in sulfuric acid solution (0.5 M) for 12 h during the fuel cell assembling. PEMFC testing was carried out on a MiniTest3000 Fuel Cell Test System (TOYO Corporation) with the operation temperature controlled at 110 °C. Flow rate of hydrogen and oxygen was set as 0.2 L/min and 0.5 L/min, respectively.

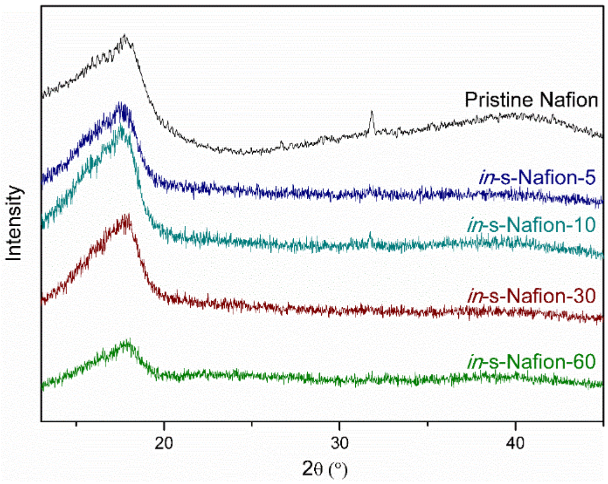

Figure S1. XRD spectra of the *in*-s-Nafion membranes and the pristine Nafion membrane.

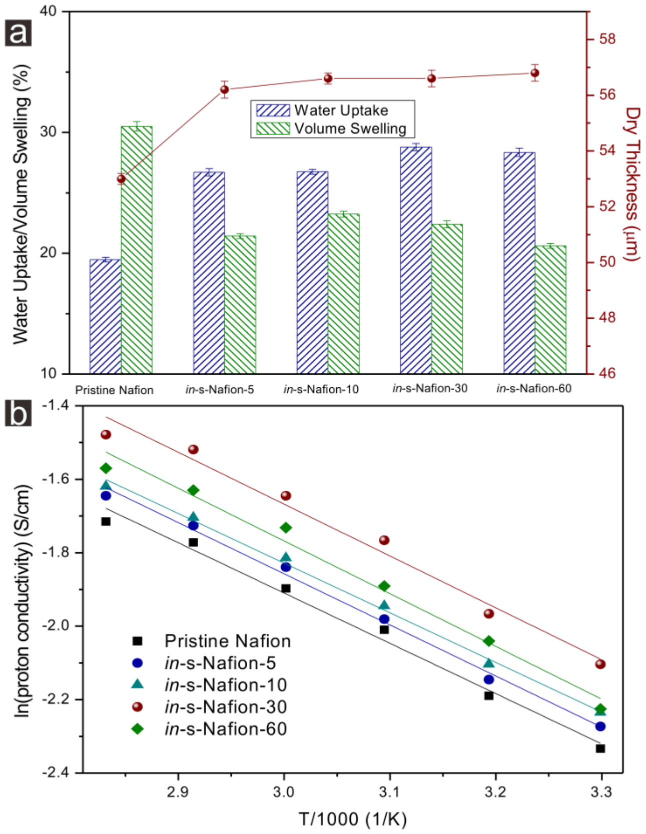

Figure S2. Fully humidify performance. (a) Dependences of dry thickness, water uptake and volume swelling ration of the *in*-s-Nafion membranes on the treating time; (b) Proton conductivity at 100% RH.

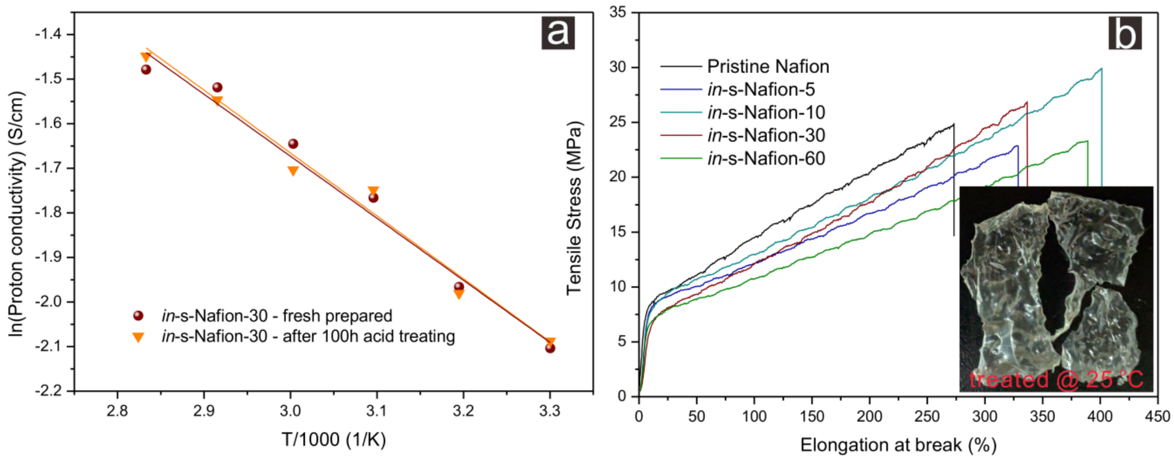

Figure S3. Stability. (a) Proton conductivity of in-s-Nafion-30 membrane measured at 100% RH before and after 100 h acid treatment. (b) Tensile-strain curves of the *in*-s-Nafion membranes and the pristine Nafion membrane (inset: photo of Nafion 212 membrane *in*-situ sol-gel treated at 25 ^{o}C for 5 min).

Table S1. Oxidative stability of the pristine Nafion membrane and the *in*-s-Nafion membranes.

Membrane	IEC (mmol/g)	Oxidative stability		
		RW-24[a)]	Reduction ratio of maximum tensile stress[b)]	Reduction ratio of proton conductivity (20%,110 °C)[c)]
Naion 212	0.914	98.4%	-1.07%	-2.2%
in-s-Nafion-5	0.909	98.6%	-0.95%	+2.0%
in-s-Nafion-10	0.905	98.5%%	-1.01%	-2.3%
in-s-Nafion-30	0.906	99.1%	-0.69%	-1.9%
in-s-Nafion-60	0.903	99.0%	-0.94%	+1.6%

a) Retained weight, b) reduction ratio of maximum tensile stress and c) reduction ratio of proton conductivity after 24 h Fenton treating at 80 °C.

Table S2. Comparison of low humidity proton conductivity and tensile strength of state-of-the-art modified Nafion membranes.

Membrane	Conductivity (S/cm)	Condition	Tensile stress (MPa)	Ref.
Nafion/DGO-2.0	0.007	80 °C, 40%RH	-	[1]
Nafion/ZrNT	0.006	80 °C, 20%RH	13	[2]
Nafion-sMC	0.0079	70 °C, 20%RH	9	[3]
Nafion/Si1-Ti2	0.011	80 °C, 25%RH	-	[4]
Nafion/SGF-3	0.012	120 °C, 20%RH	-	[5]
Nafion/HMS	0.010	120 °C, 25%RH	-	[6]
Nafion/NIM-PO3	0.019	120 °C, 30%RH	-	[7]
***in*-s-Nafion**	**0.049**	**110 °C, 60%RH**	**29.7**	**This work**

References

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