Modification of sulfonated poly(arylene ether nitrile) proton exchange membranes by poly(ethylene-co-vinyl alcohol)

Hao Liu+, [a, b], Tiandu Dong+, [b], Mingzheng Zhou+, [b], Zetian Zhang[b], Yunxi Li[b], Chuanrui Lu[b], Yichen Liu[b], Shengqiu Zhao[a], Shuhong Zheng[a], Zihan Meng[a], Haolin Tang*, [a]

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

[b] State Power Investment Corporation Hydrogen Energy Company, Ltd.Co., Beijing, China

Dimensional Change

For dimensional change measurements, dry membrane sheets were placed in oven at 80 °C under each relative humidity for 2 h. The dimensional change in membrane thickness direction (Δt) and the plane direction (Δl) were calculated from the following Equation:

$$\Delta t = \frac{t - t_s}{t_s} \tag{1}$$

$$\Delta l = \frac{l - l_s}{l_s} \tag{2}$$

where t_s and l_s refer to the thickness and length of membranes measured at dry condition, respectively; t and l are those of the membrane under each condition.

Water Stability

For water stability measurements, dry membrane sheets were placed in hot water at 80 °C for 12 h, 24h and 36h, respectively. The residual weight of membranes in hot water was calculated from the following Equation:

$$\Delta m = \frac{m - m_t}{m} \tag{3}$$

Where *m* and m_t refer to the mass of membranes before and after soaking in hot water.

Oxidative Stability

A small piece of membrane sample (1 cm×4 cm) was soaked in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 ^{O}C. The oxidative stability was evaluated 1 h later through the weight of membranes before and after the test.

Fuel Cell Performance

The active surface area of membrane electrolyte assembly (MEA) was 6.25 cm^2, and the loading amounts of Pt in both gas diffusion electrodes (GDEs) were 0.5 mg cm^{-2}. Single-cell test was performed under ambient pressure in an in-house fuel cell station (HTS-125, Shanghai Hephas Energy Co. Ltd), and the cell temperature was set at 80 ^{o}C, with varying the gas humidifier temperatures of 50–70 ^{o}C to adjust the RH condition. For each testing condition, the cell was equilibriated for at least 2 h before polarization curves were recorded. The gas flow rate (200 mL min^{-1} (H_2), 500 mL min^{-1} (air)) was fixed over the entire test.

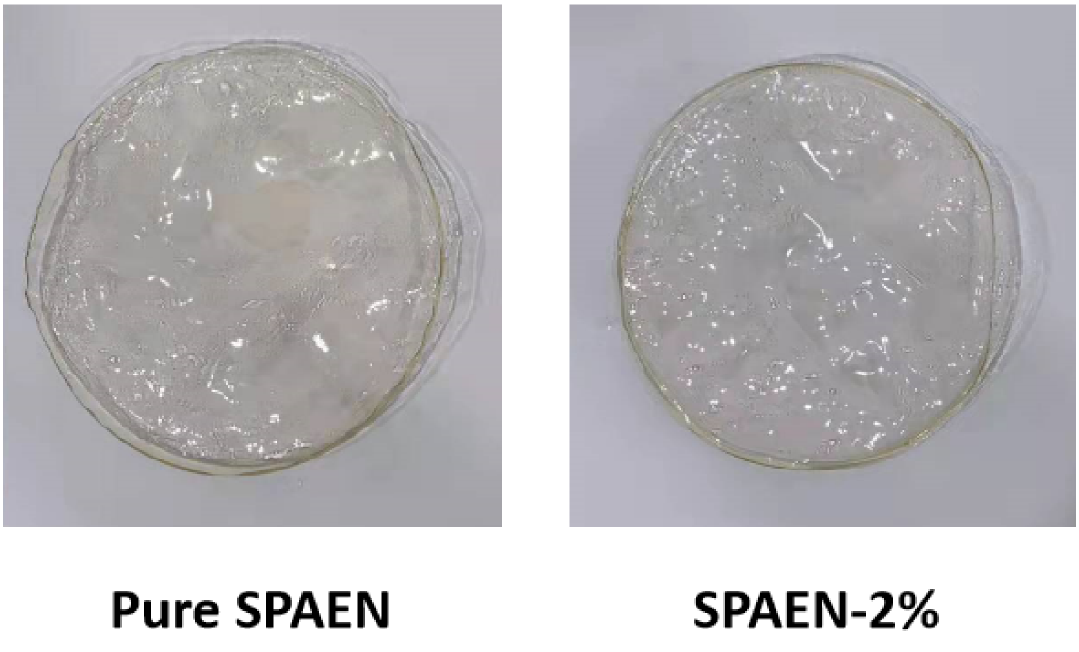

Figure S1 The photographs of Pure SPAEN and SPAEN-2%.

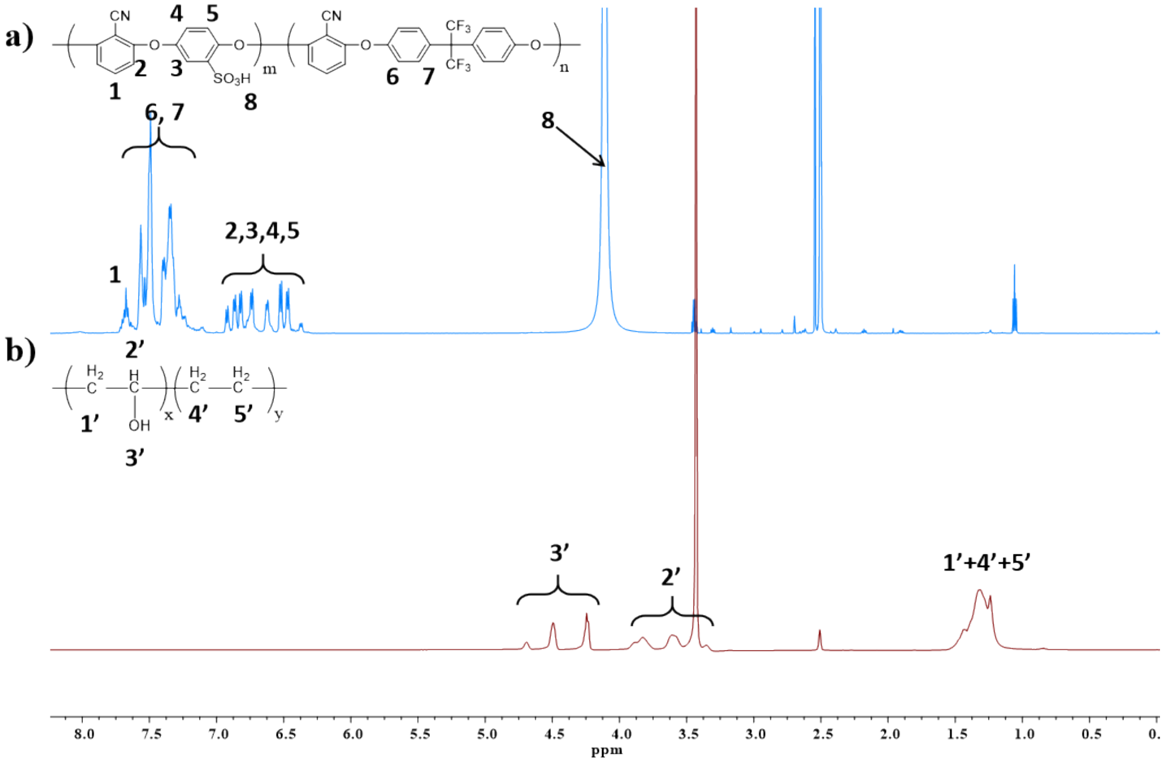

Figure S2 ^{1}H NMR spectra of a) SPAEN; b) EVOH.

Table S1 Dimensional change of SPAEN-x% membranes

Code	Dimensional change^a					
	%					
	50% RH		70% RH		95% RH	
	TP	IP	TP	IP	TP	IP
SPAEN	1.6	1.7	3.8	3.8	6.5	6.4
SPAEN-2%	1.7	1.5	4.6	4.2	7.5	7.0
SPAEN-5%	1.9	2.0	5.1	4.5	8.6	8.3
SPAEN-8%	1.8	1.6	4.9	4.6	8.1	7.8

[a] dimensional change measured at 80 ^{o}C.

Table S2 Water stability of SPAEN-x% membranes

Code	RW^a		
	%		
	12h	24h	36h
SPAEN	99.8	99.7	99.5
SPAEN-2%	99.6	99.6	99.5
SPAEN-5%	99.5	99.5	99.3
SPAEN-8%	99.7	99.6	99.6

[a] water stability measured at 80 ^{o}C in water.

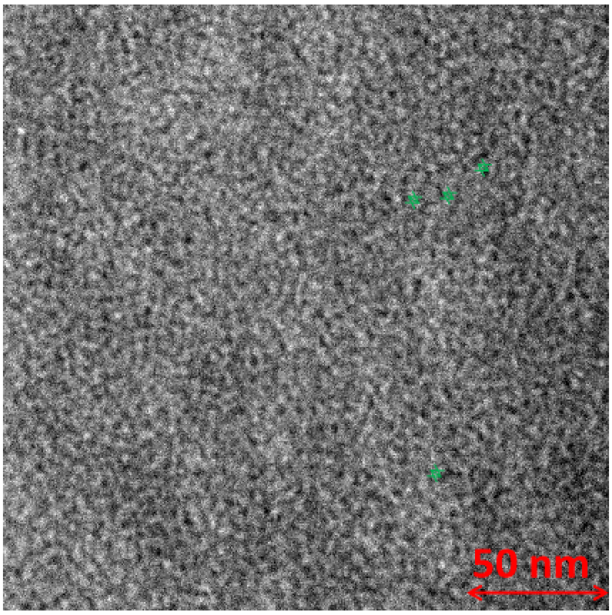

Figure S3 TEM photograph of Pure SPAEN.

Table S3 Oxidation stability of SPAEN-x% membranes

Code	RW[a]			
	%			
	First time	Second time	Third time	average
SPAEN	87.3	83.1	84.9	85.1
SPAEN-2%	89.0	91.2	88.8	89.7
SPAEN-5%	93.3	93.8	95.7	94.3
SPAEN-8%	94.5	94.0	96.4	95.0

[a] remaining weight. Measured by soaking the membrane sheets (1 cm*4 cm) in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 ^{o}C for 1 h.