

Electronic Supplementary Information for

Anion Exchange Membranes with Well-Defined Ion Transporting Nanochannels *via* Self-Assembly of Polymerizable Ionic Liquids

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Table S1 Structure Parameters for the LC Phase of C₁₂VIMBr Aqueous Mixture

Phase	[C ₁₂ VIM][Br] (wt%)	ϕ_L	a_0 (nm)	d_L (nm)	d_H (nm)	d_W (nm)
H ₁	60%	0.596	4.466		1.810	0.846
	65%	0.646	4.258		1.797	0.665
	70%	0.696	4.130		1.809	0.512
	75%	0.747	4.025		1.826	0.373
L _{α}	80%	0.797	3.398	2.709		0.689
	85%	0.847	3.315	2.810		0.505

ϕ_L is the volume fraction of hydrophobic alkyl chains in surfactant molecule; a_0 is the lattice parameters of LC phase; d_H is the radius of cylinder unit in H₁ phase; d_L is the thickness of hydrophobic domain in L _{α} phase; d_W is the thickness of water channel in LC phase.

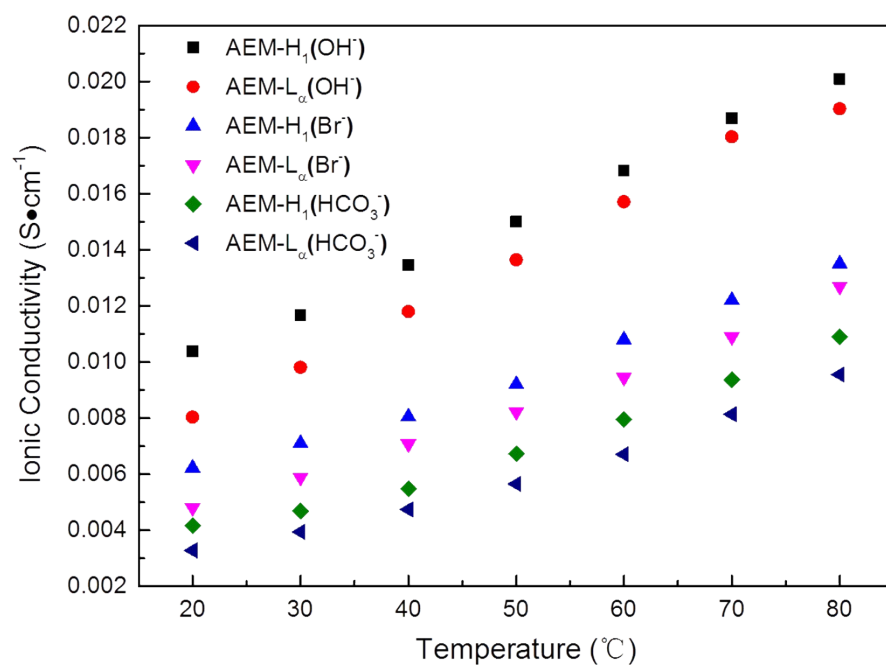


Figure. S1 The conductivities of membranes in the OH⁻, Br⁻ and HCO₃⁻ forms as a function of temperature.

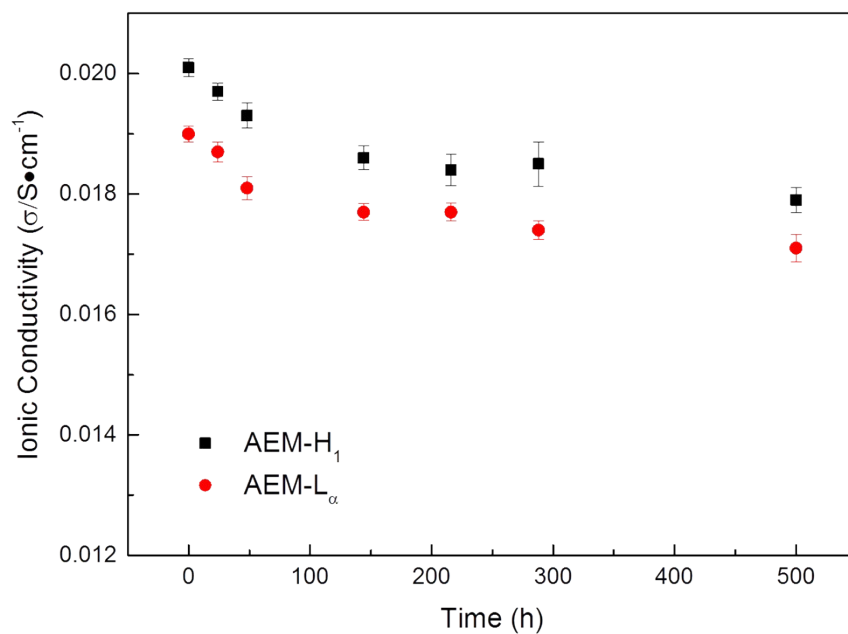
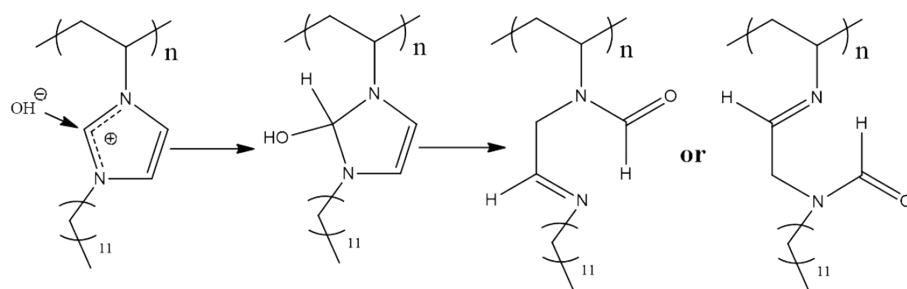


Figure. S2 The ionic conductivity stability of the AEM-H₁ and AEM-L_α membranes in 1 M KOH solution at 80 °C.



Scheme S1. A possible schematic illustrating the ring-opening degradation of imidazolium cations.

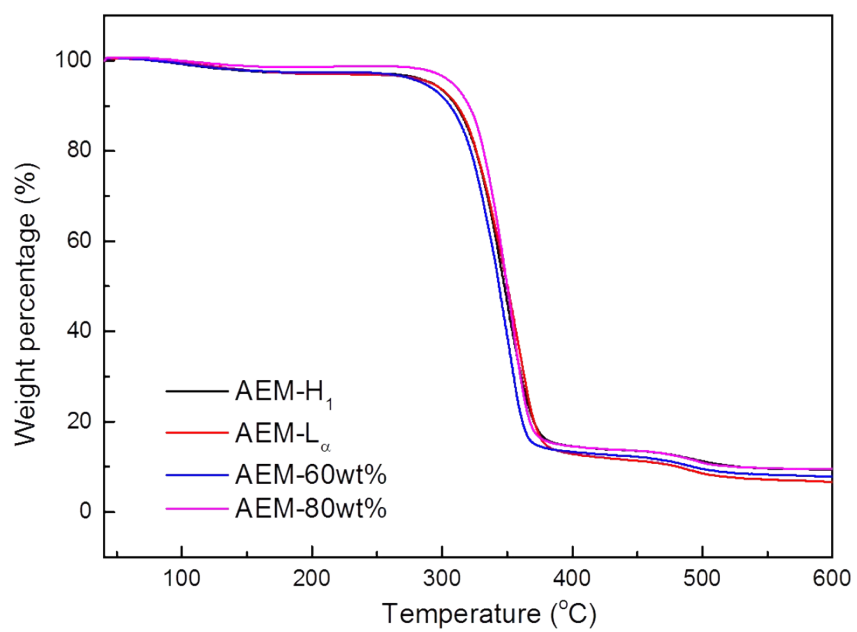


Figure. S3 TGA curves of the produced membranes under a nitrogen flow at a heating rate of 10 °C/min.

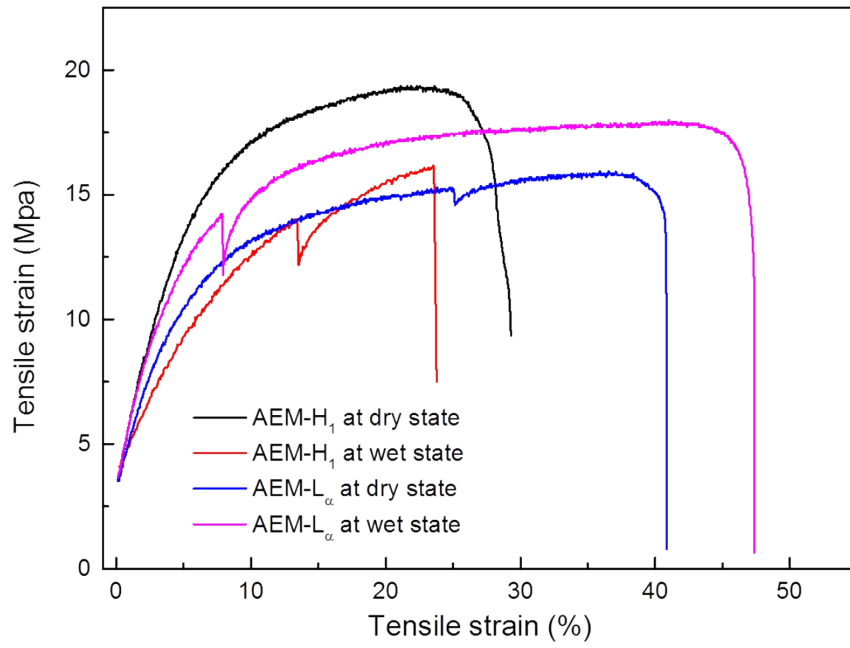


Figure. S4 Stress-strain curves of AEMs with LC nanostructures in wet and dry state.

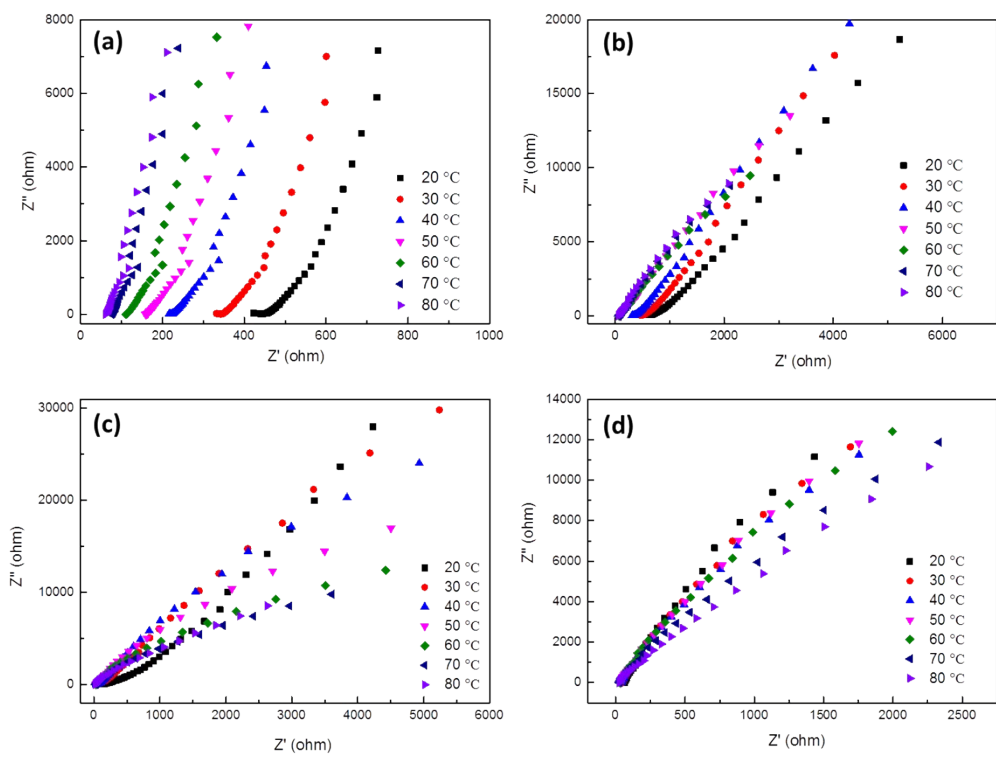
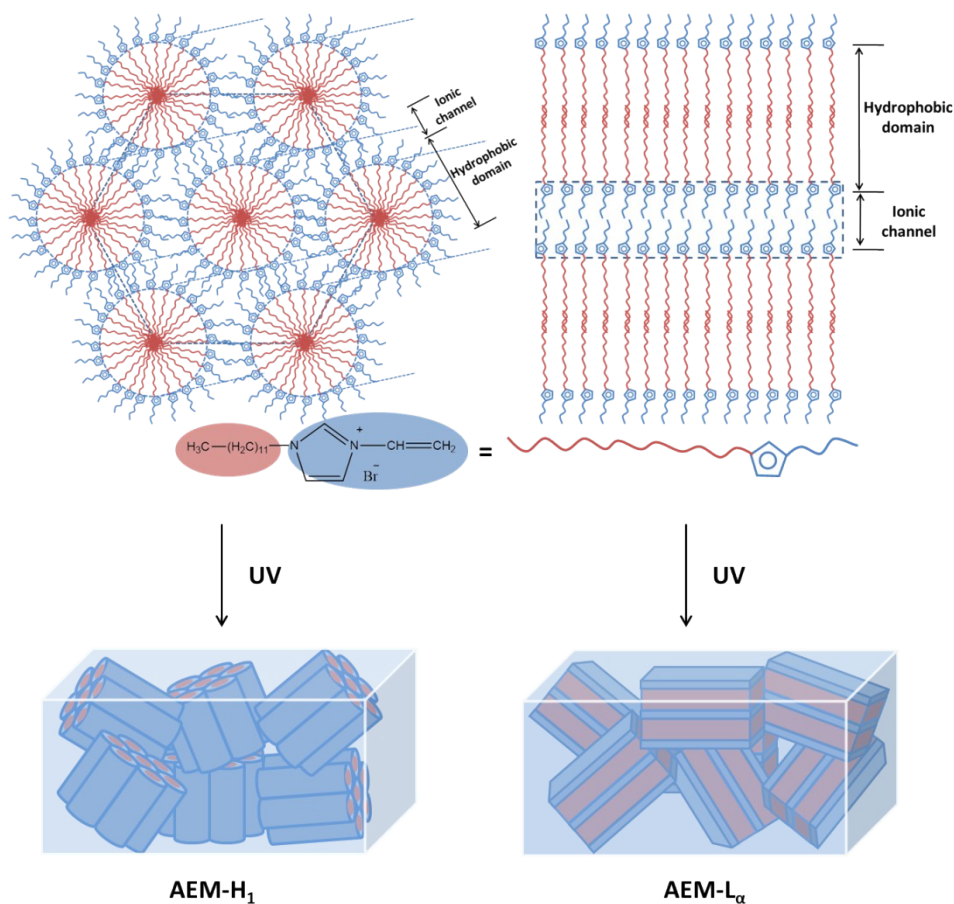


Figure. S5 Nyquist plot changes of AEMs without LC nanostructures AEM-60wt% (a), AEM-80wt% (b) and with LC nanostructures AEM- H_1 (c), AEM- L_α (d) at different temperatures.

Table S2 Water uptake, swelling degree, and conductivities of recently reported AEMs. In each cited paper, we choose the AEMs with similar IEC values for comparison with our results.

IEC (mmol/g)	w.u. (%)	s.d. (%)	conductivity ($\times 10^{-2}$ S/cm)	ref
0.49	13.5	4.2	1.8 (80°C)	1
1.03	8.74	3.91	1.90 (80°C)	This work
1.22	81.9	35.4	2.31 (60°C)	2
1.27	17.05	7.57	2.01 (80°C)	This work
1.35	68	N	4.65 (80°C)	3
1.38	39.6	N	1.59(Cl ⁻ ;90°C)	4
1.41	87.07	24.23	1.77 (60°C)	5
1.43	96.5	25.5	6.77 (80°C)	6
1.52	63	32.4	2.59 (60°C)	7
1.94	61	14	3.0 (30°C)	8
1.95	50.9	32.3	5.62 (70°C)	9
2	92	34	6.6 (23°C)	10

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Scheme S2. Schematic illustrations of hexagonal columnar structure and lamellar structure.

Theory for calculation of structural parameters of liquid crystalline phase

The lattice parameters a_0 of the hexagonal (distance between the centers of adjacent cylinders) and lamellar (lamellar periodicity) liquid crystalline phases were obtained according to Eq. (1) and (2), respectively.^{1,2}

$$q_{(h,k)} = \frac{4\pi}{\sqrt{3}a_0} \cdot (h^2 + k^2 + hk)^{1/2} \quad (1)$$

$$q_{(l)} = \frac{2\pi}{a_0} \cdot l \quad (2)$$

where $q(h,k)$ and $q(l)$ are the scattering vectors corresponding to the scattering peaks observed in the SAXS spectra for the hexagonal and lamellar phase, respectively, h , k , l are Miller indexes, and a_0 is the lattice parameter. From the results

of SAXS, several structural parameters characterizing the structure of the liquid crystalline phase could be calculated as follows.

The volume fraction of the hydrophobic long alkyl chain part in [C₁₂VIM][Br] aqueous mixture system φ_L is calculated by Eq. (3):

$$\varphi_L = \frac{\frac{W_S}{\rho_S}}{\frac{W_S}{\rho_S} + \frac{W_W}{\rho_W}} \quad (3)$$

where W_S and W_W are the weight fraction of [C₁₂VIM][Br] and water, respectively, and ρ_S and ρ_W are the densities of [C₁₂VIM][Br] and water, respectively. The density of [C₁₂VIM][Br] is obtained using a pycnometer, and the reference solvent is ethyl acetate ($\rho = 0.8944 \text{ g}\cdot\text{cm}^{-3}$).³ The densities of [C₁₂VIM][Br] and water are 1.0153 and $0.997 \text{ g}\cdot\text{cm}^{-3}$, respectively.

For hexagonal liquid crystalline, the radius of cylinder unit (d_H) and the thickness of the water channel (d_W) could be obtained using Eq. (4) and (5), respectively.

$$d_H = a_0 \sqrt{\frac{\sqrt{3}\varphi_L}{2\pi}} \quad (4)$$

$$d_W = a_0 - 2r_H \quad (5)$$

For lamellar liquid crystalline, the thickness of hydrophobic domain (d_L) and the thickness of the water channel (d_W) could be obtained using Eq. (6) and (7) respectively.:

$$d_L = a_0 \cdot \varphi_L \quad (6)$$

$$d_W = a_0 - d_L \quad (7)$$

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Ionic Conductivity Measurements. The resistance value of the produced membranes was measured using electrochemical impedance spectroscopy in the frequency of 1-10⁶ Hz using a CHI760D workstation. The temperature was varied from 20 to 80 °C by steps of 10 K. During the conductivity measurement, the membranes were immersed in N₂-saturated deionized water. The ionic conductivity was calculated as

$$\sigma = \frac{l}{RA}$$

Where l (cm) is the interelectrode separation, R (Ω) is the resistance of the membrane and A (cm²) the membrane cross-sectional area (cm²). To prepare the membranes in HCO₃⁻ form, the membranes were immersed in a 1 mol/L sodium bicarbonate solution for 24 h. The above process was repeated three times to ensure a complete displacement.

Ion Exchange Capacity (IEC) Determinations. The membrane ion exchange capacities were measured using a back-titration method. A produced membrane in OH⁻ form was soaked in standard HCl solution (0.1 mol/L, 40 mL) for 24 h. Then the resulting solution was titrated with a KOH standard solution to pH 7. The membrane ion exchange capacities can be obtained as follows

$$IEC = \frac{n_{i(H^+)} - n_{f(H^+)}}{m_{dry}}$$

Where $n_{i(H^+)}$ and $n_{f(H^+)}$ are the initial and final amounts of proton in the HCl solution determined by titration, m_{dry} is the weight of membranes in dry conditions.

The test was conducted at least three times to reach an average value.

Water Uptake and Swelling Degree. The water uptake and the swelling degree of the membranes can be evaluated by weight analysis and linear expansion ratio, respectively. The water uptake of the membrane $w.u.$ (%) and the membrane swelling degree $s.d.$ (%) can be calculated from

$$w.u. = \frac{w_w - w_d}{w_d} \times 100\%$$

$$s.d. = \frac{x_w - x_d}{x_d} \times 100\%$$

Where w_w and x_w are the weight and lengths of the hydrated membranes, respectively, while w_d and x_d are the weight and lengths of the dry membranes, respectively.

Stability Tests. To evaluate alkaline stability of the obtained AEM, the membranes were immersed in N₂-saturated 1 M KOH solution at 80 °C for 500 h. During the testing period, the KOH solution was replaced every 3 days and the change of membrane ionic conductivity was recorded. Accelerated alkaline stability test: The membranes were immersed in 4 M aqueous KOH solution at 80 °C for different time periods. Then the membranes were washed several times with deionized water and dried under vacuum. Chemical structural changes occurring in the membrane during the test were detected by ¹H NMR spectroscopy and FT-IR spectroscopy.

Mechanical Tensile Tests. Mechanical tensile tests were performed using a Universal Testing Machine (Yashima Works Ltd. Co., model RTM-IT) at room

temperature. The crosshead displacement speed of testing was set at the rate of 5 mm/min. The wet or dry membranes with thickness around 0.1 mm and size of 6 mm × 25mm were used for testing.