Supporting Information for

Highly Hydroxide Conductive Ionomers with ORR Catalytic Fullerene Functionalities

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Materials and Methods.

N-methylglycine (sarcosine, 98%) and paraformaldehyde (96%) were purchased from Energy Chemical (Shanghai, PR China) and used as received. Fullerene-C₆₀ (99.9%) was bought from Aladdin Industrial Corporation (Shanghai, PR China) and used as received. Commercialized brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) was utilized as the polymer scaffold and it can be easily prepared in the lab from commercial poly(2,6-dimethyl-1,4-phenylene oxide) according to the reported procedure¹. Other chemicals are bought from domestic chemical works and used as received.

N-methyl pyrrolidine-C₆₀ (MPC₆₀). MPC₆₀ was synthesized according to a reported procedure². Fullerene (C₆₀, 0.1011g, 0.14 mmol), paraformaldehyde (0.0220g, 0.67 mmol) and sarcosine(0.0274g, 0.28 mmol) were dissolved in toluene (130 ml). The resulting solution was heated at 120 °C for 2 h. On cooling, the solvent was removed under reduced pressure. MPC₆₀ was obtained as brown powder by silica gel chromatography (with toluene as eluent). The purified MPC₆₀ was dissolved in CS₂ and CDCl₃ for NMR characterization.

Quaternized n-methyl pyrrolidine- C_{60} (QMPC₆₀). To a solution of MPC₆₀ in toluene, excess amount of methyl iodide was added. The resulting solution was kept

at room temperature in dark for 48h. $QMPC_{60}$ would precipitate once formed. The solution was then filtered and $QPMC_{60}$ was collected. It was dissolved in d6-DMSO for NMR characterization. It should be noted that in some reports DMSO was used as solvent for the quaternization of MPC_{60} . However, we found that DMSO would react with CH_3I and formed a white solid which we assumed was trimethyl-sulfoxonium iodide. Therefore, toluene was employed here as solvent.

Preparation of BPPO-MPC₆₀ anion exchange membrane. To prepare the BPPO-MPC₆₀ anion exchange membrane, BPPO and MPC₆₀ (mole ratio= 5:1) were dissolved in a large amount of toluene and the resulting solution was stirred at 50 °C for 96h. On cooling, the solvent was removed under reduced pressure using rotatory evaporator. The solid residue was then dissolved in NMP and centrifuged. The top liquid solution was then cast on a clean glass plate and heated at 60 °C for 48h. The obtained membrane was then peeled off for further characterization. The weight percentage of MPC₆₀ in the final membrane is around 22.7wt%.

Nuclear magnetic resonance (NMR). ¹H-NMR spectra of the synthesized MPC₆₀ and QMPC₆₀ was attained on a Bruker AscendTM 400M spectrometer.

Cyclic voltammetry (CV). CV experiments were conducted on a glassy carbon (GC) electrode. The GC electrode was polished using 0.05 μ m alumina slurry, rinsed with deionized water, then ultrasonically treated in water for 30 s and washed. This procedure was repeated three times. A catalyst ink was prepared by adding 2mg of MPC₆₀ or QMPC₆₀ into 1 mL ethanol containing 10 μ L 5% Nafion (D520, Dupont Inc., USA). Ten microliters of the catalyst ink was then deposited on the GC electrode (with a surface area of 0.196 cm²). Electrochemical activities was conducted on a CHI 660D potentiostat in a three-electrode electro-chemical cell with a platinum counter electrode, an Ag/AgCl reference electrode and with 0.1 M KOH as the electrolyte. Electrolyte was saturated with oxygen prior to each experiment. O₂ flow over the electrolyte was maintained during the measurements to ensure O₂ saturation. The scan rate was 50 mV/s, and at least 10 cycles were performed before collecting the data.

Linear sweep voltammetry (LSV). LSV measurements of the catalysts were conducted on a rotating disk electrode (RDE) (Pine Research Instrumentation). The

working electrode was prepared by the same procedure as for CV. The scan rate of working electrode was 10 mV/s with rotating speed of 1600 rpm. To compare the efficiency of the catalyst in this work, commercial Pt/C catalyst was also characterized using the same method.

Ion exchange capacity (IEC) titration. IEC value was measured by the Mohr method. Typically, the membrane samples (in Cl⁻/Br⁻ form) were immersed in aqueous Na₂SO₄ solution (0.3 mol/L). The Cl⁻/Br⁻ ions released from the membranes were titrated with aqueous AgNO₃ solution (C_{AgNO_3} =0.01 mol/L) using K₂CrO₄ as an indicator. The IEC values were calculated from the amount of AgNO₃ consumed (V_{AgNO_3}) and the weight of dry membrane samples (m_{dry}).

$$IEC(\text{mmol/g}) = \frac{V_{AgNO_3} \times C_{AgNO_3}}{m_{dry}}$$
(S1)

Ionic conductivity (σ). Measurement of ionic conductivity was conducted on the four-point probe technique (Autolab[®] PGSTAT 30) using galvanostatic mode with an a.c. current amplitude of 0.1 mA and a frequency range of 1 MHz-100 Hz. Bode plots were used to determine the frequency region over which the magnitude of impedance was constant. Ionic resistance was then obtained from the associated Nyquist plot. The membrane sample being studied was set into a Teflon cell where it was in contact with two current collecting electrodes and two potential sensing electrodes (the distance between electrodes was 1cm). The cell was completely immersed in deionized water and the impedance spectrum was collected. This was done quickly to minimize the potential error caused by reaction of the hydroxide ions in the membrane with dissolved carbon dioxide. The ionic conductivity was calculated according to the following equation.

$$\sigma = \frac{L}{RWd}$$
(S2)

Where, R is the membrane resistance, L is the distance between potential sensing

electrodes. W and d are the width (here 1 cm) and thickness of the membrane respectively.

Thermal gravimetric analysis. The thermal stabilities of the samples were measured using a TGA Q5000 (TA Instruments) thermo-gravimetric analyzer under nitrogen atmosphere and with a heating rate of 10 °C/min over temperature range of 25 °C to 800 °C.



Figure S1 NMR spectroscopy of N-methyl pyrrolidine- C_{60} (MPC₆₀).A mixture of CS₂/CDCl₃ (2:1, v/v) is used as solvent. ¹H-NMR (400 MHz): 2.99 (s, 3H), 4.38 (s, 4H)².



Figure S2 Image of the anion exchange membrane made from BPPO-MPC₆₀ anion exchange ionomers. Photo is taken by Canon Powershot[®] G15 camera. The thickness

of the membrane is around 30 μ m.



Figure S3 Cyclic voltammetic curve of N-methyl pyrrolidine-C60 (MPC60) in a mixture of 1M MeOH and 0.1 M KOH.



Figure S4 Quaternization of N-methyl pyrrolidine-C₆₀ (MPC₆₀)



Figure S5 NMR spectroscopy of quaternized N-methyl pyrrolidine- C_{60} (QMPC₆₀). DMSO-d6 is used as solvent.



Figure S6 Linear sweep voltammetry (LSV) curves of the MPC₆₀ and QMPC₆₀ compared with Pt/C (20%) electrocatalyst by RDE in O₂-saturated 0.1 M KOH solution



Figure S7 Thermal gravimetric analysis of the BPPO-MPC₆₀ ionomer from room temperature to 800 $^{\circ}$ C under N₂ atmosphere at a heating rate of 10 $^{\circ}$ C/min



Figure S8 FTIR spectra of BPPO and BPPO-MPC60 membrane

-	L	0	1 5	U	
Temperature(°C)	40	50	60	70	80
Water Uptake	3.62%	2.92%	2.59%	3.11%	3.65%

temperature.	The ion	exchange	capacity is	0.62 mmol/g
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Reference:

- (1) Tongwen, X.; Weihua, Y. J. Membr. Sci. 2001, 190, 159.
- (2) Maggini, M.; Scorrano, G.; Prato, M. J. Am. Chem. Soc. 1993, 115, 9798.