

Supporting information

Synergistic proton transfer through nanofibrous composite membranes by suitably combining proton carriers from nanofiber mat and pore-filling matrix

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1. Photographs of nanofiber mats and NFCMs

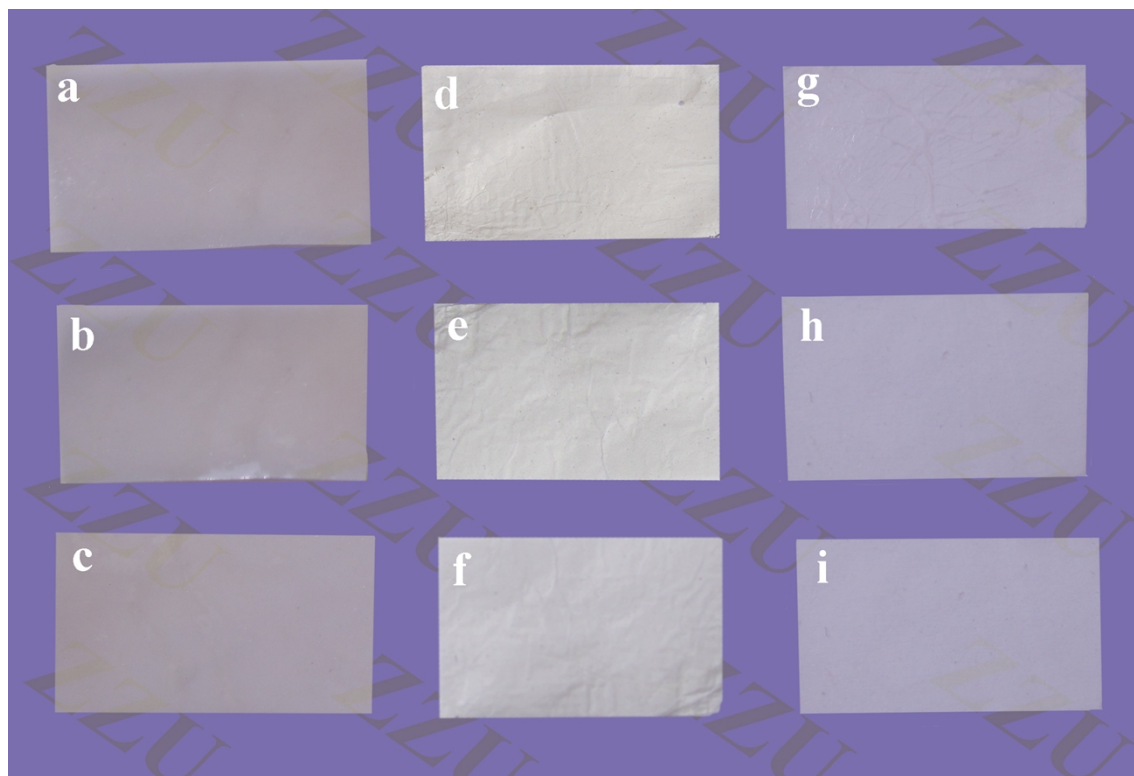


Fig. S1. Photographs of (a) SP/NF-OH, (b) SP/NF-NH₂, and (c) SP/NF-SO₃H; (d) NF-OH, (e) NF-NH₂, and (f) NF-SO₃H; (g) CS/NF-OH, (h) CS/NF-NH₂, and (i) CS/NF-SO₃H.

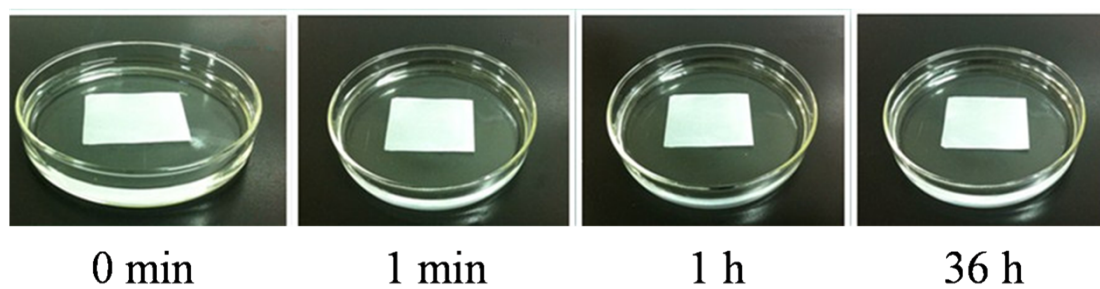


Fig. S2. Solubility of NF-OH in de-ionic water at 25 °C.

2. SEM images, TGA, DSC, and XRD curves of nanofibers

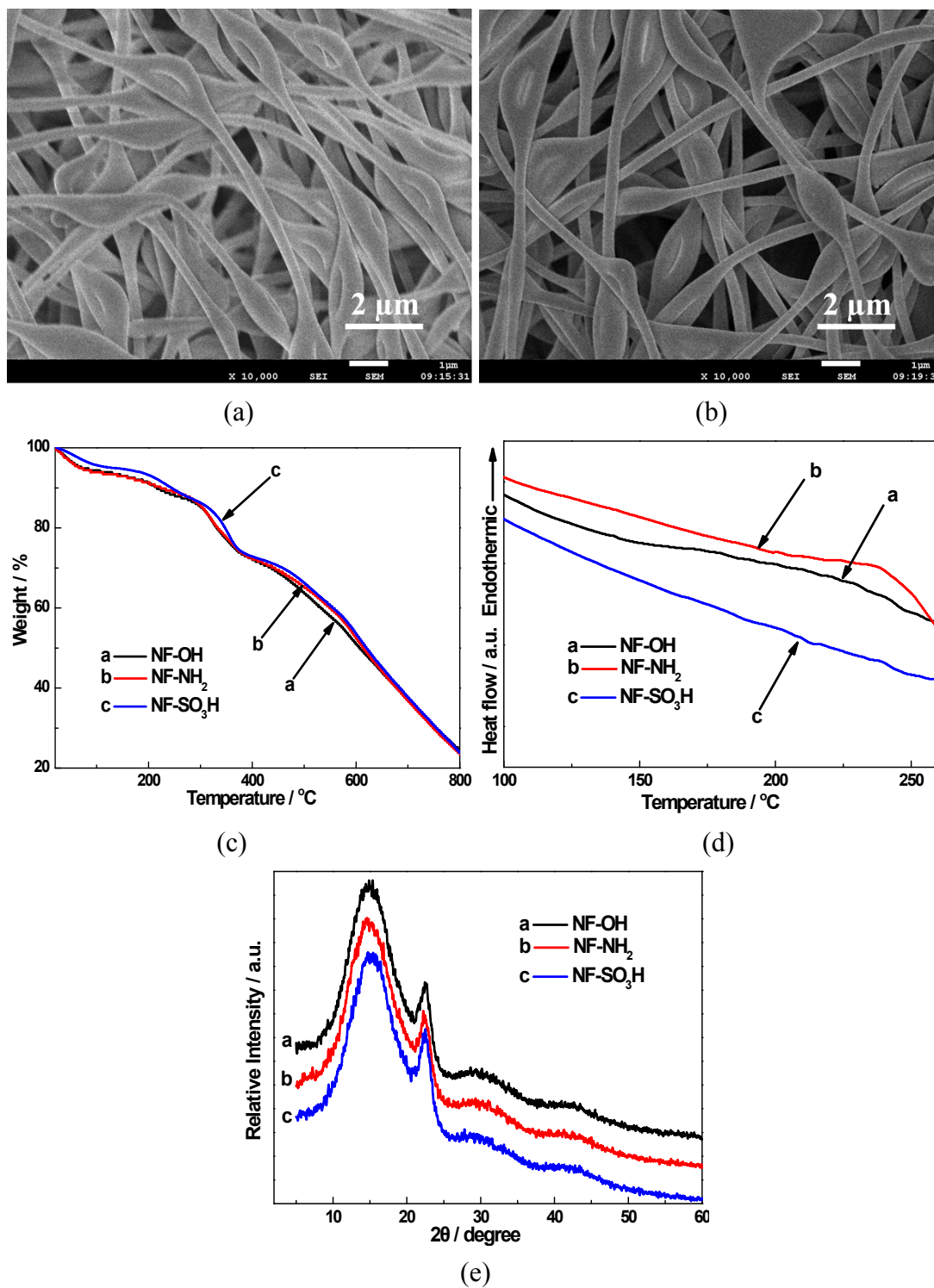


Fig. S3. SEM images of (a) NF-NH₂ and (b) NF-SO₃H; (c) TGA, (d) DSC, and (e) XRD curves of nanofibers.

3. SEM images of cross-sectional NFCMs

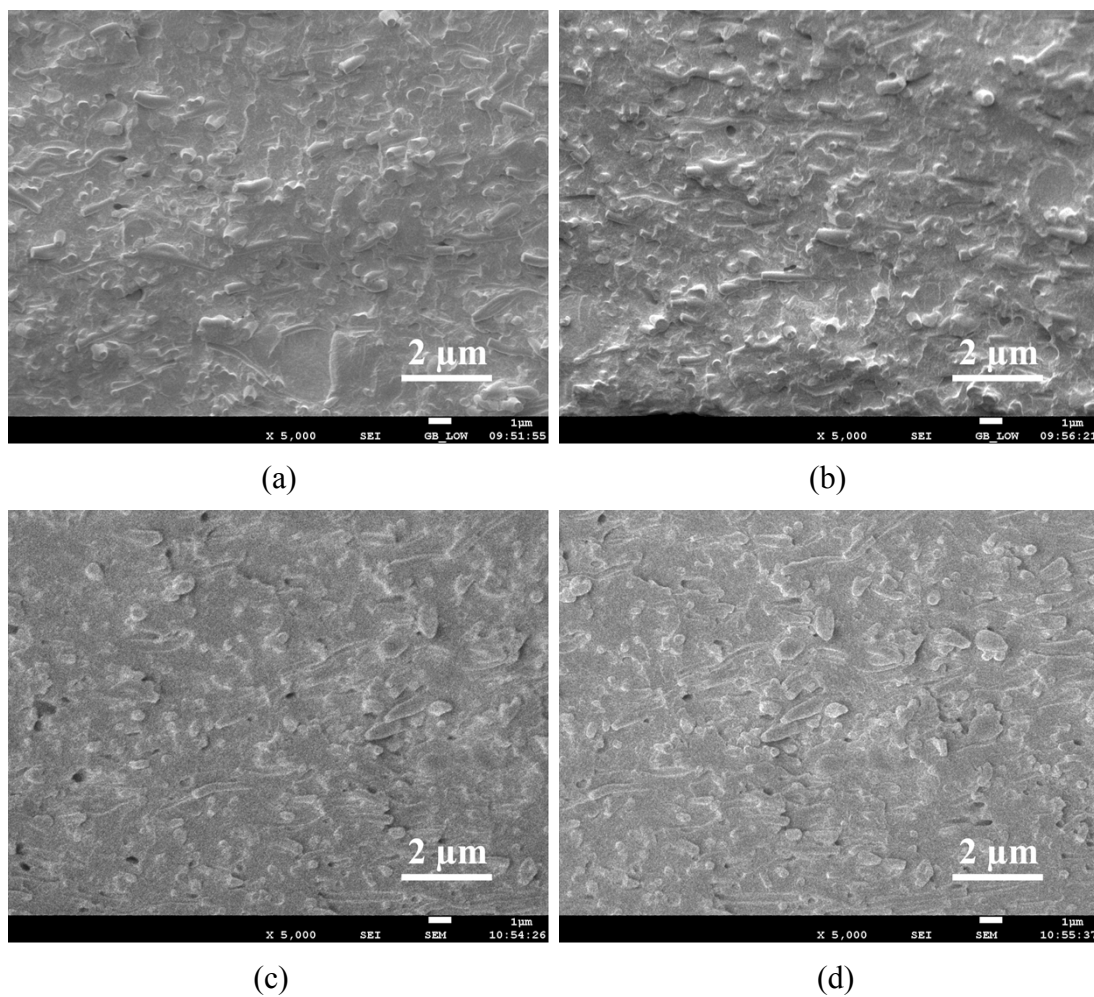


Fig. S4. SEM images of cross-sectional (a) SP/NF-OH, (b) SP/NF-SO₃H, (c) CS/NF-OH, and (d) CS/NF-NH₂.

4. Measurement of the bonded sulfuric acid content in cross-linked chitosan membrane

(1) Titration method: a certain amount of uncross-linked CS membrane was immersed in 1 M H_2SO_4 solution (200 mL) for 24 h. Afterwards, the cross-linked membrane was taken out and washed thoroughly with de-ionized water until pH was 7.0. The washing solution was collected and mixed with the residual H_2SO_4 solution. The total volume (V , L) could be measured by a graduated cylinder, and the concentration (c , mol L^{-1}) was determined through titration using NaOH aqueous solution. Therefore, the amount of bonded H_2SO_4 could be calculated by: n (mol) = $0.2-cV$. The results showed that the bonded H_2SO_4 in per weight CS was around 3.06 mmol g^{-1} and the molar ratio of nitrogen to sulfur ($n_{\text{N}}/n_{\text{S}}$) was 2.38:1.

(2) Elemental analysis method: the elemental content of chitosan membrane before and after cross-linking was characterized using an elemental analyzer (vario EL cube) and the results were shown in the table below:

Table R1. Elemental analysis of chitosan membrane before and after cross-linking

	Elemental content (wt. %)				$n_{\text{N}}/n_{\text{S}}$
	C	H	N	S	
Before	38.81	7.673	6.28	0	---
After	29.27	7.017	5.44	5.734	2.16

5. FTIR, DSC, TGA and XRD curves of membranes

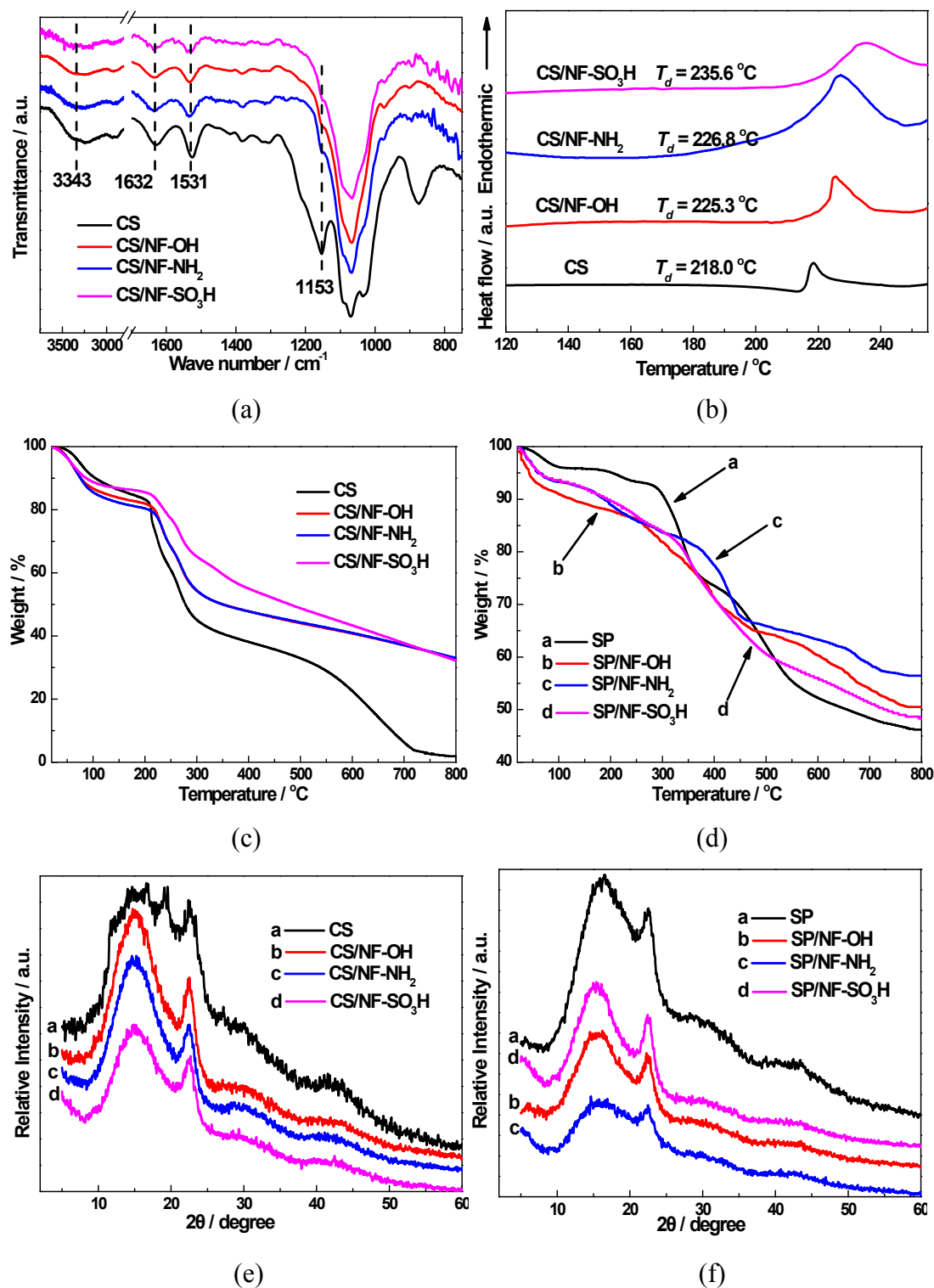


Fig. S5. (a) FTIR and (b) DSC curves of CS-filled membranes; TGA curves of (c) CS-filled membranes and (d) SPEEK-filled membranes; XRD curves of (e) CS-filled membranes and (f) SPEEK-filled membranes.

6. Mechanical stability of CS-filled membranes

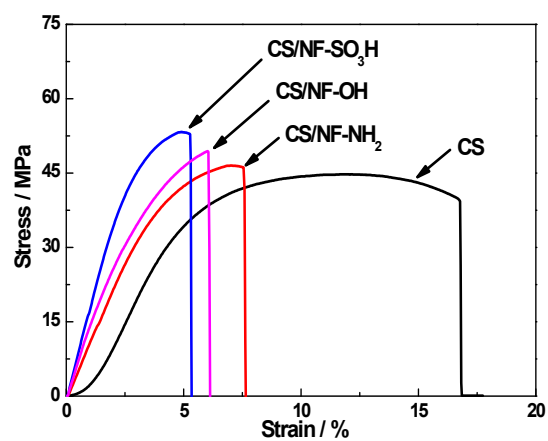


Fig. S6. Stress-strain curves of CS-filled NFCMs.

7. Water uptakes and area swellings of membranes

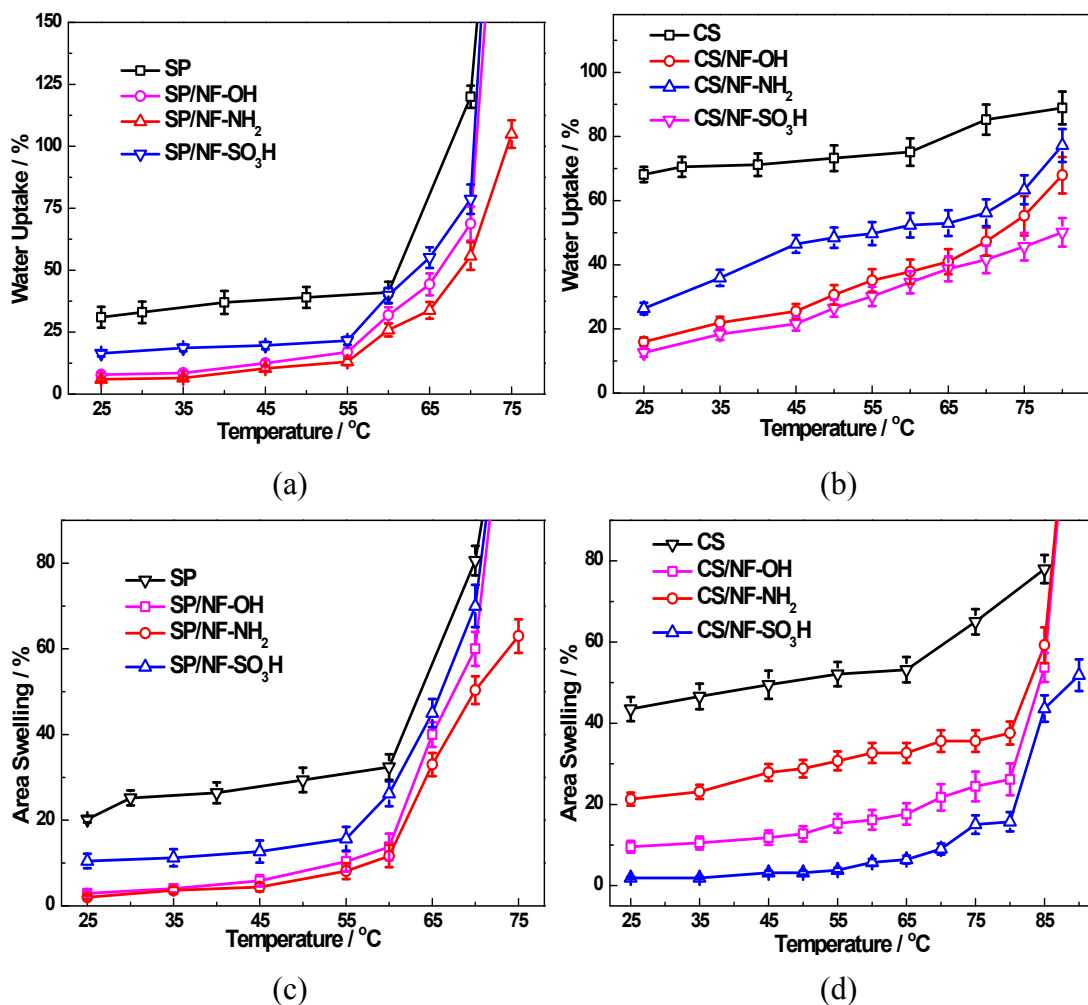


Fig. S7. Water uptakes of (a) SPEEK-filled membranes and (b) CS-filled membranes; area swellings of (c) SPEEK-filled membranes and (d) CS-filled membranes.

8. Stability of proton conductivities

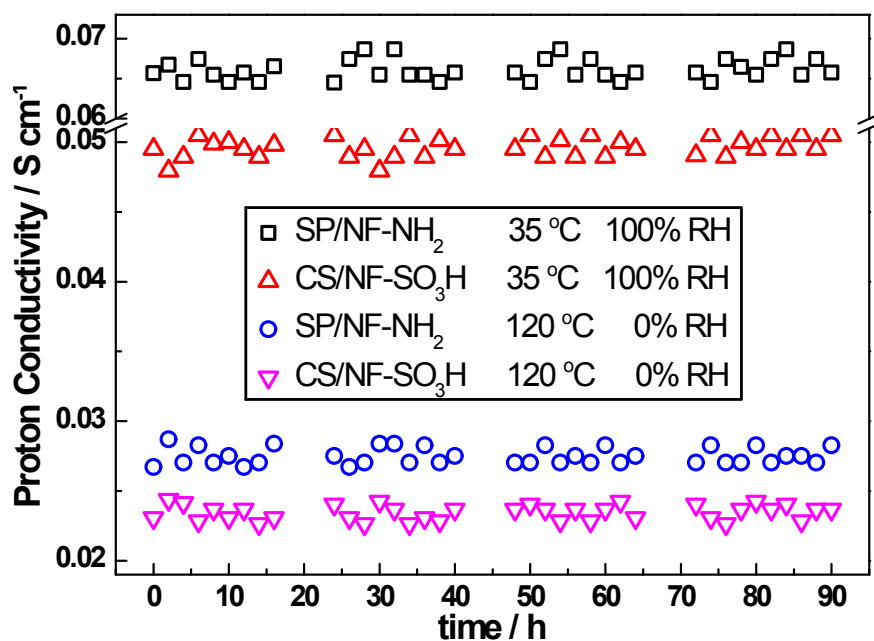


Fig. S8. Time-dependent conductivities of SP/NF-NH₂ under 35 °C and 100% RH (square) and 120 °C and 0% RH (circle); time-dependent conductivities of CS/NF-SO₃H under 35 °C and 100% RH (upper triangle) and 120 °C and 0% RH (lower triangle).