Supporting Information

Piperidinium-functionalized Anion Exchange Membranes and its application in Alkaline Fuel Cell and Water Electrolysis

Xiaomeng Chu,[ab] Yan Shi, [de] Lei Liu,[ac]* Yingda Huang, [a]* and Nanwen Li [ab]*

[a]State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, China.

[b]Center of Materials Science and Optoelectronics Engineering，University of Chinese Academy of Sciences, Beijing 100049, China.

[c]Key Laboratory of Functional Molecular Solids, Ministry of Education, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, China.

[d]Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, 510640, China

[e]Key Laboratory of New and Renewable Energy Research and Development of Guangdong province, Guangzhou, Guangdong 510640, China

Corresponding author: L. Liu (liulei@ahnu.edu.cn); Y. Huang (huangyd@sxicc.ac.cn); N. Li (linanwen@sxicc.ac.cn)

Experiment Section

Materials. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was purchased from Sigma-Aldrich with a molecular weight of 20,000 g/mol. 2,2'-azobis-isobutyronitrile (AIBN) was recrystallized from methanol twice. 1-Methylpiperidine, *N*-bromosuccinimide (NBS), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA), propargyl bromide, 6-chloro-1-hexyne and copper bromide (CuBr) were purchased from Sigma-Aldrich and used as received. Bromomethylated PPO (PPO-Br) and corresponding azided PPO copolymer (PPO-N_3) with the degree of functionalization (DF) of 30% was synthesized according to the previous reports. [1,2]

Synthesis of 1-Methyl-1-Propargyl Piperidinium Bromide Salt (PPi). Propargyl bromide (5 mL, 63 mmol), 1-methylpiperidine (9.3 mL, 76 mmol), and 50 mL toluene were placed into a 100 mL round-bottomed flask. The mixture was stirred at room temperature for 48 h. The white precipitate was filtered, washed with toluene, and dried in a vacuum with the yield of 95%.

Synthesis of 1-Methyl-1-Hexynyl Piperidinium Chloride Salt (HPi). 6-Chloro-1-hexyne (1 mL, 8.3 mmol), 1-methylpiperidine (1.2 mL, 9.8 mmol) and 10 mL acetonitrile were added to a 100 mL round-bottomed flask, and then the solution was stirred at 80 °C for 24 h under nitrogen atmosphere. A white solid was obtained after the mixture was precipitated in a large amount of diethyl ether. The product was filtrated, washed with ether several times, and dried in vacuum at room temperature (yield: 85%).

Synthesis of Piperidinium-Functionalized PPO Copolymers by Click Reaction. Anion conductive PPO copolymers containing side-chain-type or long side-chain-type piperidinium (SCPi or LSCPi) were synthesized by "click" reaction between PPO-N_3 copolymer and piperidinium-functionalized alkyne (PPi or HPi), respectively. Typically, PPO-N_3 (1.56 g, DF=30%, 3.21 mmol azide group), PPi (0.84 g, 3.86 mmol), PMDTEA (0.40 mL, 1.93 mmol), CuBr (0.14 g, 0.96 mmol), and NMP (16 mL) were placed in to a Schlenk flask. The flask was degassed by three freeze-pump-thaw cycles, then left under vacuum, and finally placed in a 50 °C bath for 12 h. After cooling to room temperature, the mixture was precipitated in 200 mL water, and then washed with water three times. The obtained SCPi copolymer was filtered and dried under vacuum at 60 °C for 24 h (yield: 92%).

The LSCPi copolymer was synthesized according to the above procedure by replacing the PPi with HPi monomer during the click reaction.

Synthesis of BPi Copolymer. PPO-Br (1.00 g, DF=30%, 1.91 mmol bromine group) and 1-methylpiperidine (0.20 mL, 2.30 mmol) was dissolved in 10 mL NMP, and the solution was stirred at 60 °C for 24 h. After cooling to room temperature, the mixture was precipitated in 100 mL water, and then washed with water three times. After filtration and drying under vacuum at 60 °C for 24 h, BPi copolymer was obtained with the yield of 95%.

Membrane Preparation and Ion Exchange. Anion-conductive copolymers in bromide or chloride form were dissolved in NMP (10 wt%) and cast on a flat glass plate. The membranes with the thickness of 50±5 μm was obtained after drying at 80 °C for 12 h and then at 80 °C under vacuum for 24 h. Membranes in hydroxide and bicarbonate form were obtained by treating the membranes in 1 M NaOH or 1 M $NaHCO_3$ at room temperature for 48 h, then washed with deionized water until neutral, and finally placed in deionized water which was degassed with argon gas for 30 min.

Characterization and Measurements. ^{1}H NMR spectra were obtained from a BrukerDPX-400 spectrometer at room temperature using $CDCl_3$ or DMSO-d_6 as solvent. Fourier transform infrared spectroscopy (FTIR) was measured on a PE-1710 spectrometer from 4000 to 400 cm^{-1} with a 4 cm^{-1} resolution in 64 scans using polymer thin films. The thermal stability of membranes was determined by thermo-gravimetric analysis (TGA) (Perkin-ElmerTGA-7) under a N_2 flow with the heating rate of 10 °C/min. Tensile measurements of PPO AEMs in the dry state were carried out with an CMT-4502 (MTS SYSTEMS CO., LTD., CHINA) mechanical testing instrument at a cross head speed of 5 mm·min^{-1}. To measure the atomic force microscopy (AFM) images of the ionomers, the obtained ionomers solution in DMF (1 wt%) was sprayed onto a pristine mica substrate. After the evaporation of solvent at 60 °C, AFM tapping-mode height profiles were collected with a Veeco Multimode V.

Water uptake (WU) of membranes in hydroxide form was measured at different temperature. Before dried at 60 °C in a vacuum for 12 h, the membrane was immersed in water at given temperatures for 24 h, and then weighed on an analytical balance until a constant mass was obtained. The water uptake of membrane was calculated using the following equation.

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

where w_{wet} and w_{dry} are the mass of fully hydrated and dried membrane, respectively.

The swelling ratio was calculated based on the equation,

$SR = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\%$, where L_{wet} and L_{dry} are the length of the hydrated and dry membranes at 20 °C, respectively.

The hydroxide number (λ), defined as number of absorbed H_2O per cation group tethered on the polymer backbone, was calculated as

$$\lambda = \frac{(w_{wet} - w_{dry}) \times 1000}{IEC \times w_{dry} \times 18}$$

The titrated gravimetric ion exchange capacity (*IEC*) of membranes in bromide salt form was determined by Mohr titrations. Membranes were first dried under vacuum for 24 h at 80 °C and weighted before immersion in 100 mL 0.1 M $NaNO_3$ for 24 h, and then the solution was titrated with a standardized $AgNO_3$ solution using potassium chromate as indicator. The IEC_{titr} was calculated from the equation, $IEC_{titr} = \frac{C \times V}{W_{dry}}$, where V and C is the volume of consumed $AgNO_3$ solution and concentration of $AgNO_3$ solution, respectively. w_{dry} is the weight of dried membrane.

The ionic conductivity (σ, mS/cm) of membranes was calculated from the equation, $\sigma = d/LWR$ (d is the distance between reference electrodes, and L and W are the thickness and width of the membrane, respectively). R is the membrane impedance, which was measured in a two-probe cell using an impedance/ gain-phase analyzer (Bio-Logic VSP-300, FR) in the frequency range from 100 mHz to 100 kHz. The ionic conductivity measurement was carried out under fully hydrated conditions with the cell immersed in water which was degassed and blanketed with flowing Ar gas.

Alkaline stability of membranes was evaluated at 60 and 80 °C in 1 M aqueous NaOH. After pre-determined times, the membranes were washed with deionized water several times until neutral, and then the change in ionic conductivity was monitored.

Fuel Cell Test. To fabrication of membrane/electrode assemblies (MEA), the Pt/C catalysts (40 wt%, Johnson Matthey), deionized water, 1-propanol, and ionomer solution (AS-4, 5 wt%, Tokuyama corporation, Japan) were mixed using magnetic stirring and ultrasonication. The well-dispersed catalyst ink was sprayed onto the both sides of the AEM to form the anode and cathode. The load amounts of catalyst and ionomers is 0.5 mg/cm^2 and 20 wt%, respectively. The catalyst-coated membrane was sandwiched between two sheets of carbon paper (HCP120, HESEN, Shanghai, China) to prepare the MEA.

The MEA with electrode size of 5 cm^2 was mounted in a single cell test system (Smart2 PEM/DM, WonATech, Korea). The fuel cell performance was tested at 60 ℃ with a flow rate of 200 sccm for both H_2 and O_2 under fully humidified conditions with no backpressure. After full activation under potentiostatic mode, the polarization curve was measured. The lifetime test was conducted when a current density of 100 mA/cm^2 was applied to the fuel cell, and the cell voltage as a function of time was recorded.

Water Electrolysis Test. For fabrication of MEA for water electrolyzer, both anode and cathode were prepared by catalyst-coated substrate (CCS) method. Anode was prepared as follows: IrO_2 powder (Shanxi Kaida, China) were mixed with de-ionized water and isopropanol. Then PTFE emulsion were added. After ultra-sonicated for 30 min, the catalyst ink was put in the water bath at 85 ℃ under stirring for evaporating water and isopropanol. The obtained paste was coated on platinized porous Ti plate. The ionomer solution (5 wt% LSCPi or SCPi copolymer in ethanol) was also sprayed on the surface of catalyst layer, and the loading of dry ionomer and IrO_2 in anode was 1.5 and 8 mg/cm^2 respectively. For cathode preparation, Pt/C (40 wt%, Johnson Matthey), de-ionized water, isopropanol, and PTFE emulsion (6 wt% in the cathode) was mixed. Then as-prepared ink was ultra-sonicated for 30 min, and sprayed on the carbon paper (HCP120, HESEN, Shanghai, China) with Pt loading of 0.4 mg/cm^2. The ionomer solution was also sprayed on the surface. (1.5 mg/cm^2). The area of electrode was 8 cm^2. Finally, two electrodes and membrane were immersed in 1M NaOH for 24h for ion exchange, and rinsed with the de-ionized water several times before using.

The electrolyser was assembled by sandwiching the membrane between cathode and anode. A platinized porous Ti plate was used in cathode as the current collector. The electrochemical test was operated in de-ionized water both in anode and cathode, the temperature was maintained at 50 °C. Polarization curves were obtained by measuring the cell voltages at different current density, and the durability was evaluated under a constant current of 200 mA/cm^2 at 50 °C.

References

1. N. Li, M. D. Guiver and W. H. Binder, *ChemSusChem*, 2013, **6**, 1376-1383.

2. L. Liu, S. He, S. Zhang, M. Zhang, M. D. Guiver and N. Li, *ACS Appl. Mater. Interfaces*, 2016, **8**, 4651-4660.

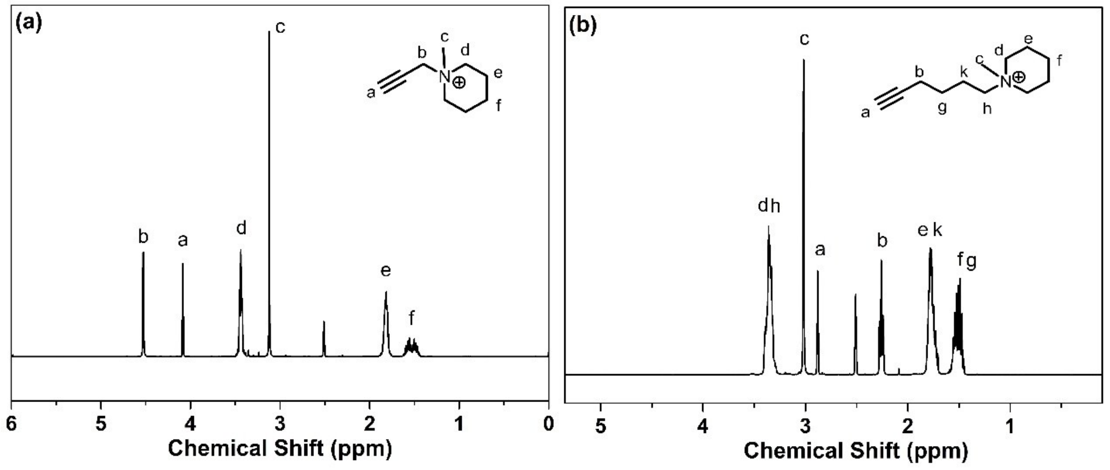

Fig. S1 ^{1}H NMR spectra of (a) PPi and (b) HPi monomers in DMSO-d_6.

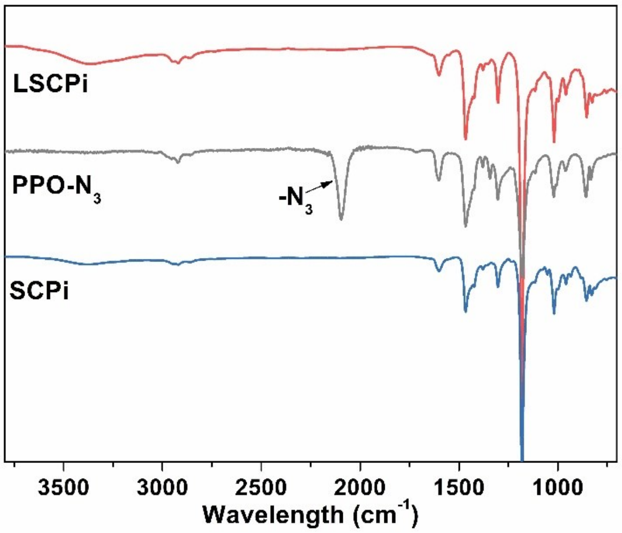

Fig. S2 FT-IR spectra of PPO-N$_3$, SCPi and LSCPi copolymers.

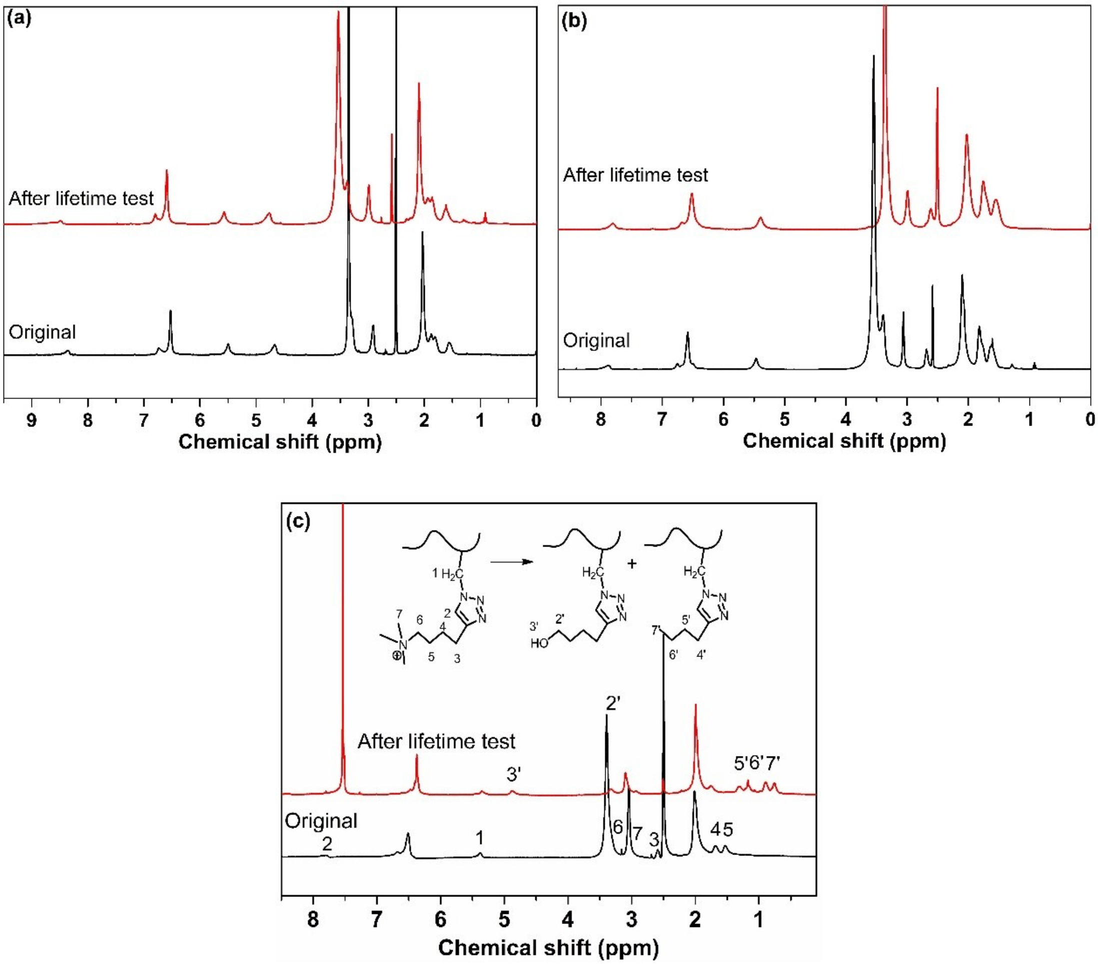

Fig. S3 ^{1}H NMR spectra of (a) SCPi, (b) LSCPi and (c) LSCQA membrane before and after fuel cell durability test.

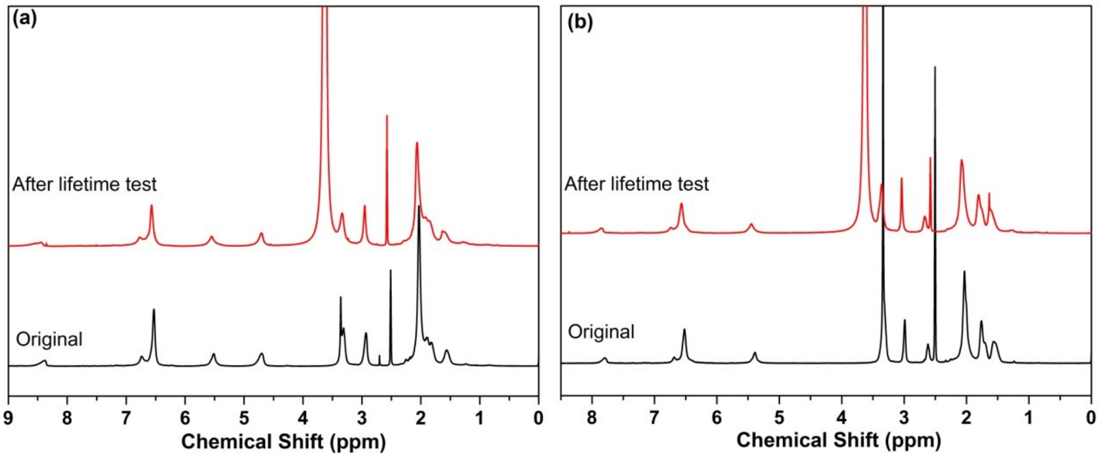

Fig. S4 ^{1}H NMR spectra of (a) SCPi and (b) LSCPi membrane before and after water electrolysis durability test.