

Supplementary Information

How does a Small Structural Change of Anode Ionomer Make a Big Difference in Alkaline Membrane Fuel Cell Performance?

Eun Joo Park,^{a,†} Sandip Maurya,^{a,†} Albert S. Lee,^a Daniel P. Leonard,^a Dongguo Li,^a Jong Yeob Jeon,^b Chulsung Bae,^b and Yu Seung Kim^{a,*}

^a MPA-11, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

^b Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, Troy, New York 12180, USA

Experimental Methods

Materials. All reagents and solvents were purchased from Sigma Aldrich, Oakwood Chemicals, Acros, and Strem Chemicals and were used without further purification. 7-Bromo-1,1,1-trifluoro-2-heptanone was prepared according to a procedure in the literature.¹ BPN was prepared according to our previous study.²

Instrumentation. ¹H NMR spectra were collected from Bruker 500 NMR spectrometer at room temperature, and chemical shifts were referenced to the solvent residue peaks of CDCl₃ and DMSO-d₆ at 7.26 ppm and 2.50 ppm, respectively.

Synthesis of o,o'-bitolyl. In a 250 mL of round bottom flask, 2-bromotoluene (5.1 g, 30 mmol), 2-tolylboronic acid (4.9 g, 36 mmol, 1.2 equiv.), tetrakis(triphenylphosphine)palladium (1.7 g, 1.5 mmol, 5 mol%) were dissolved in anhydrous tetrahydrofuran (100 mL), and aqueous potassium carbonate solution (2 M, 60 mmol, 2.0 equiv.) was added. The mixture was refluxed with stirring for 24 h. The reaction was cooled to room temperature. Ethyl acetate (50 mL) and water (50 mL) were added, and the organic layer was washed with water (2 × 50 mL) and dried over MgSO₄. The colorless oil was obtained after column chromatography using hexane (R_f=0.5). ¹H NMR (CDCl₃): δ (ppm) 7.31-7.26 (6H, m), 7.16-7.14 (2H, d), 2.10 (6H, s).

Synthesis of o-BTBr polymer. A mixture of o,o'-bitolyl (0.50 g, 2.75 mmol), 7-bromo-1,1,1-trifluoro-2-heptanone (0.81 g, 3.29 mmol, 1.2 equiv.), dichloromethane (3.0 mL), and a magnetic stirring bar were placed in a 25 mL round-bottom flask and cooled in an ice bath. Trifluoromethanesulfonic acid (3.0 mL) was added in one portion, and the mixture was stirred at room temperature for 12 hours under nitrogen. The resulting dark-brown mass was poured into methanol, and the precipitate formed was filtered and washed with warm methanol. After drying

under vacuum, 1.06 g of white solid was obtained (95% yield). ^1H NMR (CDCl_3): δ (ppm) 7.20-7.05, 3.31, 2.37, 2.01, 1.78, 1.41, 1.25.

Synthesis of o-BTN polymer. Trimethylamine aqueous solution (1.0 mL) was added to the solution of *o*-BTBr (1.2 g) in THF (2.4 mL) then stirred at room temperature. The ionic polymer was precipitated after 24 hours, and deionized water (1.0 mL) was added to the solution to dissolve the precipitate. A sequence of addition of trimethylamine and dissolution of the precipitate with addition of water while stirring at room temperature were repeated again. Upon the evaporation of the volatiles, the ionic polymer *o*-BTN was precipitated by adding ether, filtered, and dried under vacuum (98% yield). ^1H NMR ($\text{DMSO-}d_6$): δ (ppm) 7.30-6.97, 3.25, 3.04, 2.37, 1.93, 1.60, 1.25.

Synthesis of TEA-o-BTN polymer. Triethylamine (0.50 mL) was added to the solution of *o*-BTBr (0.50 g) in *N,N*-dimethylacetamide (1.0 mL) then stirred at 80 °C for 12 h. After cool to room temperature, the ionic polymer TEA-*o*-BTN was precipitated by adding ether, filtered, and dried under vacuum (98% yield). ^1H NMR ($\text{DMSO-}d_6$): δ (ppm) 7.32-6.97, 3.20, 3.05, 2.51, 1.96, 1.51, 1.28, 1.14.

Ionomer characterization. The ion exchange capacity (IEC) values of the ionomers and the membrane were calculated from ^1H NMR spectra, using the integral ratio of the methyl proton peak (2.01 ppm) and the trimethylammonium proton.

Water uptake. Ionomers in OH^- form was immersed inside the water at room temperature for 24 h and weighed right after blotting the excess water from the surface (W_{wet}). The ionomers were then dried at 80 °C under vacuum for 12 h and weighed again (W_{dry}). Water uptake (%) was then calculated from:

$$\text{Water uptake (\%)} = [(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}] \times 100\%.$$

Ion conductivity. The solution ionic conductivity of the ionomers was measured with the AC electrochemical impedance spectroscopy (Solartron 1260 gain phase analyzer) using custom liquid cell of 1 π cm diameter stainless steel electrode area with 1 cm distance apart encased in polypropylene casing. All samples were prepared at $[QA^+] = 0.16$ M in anhydrous DMSO to mitigate solvent effects.

H₂ diffusion coefficient measurement using pulse-field-gradient, PFG-¹H NMR. A 2 wt% ionomer dispersion in DMSO-*d*₆ was dried over anhydrous MgSO₄ to eliminate all water content which may limit H₂ solubility in DMSO. After syringe filtering this solution into a dry glass vial, the solution was degassed by sonication for 5 min and ultra-high purity H₂ gas was directly bubbled into the solution for 30 min. This solution was immediately injected into a standard glass NMR tube and hermetically sealed. For pulse-field gradient ¹H NMR experiments, a 500 MHz Bruker Advance instrument was used. The experimental parameters used followed a literature procedure.³ Briefly, the 90° pulse was recalibrated at each temperature, with the total inverse-recovery pulse sequence of: relaxation delay $\rightarrow \pi \rightarrow \tau \rightarrow \pi/2 \rightarrow$ acquire for variable delays between $\tau = 0.1$ -50 μ s in increments of 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 30, 40, and 50 μ s. Exponential fit of the logarithmic normalized peak area, S, for H₂ at 4.5 ppm plotted as function of gradient pulse area, $q^2 = \gamma^2 g_z^2 \delta^2$, where γ is the magnetogyric ratio of hydrogen, g is the gradient pulse, and δ is the gradient pulse width, gave the diffusion coefficients through the Stejskal-Tanner equation: $S = S_0 e^{-Dq^2\Delta}$.

Microelectrode experiment. Rotating disk electrode (RDE) and microelectrode measurements were conducted using an SP-200 potentiostat from Bio-Logic. For RDE experiment, tetramethylammonium hydroxide (25 wt. water solution, EMD) and tetraethylammonium hydroxide (1M water solution, Sigma Aldrich) were diluted by MilliQ water to make 0.1 M electrolyte solution. The 3-electrode setup includes a platinum polycrystalline electrode (5 mm in

diameter, Pine) as working electrode, a graphite rod as the counter and a Hg/HgO electrode as the reference. The hydrogen oxidation curves were recorded in hydrogen saturated electrolyte at 900 rpm with iR compensation. For the microelectrode experiment, the setup was modified from our previous publication,⁴ a glassy carbon disk of 5 mm was used as the working electrode. Aqueous ink of Pt/C catalyst from Alfa Aesar (60% wt. Pt) was deposited on top of the glassy carbon to make the 46 $\mu\text{g}/\text{cm}^2$ Pt loading. 15 microliters of 1% wt. *o*-BTN or TEA-*o*-BTN ionomer (Hydroxide form, dispersed in dimethylacetamide) was pipetted on top of the catalyst layer and dried in air. Quaternary ammonium tethered poly(phenylene) membrane⁵ was used to bridge the working electrode with the reference (Hg/HgO) and counter (Graphite rod) electrodes via 0.1 M NaOH solution, which is a few centimeters underneath the working electrode. Additional alkaline ionomer was added on the side wall of the glassy carbon disk to ensure good ion conductivity and adhesion between the membrane and working electrode. Nitrogen or hydrogen was bubbled through the NaOH solution. The hydrogen oxidation polarization curves were corrected for iR drop.

MEA fabrication and AMFC performance measurement. The 5 wt.% ionomer solution in 50:50 wt% isopropanol-ethanol solution was prepared by dissolving hydroxide form of BPN, *o*-BTN and TEA-*o*-BTN polymers. The catalysts inks were prepared by dispersing 10 mg of Pt/C (60 wt% Pt on high surface area carbon, HISPEC 9100, JM catalysts) or Pt-Ru/C (50 wt% Pt – 25 wt% Ru on high surface area carbon, HISPEC 12100, JM catalysts) catalysts and 70 mg of 5wt.% ionomer solution in 2000 mg of 80:20 wt% isopropanol – water solution. The catalysts inks were then painted on gas diffusion layer (BC-29, SGL carbon) followed by drying on vacuum table at 60 °C for 1 h. The ionomer to catalyst ratio was kept 17 wt% for both electrodes. Prior to the MEA fabrication, electrodes were immersed in 1 M NaOH solution to convert ionomers in hydroxide

form and remove any carbonation occurred during electrode preparation. These revitalized electrodes were used to sandwich the hydroxide form *m*-TPN membranes (treated with 1 M NaOH), followed by placing MEA in fuel cell hardware (active area 5 cm², fuel cell technologies). The MEAs were washed in-situ with plenty of deionized water till pH of effluent water was neutral. The fuel cell break-in was carried out as discussed elsewhere⁶ using commercial fuel cell test station (Fuel cell Technologies, US). The fuel cell performances were recorded at 80 °C with a flow rate of 500 or 2000 sccm for hydrogen and 300 or 1000 sccm for oxygen under 100% humidity with 285 kPa backpressure. After break-in, the polarization curves were measured under constant voltage mode at the interval of 0.05 V. Further, the durability test was conducted with a flow rate of 2000 sccm for hydrogen and 300 sccm for oxygen at 147 kPa backpressure. For the durability assessment, a current density of 0.6 A/cm² was applied and the cell resistance and voltage were recorded as a function of time.

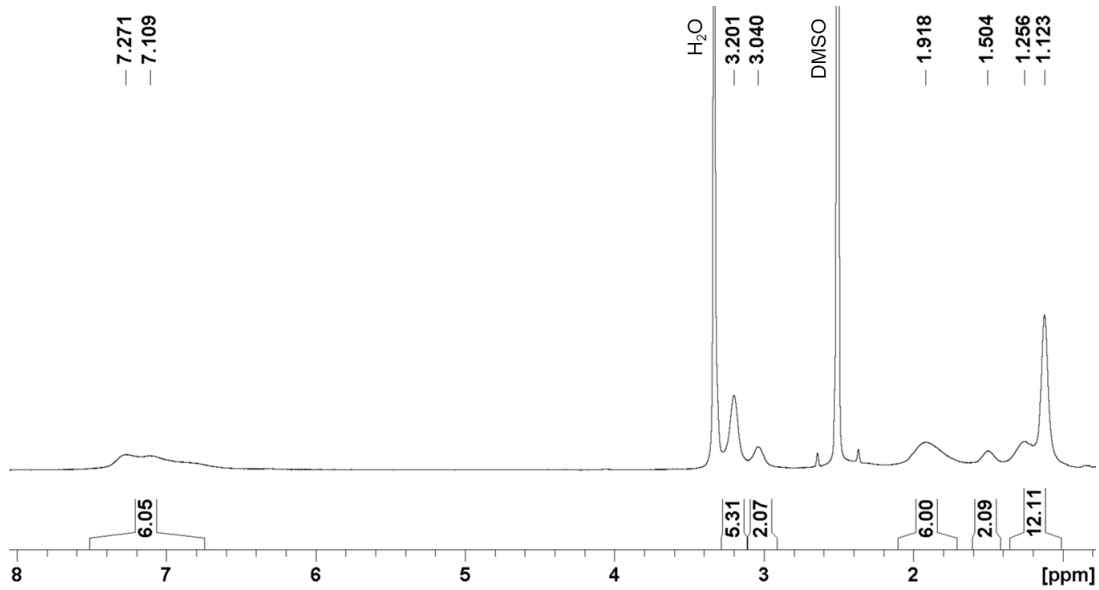


Fig. S1 ¹H NMR spectra of TEA-*o*-BTN after the alkaline stability test of 500 h (1 M NaOH, 80 °C).

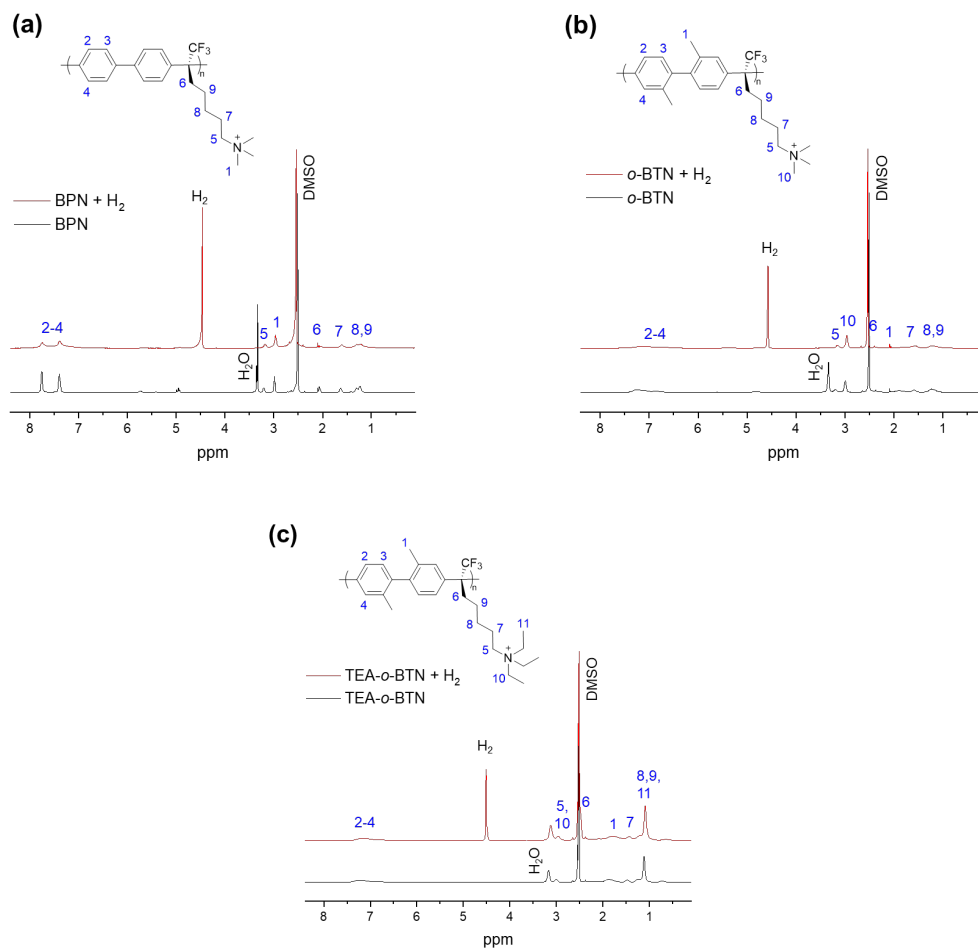


Fig. S2 ^1H NMR spectra of (a) BPN, (b) *o*-BTN and (c) TEA-*o*-BTN before and after H_2 bubbling.

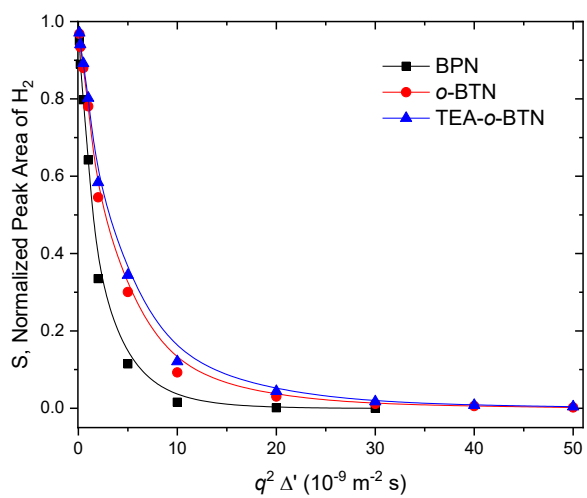


Fig. S3 Diffusion-dependent signal attenuation of the H₂ peak assigned at 4.5 ppm at 25 °C.

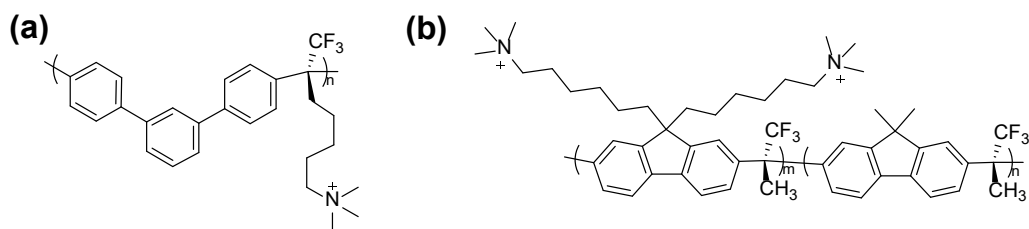


Fig. S4 The chemical structure of (a) *m*-TPN membrane and (b) FLN ionomer.

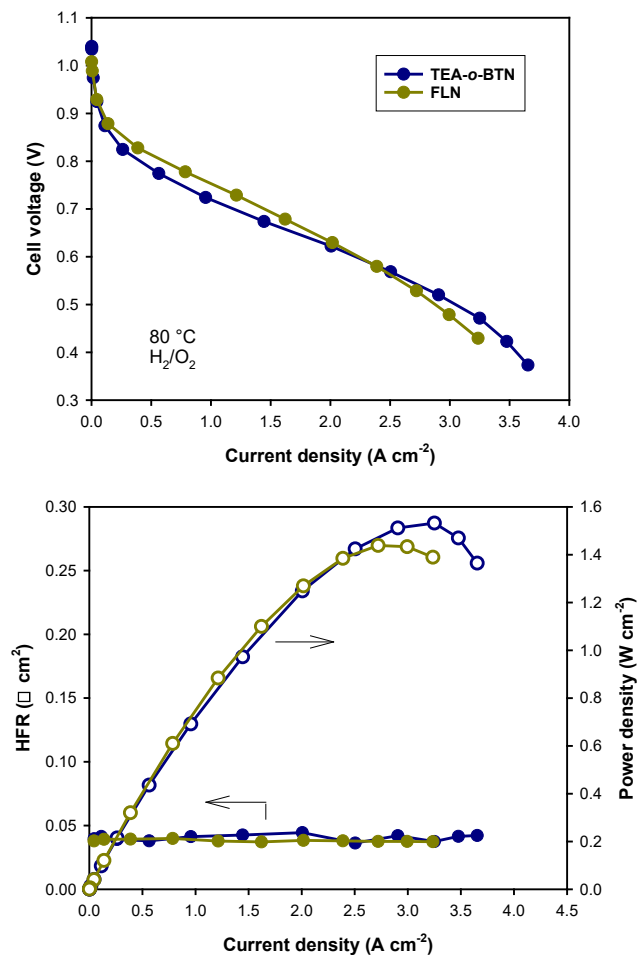


Fig. S5 Comparison of AMFC performance of MEAs employing TEA-*o*-BTN and FLN ionomers. Measured the performance at 80 °C under fully humidified H₂/O₂ (2,000/1000 sccm) at 285 kPa backpressure. AEM: *m*-TPN (35 μm for the TEA-*o*-BTN cell and 30 μm for the FLN cell, IEC = 2.1 meq. g⁻¹); anode: Pt-Ru/C (0.5 mg_{Pt} cm⁻²); cathode: Pt/C (0.6 mg_{Pt} cm⁻²), humidification: 100%.

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