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Electronic Supporting Information for

Ammonia-assisted Dehydrofluorination between PVDF and Nafion for Highly Selective and Low-cost Proton Exchange Membranes: A Possible Way to Further Strengthen the Commercialization of Nafion

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1. Membrane preparation.

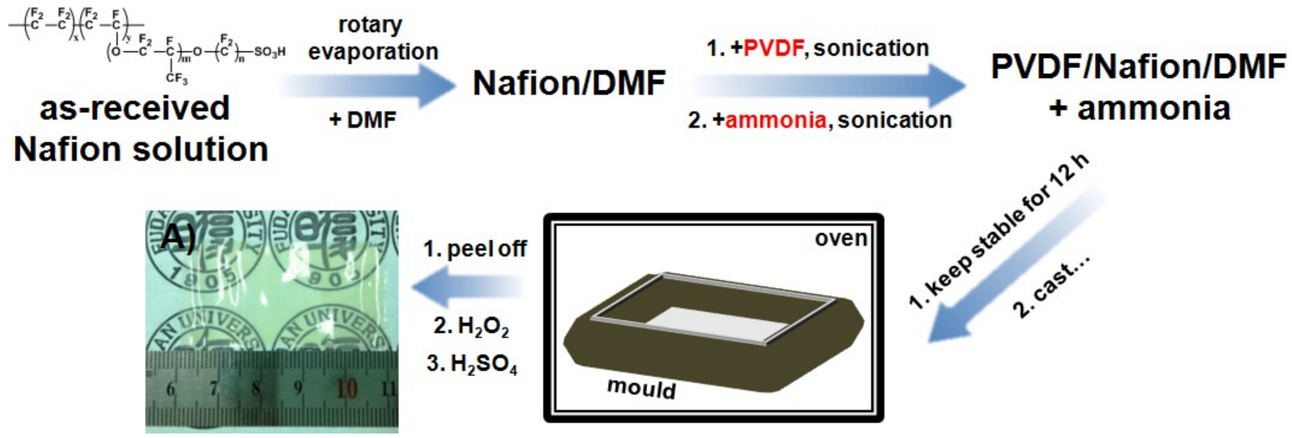

Fig. S1. Preparation procedures of A-Nafion+PVDF. (A) A digital photo of A-Nafion+PVDF.

Fig. S1 presents the typical preparation procedure of the ammonia-modified PVDF+Nafion composite PEM (A-Nafion+PVDF). First, most of the solvent of the as-received Nafion solution was exchanged by dimethylformamide (DMF) with the aid of rotary evaporation. Then, 30 wt% PVDF powder was added into the Nafion/DMF solution, followed by being sonicated for 30 min to completely dissolve PVDF. Subsequently, 300 v/w% (mL/g) ammonia was put into the PVDF/Nafion/DMF mixture and then the system was sonicated for another 4 h. The quantity of PVDF and ammonia were determined according to the Nafion polymer. After being kept stable for at least 12 h, the “PVDF/Nafion/DMF + ammonia” solution was cast onto a glass mould. The mould was dried in a vacuum oven by slowly increasing the temperature from 70 to 120 ^{o}C for 6 h, and then further dried under vacuum at 120 ^{o}C overnight. Subsequently, the transparent A-Nafion+PVDF was immersed in 3 wt% H_2O_2 solution under 70 ^{o}C for 2 h, and then immersed in 1 M H_2SO_4 solution at 80 ^{o}C for 1 h to convert the membrane into H^+ form. At last, the membrane was rinsed by deionized H_2O for several times before latter characterizations. The recast Nafion membrane was prepared via the same method.

2. Membrane characterizations.

XPS characterizations were carried out on Axis Ultra DLD XPS equipment (Kratos, England). NMR spectra were obtained on Varian Mercury plus 400 M spectrometer with D-DMSO as the solvent and tetramethylsilane (^1H) or benzotrifluoride (^{19}F) as the internal reference. TGA was performed on Perkin Elmer Thermal Analyzer. FTIR characterizations were carried out on a Nicolet Nexus 470 spectrometer with a resolution of 4 cm^{-1} and 64 scans. Energy dispersive X-ray fluorensence spectrometer (EDX) analysis was obtained by the field emission scanning electron microscopy (Ultra 55, Zeiss, German). The sample was coated with gold before the EDX characterization.

Cross-linking degree of the membrane was characterized by its gel fraction. First, the membrane was immersed in DMF under 100 °C for 24 h to dissolve those uncrosslinked Nafion/PVDF chains. Second, the precipitation was collected and dried until a constant mass was obtained. The gel fraction of the membrane was calculated as $GF(\%) = \frac{W_p}{W_o} \bullet 100$, where W_p and W_o is the mass of the precipitation and the original sample.

Water uptake (WU) was obtained by the following steps[1]: first, W_{dry} was measured after the PEM was dried at 80 °C for 24 h. Then, the PEM was saturated with H_2O by being immersed in deionized H_2O at room temperature for 24 h. After that, the PEM were taken out followed by being quickly sandwiched between two pieces of filter paper to remove the water on the membrane surfaces. Subsequently, the PEM was immediately put into a sealed weighing bottle, and weighted (W_{wet}). Thereby, WU was calculated by the following equation: $WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \bullet 100$. The membrane areas of dry (A_{dry}) and wet (A_{wet}) PEMs in methanol or H_2O were obtained via the same treatment processes as described above. The membrane swelling ratio in methanol or H_2O was calculated as:

$$Swelling\quad ratio(\%) = \frac{A_{wet} - A_{dry}}{A_{dry}} \cdot 100 \cdot {}^{1}$$

Proton conductivity was obtained by a four-electrode method using AC impedance spectroscopy between 0.1 MHz and 1 Hz with potentiostat control (CHI660d model).[1] The investigated temperature and humidity were controlled by a temperature-and-humidity test chamber during the entire measurement. All the samples were placed under the desired temperature and humidity for 8 h before the measurement of proton conductivity.

Methanol permeability was measured under 50 ^{o}C with the aid of a home-made equipment (Fig. S2).[2] First, a dry PEM was put onto a ZnSe crystal in the ATR cell (Nicolet Nexus 470 FTIR spectrometer) and then sandwiched by the ZnSe crystal and a PTFE mould. Second, continuous FTIR data were collected as soon as 0.5 ml of 80 v/v% methanol/H_2O solution was injected into the PTFE mould through a little hole (Fig. S2). The little hole was blocked during the entire measurement to avoid any evaporation of methanol/H_2O. Using a macro program, the FTIR data, based on 4 cm^{-1} spectral resolution, were taken as a function of time with acquisition time interval of 40 s. Third, according to the increase in the peak area corresponding to the $-CH_3$ stretching vibration, the Fickian diffusion equation (eq 1) put forward by Fieldson and Barbari[3] was used to estimate the diffusion coefficients of methanol in the PEMs.[4]

Fig. S2. Schematic illustration of the home-made equipment used to characterize the methanol permeability of PEMs.[2]

$$\frac{A_t}{A_\infty} = 1 - \frac{8\gamma}{\pi[1-\exp(2L\gamma)]} * \sum_{n=0}^{\infty}[\frac{\exp(g)[f\exp(-2L\gamma)+(-1)^n(2\gamma)]}{(2n+1)(4\gamma^2+f^2)}] \quad (1)$$

Where $g = \frac{D(2n+1)^2\pi^2 t}{4L^2}$; A_t is the absorbance are at time t, and A_∞ is the equilibrium area; L denotes the thickness of PEMs; D refers to diffusion coefficient; n and π are constants. The parameter γ is defined as $\gamma = \frac{2n_2\pi\sqrt{\sin^2\theta - \left(\frac{n_1}{n_2}\right)^2}}{\lambda}$, where λ is the wavelength of infrared beam in the ATR element; θ ($\theta = 45^o C$) is the angle of the incidence of the infrared radiation; n_1 and n_2 are the refractive indexes of Nafion and the ATR crystal.

3. Supporting results.

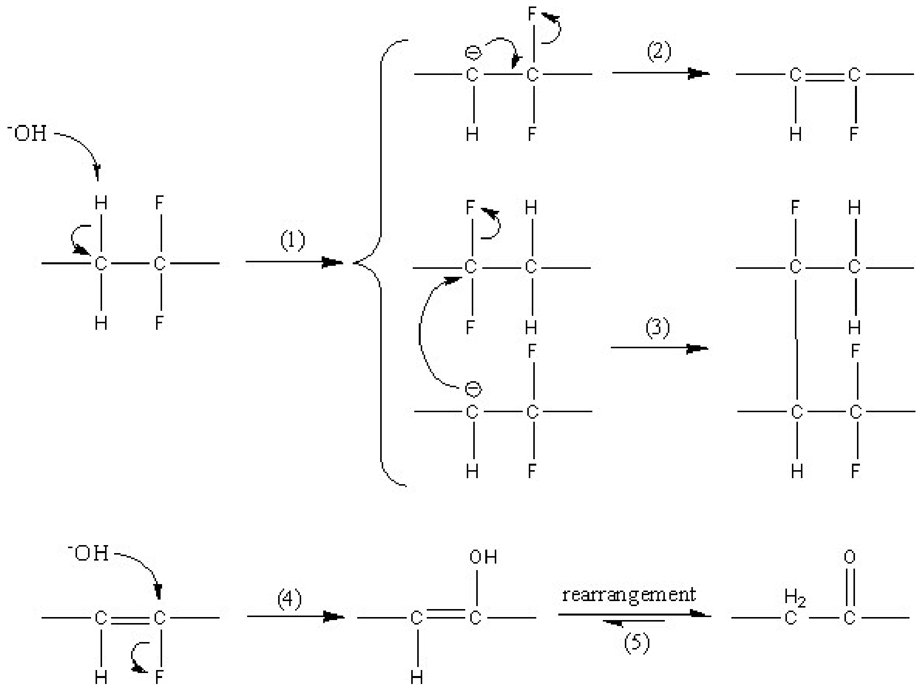

Fig. S3. Proposed dehydrofluorination mechanism of PVDF in the presence of ammonia.

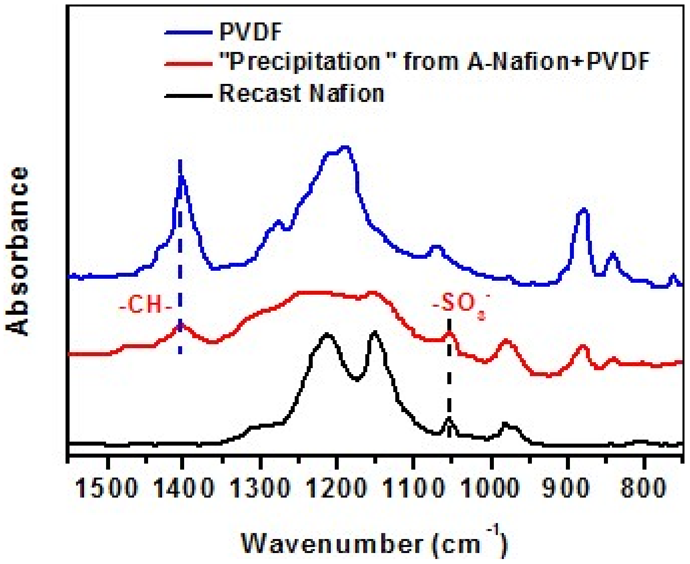

Fig. S4. FTIR spectra of recast Nafion, PVDF, and the “precipitation” derived from A-Nafion+PVDF by immersing it into DMF under 100 °C for 24 h.

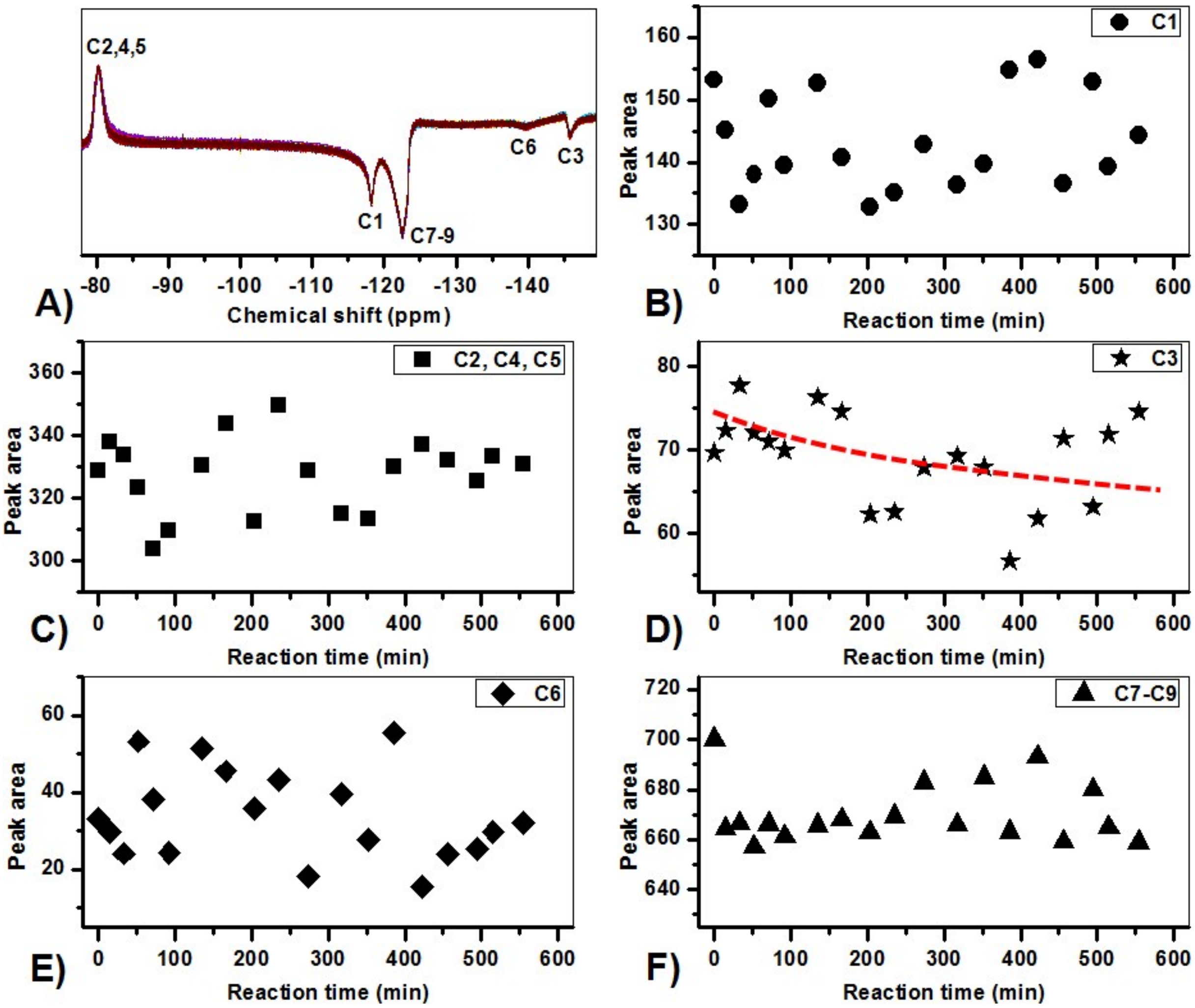

Fig. S5. (A) time-dependent ^{19}F NMR technique *in situ* tracing the changes of Nafion polymer chains in the presence of ammonia (300 v/w% (mL/g)); (B-F) changes of the ^{19}F NMR peak areas of different C-F$_{(1/2/3)}$ groups of Nafion (as labeled in Fig. 1 (C)).

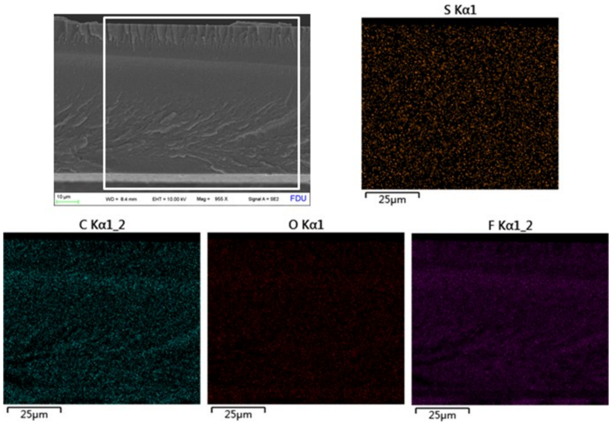

Fig. S6. Cross-sectional EDX mapping of A-Nafion+PVDF.

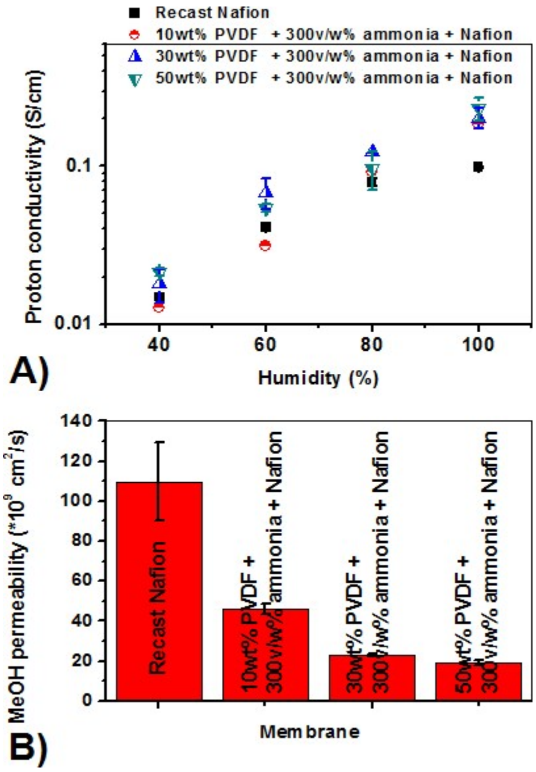

Fig. S7. (A) Humidity-dependent proton conductivity (80 °C) and (B) methanol permeability (50 °C, 80 v/v% methanol/H_2O) of the A-PVDF+Nafion membranes with 10/50 wt% PVDF contents. For comparison, those of recast Nafion[1,2] and 30 wt% A-PVDF+Nafion are also provided here.

Notes and references

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