Supporting Information

Preparation and Application of Piperidinium-Functionalized Cross-Linked Polynorbornene-Based Anion-Exchange Membranes

Haixia Zhang,[a,b,†], Yubing Xiao,[a,b,†] Hesong Guo,[c] Xiang Li,[c] Yu Wang,[a,*], and Wei You[a,b,*]

[a] Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China.

[c] Beijing Cleanway Technology Co., Ltd., Beijing 102611, China.

Corresponding Authors

* Wei You: Email: weiyou@iccas.ac.cn

* Yu Wang: Email: ywang507@iccas.ac.cn

† These authors contributed equally to this work.

Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Fisher Nicolet 6700 FT-IR spectrometer. The measurement was carried out in the range of 4000–650 cm^{-1} with the number of scans per spectrum of 32 and the spectrum resolution of 4 cm^{-1}. Scanning electron microscopy (SEM) imaging (Hitachi S-8020) was performed to observe the morphology. Simplicity®UV was used to afford the ultrapure water (18.2 $M\Omega/cm^2$ at 25 °C).

D-2 Copolymer Synthesis.

The copolymerization was performed in a N_2-filled glovebox. $Pd_2(dba)_3$ (6.9 mg, 0.0075 mmol), PCy_3 (8.4 mg, 0.030 mmol), and LiFABA (22.8 mg, 0.030 mmol) were mixed in toluene (3.0 mL) and stirred for 1 h to obtain the activated catalyst solution. BrNB (2.0 mmol) and DCPD (1.0 mmol) were mixed in toluene (3.0 mL) to obtain the monomer solution. Then, the activated catalyst solution was filtered and injected into the monomer solution and the polymerization was carried out at room temperature for over 12 h. Lastly, the solution was precipitated in methanol and collected by filtration to obtain the copolymer (D-2) in 95 % yield.

Cryo-ultramicrotoming and transmission electron microscope (TEM) observation.

The morphology of the D-2-Pip AEM was characterized by transmission electron microscopy (TEM). Ultrathin sections (<100 nm) were prepared by cryo-ultramicrotomy at –60 °C using a Leica EM UC6 ultramicrotome and mounted on copper grids. Imaging was performed on a Hitachi HT7700 TEM operated at 100 kV.

DSC

Melting (T_m) and glass transition (T_g) temperatures of the studied membranes were determined by using a TA Q200 differential scanning calorimetry (DSC) under a nitrogen atmosphere. The samples were heated under the nitrogen atmosphere from

20 °C to 200 °C, and then cooled to –50 °C, followed by heating to 200 °C. All the heating/cooling rate are 10 °C per minute.

TGA

The thermal stabilities of studied membranes were compared by using a TGA 8000 (PerkinElemer) from 50 °C to 750 °C under a nitrogen atmosphere (20 °C /min).

Ion exchange capacity (IEC):

First, the membranes in the Cl^- form was prepared by immersing in 1 M NaCl solution for 24 h, washed with DI water for three times, dried in vacuo at 60 °C for 24h. The weights of the dried samples were recorded (W_{dry}, g). Then, the samples were immersed in 1 M KNO_3 solution for 48 h to replace Cl^- in aqueous solution. Finally, the Cl^- in the solution was titrated use $AgNO_3$ solution. The concentration and the used volume of the $AgNO_3$ solution were recorded as C_{AgNO3} (mmol L^{-1}) and V_{AgNO3} (L), respectively. The IEC was then calculated according to the following equation as the average of three samples:

$$\mathrm{IEC(mmol\ Cl^-/g)} = \frac{\mathrm{C_{AgNO3} \times V_{AgNO3}}}{\mathrm{W_{dry}}}$$

Water uptake (WU) and swelling ratio (SR)

The studied membranes were saturated via immersion in DI water for 24 h at 25 °C. After removing the residual water with tissue paper, the length and weight of the saturated membrane were quickly recorded (L_{wet} and W_{wet}). The samples were then dried at 60 °C in vacuo until reaching a constant weight, with the length recorded as L_{dry} and the weight recorded as W_{dry}. The water uptake (WU) and swelling ratio (SR) were calculated according to the following equation as the average of three sample:

$$\mathrm{WU} = \frac{W_{\mathrm{wet}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}} \times 100\%$$

$$\mathrm{SR} = \frac{L_{\mathrm{wet}} - L_{\mathrm{dry}}}{L_{\mathrm{dry}}} \times 100\%$$

Conductivity in bulk DI water

The in-plane chloride conductivity of the AAEM sample was measured by four-probe electrochemical impedance spectroscopy (EIS) using an Ivium Vertex.C.EIS electrochemical workstation. The conductivity cell BT-112 was purchased from BekkTeck LLC, and a helpful schematic description of a similar experimental setup has been reported[1]. The membrane samples in the Br^- form were clamped into the cell and the cell was completely immersed in bulk DI water at room temperature during the measurement time. Electrochemical Impedance Spectroscopy (EIS) was performed by imposing a small sinusoidal (AC signal) voltage, 10 mV, across the membrane sample at frequencies between 1 MHz and 1 Hz (scanning from high to low frequencies) and measuring the resultant current response. A Bode plot was used to assess the frequency range over which the impedance approached a constant and the phase angle approached zero. In a Nyquist plot of the data, the high frequency intercept on the real impedance axis was taken to be the resistance of the membrane. The Br^- conductivity was then calculated according to the following equation:

$$\sigma = \frac{L}{R \times W \times d}$$

Where L represents the distance between two electrodes in the BT-112 Membrane Conductivity Cell (0.425 cm); R is the membrane resistance; W and d are the width and thickness of the samples, respectively.

In situ de-carbonation under humidified conditions

A similar set-up was adopted from the literature to measure "true hydroxide conductivities" under humidified conditions.[2, 3] The samples in the HCO_3^- form were clamped into the abovementioned BT-112 Membrane Conductivity Cell, which was located in the corresponding Scribner Associates (SAI) and connected with an FD-HG temperature and humidity controller (Furande Experimental Equipment Co., Ltd., Suzhou, China). The HCO_3^- conductivity was measured for two hours to ensure the stabilization of the membrane in the temperature and humidity atmosphere. Through

the external electrodes, a constant direct current of 200 μA was applied to the membrane under nitrogen flow (100 mL/min) at 40 °C and relative humidity (RH) of >98%. Every 10 min, the ionic resistance of the membrane was measured using the abovementioned 4-probe EIS technique, and the in-plane conductivity was then calculated using the equation:

$$\sigma = \frac{L}{R \times W \times d}$$

Where L represents the distance between two electrodes in the BT-112 Membrane Conductivity Cell (0.425 cm); R is the membrane resistance; W and d are the width and thickness of the samples, respectively.

The anion conductivity was continuously measured until conductivity reached a stable value (<0.1 kΩ change in resistance of 3 h). The operating temperatures of the testing cell and the feeding gas were increased to 50 °C, 60 °C, 70 °C and 80 °C while maintaining RH, and the conductivities were continuously measured.

Mechanical properties

The tensile tests were performed on an Instron 3365 universal testing machine. D-2-Pip aqueous AEM was cut into Dumbbell shape (the length and width of the rectangle area in the Dumbbell bars are 10 mm and 3 mm, respectively), and the thickness was measured separately before the test. The mechanical properties of the samples were assessed with a strain rate of 2 mm min^{-1}. All the membranes were tested upon 5 duplicates.

Alkaline stability

The as-prepared membranes were soaked in an aqueous 1 M KOH solution at 80 ºC. Every seven days, the samples were washed with DI water several times to remove the residual K^+ and OH^- ions, and then immersed in an aqueous 1 M $NaHCO_3$ solution for 24 hours. After washing with DI water, HCO_3^- conductivities of the samples were measured according to the abovementioned method, and HCO_3^- conductivities were obtained as the average of three samples.

Dynamic mechanical analysis (DMA)

The measurements were performed on a TA Instruments DMA 800. The D-2-Pip AEM was cut into strip-shaped samples measuring 20 mm in length, 5 mm in width, and approximately 130 μm in thickness. The samples were heated from 0 ºC to 90 ºC at a rate of 3 °C/min under the nitrogen atmosphere.

SAXS

The small angle X-ray diffraction (SAXS) experiments at 21.7 °C /19.9 °C were conducted on a Xeuss 2.0 SAXS system (Xenocs SA). X-ray radiation with a wavelength of 1.5418 Å was generated with a Cu K_α X-ray source (GeniX3D Cu ULD). The sample-to-detector distances were 2501 mm for the SAXS experiments, respectively. The 2-D SAXS patterns were subsequently collected for an image acquisition time of 1200 s by using a semiconductor detector (Pilatus 300k, DECTRIS) with a resolution of 487×619 pixels (pixel size of 172×172 μm^2). Both the obtained SAXS patterns were corrected for detector noise, air scattering, and sample absorption. 1-D intensity profiles were integrated from the background-corrected 2-D SAXS patterns.

Alkaline water electrolysis

The MEA was prepared through the catalyst-coated substrate (CCS) technique. The anode catalyst was nickel–iron-based electrocatalyst[4], while the cathode catalyst was Pt/C and it was dispersed in the presence of CLi-01 ionomer on the carbon paper gas diffusion layer. A 1 cm × 1 cm piece of HER catalyst layers and a 1 cm × 1 cm piece of OER catalyst layers were used to assemble in a Mainz-01 water electrolyzer cell (Anhui Mainz Laboratory Equipment Co., Ltd, Hefei, China) with membranes. A SS-L3010SPD battery test station was purchased from Bufan Electronics Co., Ltd, Dongguan, China to control the electrolyzer. 0.1 M, 0.5 M or 1 M KOH were studied for their AEMWE performance by using polarization curves with an applied voltage

from 1.3 V to 2.2 V at 60 °C. Moreover, 1 M KOH were studied for their AEMWE performance by using polarization curves with an applied voltage from 1.3 V to 2.2 V at 40 °C, 60 °C or 80 °C Long-term durability tests were conducted with a 1 M KOH aqueous solution at 60 °C, using a galvanic mode of 1 A cm^{-2}.

XPS

XPS measurements were performed on a VG ESCALAB 250XI spectrometer. The D-2-Pip AEMs was immersed in 1 M $NaHCO_3$ solution for 12 h to exchange the Br^- with HCO_3^-, thereby eliminating potential interference from bromine during subsequent XPS characterization.

Table S1. The influence of different piperidine concentrations and reaction times on conductivity of D-2-pip membranes

	0.5 h	1 h	2 h	4 h	6 h	12 h
$\sigma^{[a]}$ (Br^-, mS/cm) at 40 °C			N.A.			10.5
$\sigma^{[a]}$ (Br^-, mS/cm) at 60 °C			N.A.			14.4
$\sigma^{[b]}$ (Br^-, mS/cm) at 80 °C	10.5	11.6	12.5	12.8	N.A.	16.7

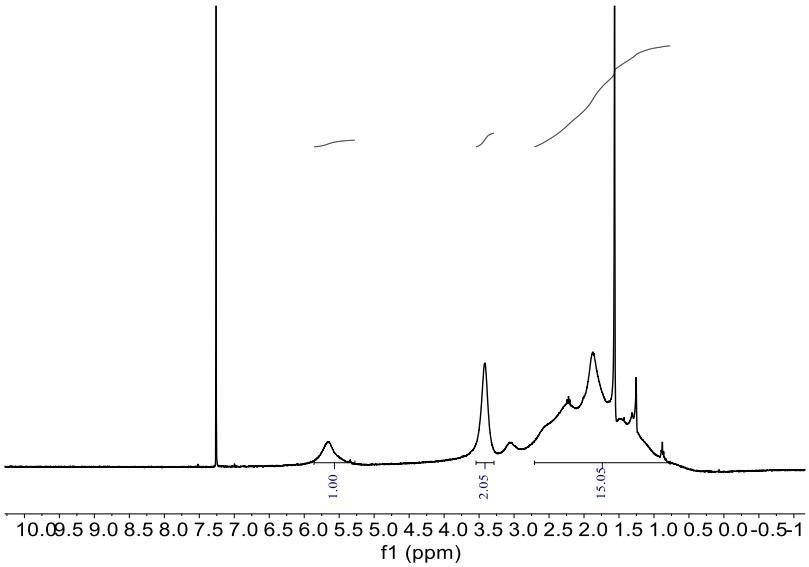
[a] The concentration of the 1-methylpiperidine solution used was 30 vol%. [b] The concentration of the 1-methylpiperidine solution used was 5 vol%.

Table S2. Performance comparison between D-2-Pip AEM and other membranes.

	Stress-at-break (MPa)	Strain-at-break (%)	σ at 80 °C (OH^-, mS/cm)
D-2-Pip	9±5.5	38±8.5	138
x-PFTP-DP-C10-10[5]	86	34	165
FPAP-3[6]	84	40	148

Table S3. The XPS of **D-2-Pip** AEM

	Br	C	N	O
Atomic/%	0.1	85.49	2.88	11.53



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190 **Figure S1.** The ^{1}H NMR of **D-2**

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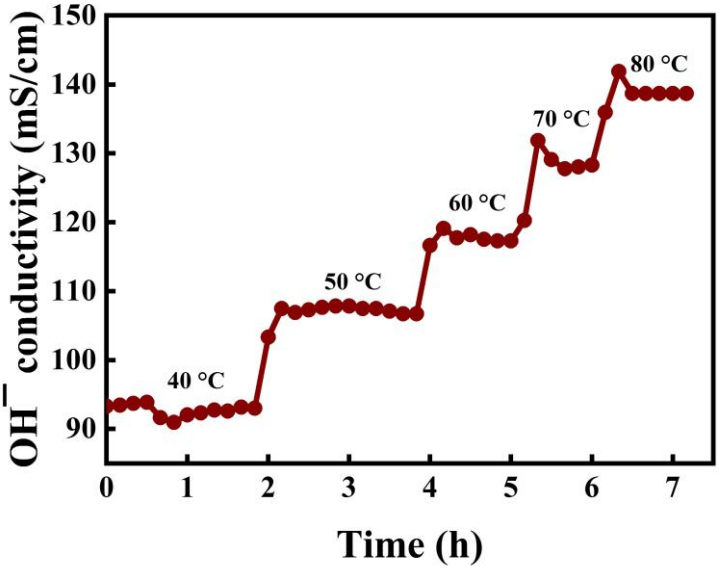

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195 **Figure S2**. Hydroxide conductivities of D-2-Pip AEM

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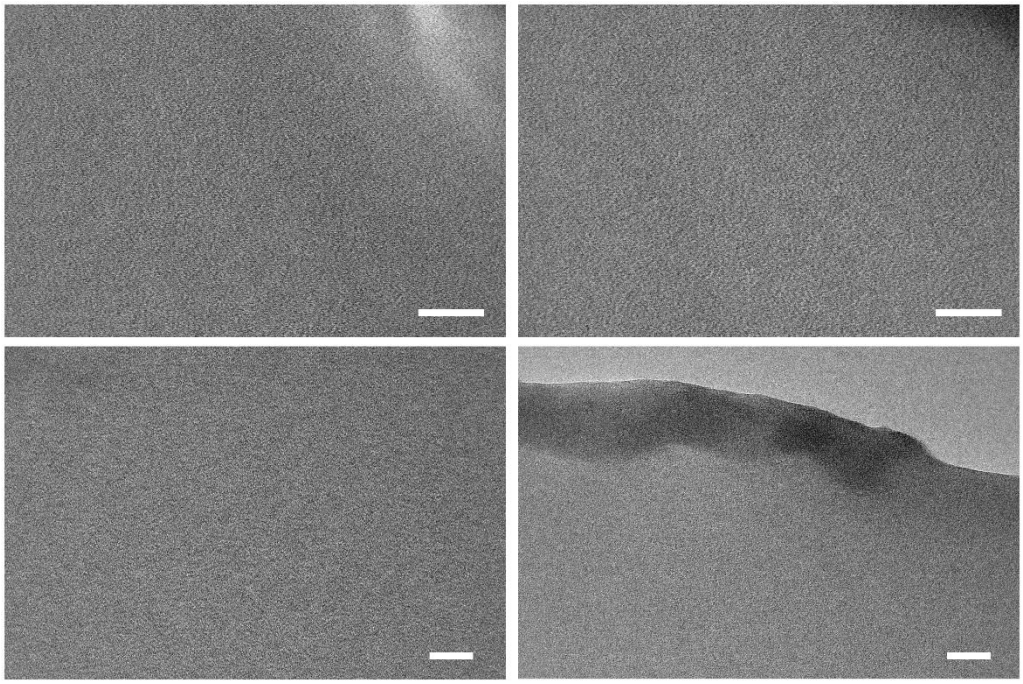

Figure S3. TEM images of **D-2-Pip** membranes obtained at different locations. Scale bar represents 50 nm in length.

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