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Highly Stable, Low Gas Cross-Over, Proton-Conducting Phenylated Polyphenylenes

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Abstract: Two classes of novel sulfonated phenylated polyphenylene ionomers are investigated as polyaromatic-based proton exchange membranes. Both types of ionomer possess high ion exchange capacities yet are insoluble in water at elevated temperatures. They exhibit high proton conductivity under both fully hydrated conditions and reduced relative humidity, and are markedly resilient to free radical attack. Fuel cells constructed with membrane-electrode-assemblies containing each ionomer membrane yield high in situ proton conductivity and peak power densities that are greater than obtained using Nafion reference membranes. In situ chemical stability accelerated stress tests reveal that this class of the polyaromatic membranes allow significantly lower gas crossover and lower rates of degradation than Nafion benchmark systems. These results point to a promising future for molecularlydesigned sulfonated phenylated polyphenylenes as protonconducting media in electrochemical technologies.

Hydrocarbon-based proton exchange membranes (PEMs) and ionomers, intended for electrochemical applications (fuel cells, electrolyzers, and water treatment)^{[/1][2]} are actively sought after as alternatives to traditional perfluorosulfonic acid (PFSA) ionomers^{[2][3][4]} due to their ease of synthesis, low cost, low gas crossover, high T₉, and fewer environmental concerns.^{[5][6]} Many different ion-containing polymers have been investigated with significant focus on those incorporating aromatic groups as part of the polymer main chain, such as sulfonated derivatives of poly(arylene ether)s,^[7] poly(arylene ether ketone)s,^{[8][9][10]} poly(arylene sulfone)s,^[9] poly(imide)s,^[11] poly(benzimidazole)s,^{[2][12]} and poly(*para*-phenylene)s.^{[8][13][14]} However, it is the general consensus that hydrocarbon-based ionomers to date are inhibited by a greater sensitivity to oxidative degradation either *ex situ* (e.g., Fenton's Reagent test) and/or *in situ* (e.g., in PEM fuel cells).^{[2][8]} Recent attention has therefore focused on the rational design of hydrocarbon ionomers with enhanced chemical stability.^{[6][15][16]}

Sulfonated phenylated polyphenylenes (**sPPPs**) have been of particular interest as PEMs due to the inherent chemical and mechanical stability of a fully aromatic backbone.^{[17][18]} Work in this area, however, had been limited by the challenge of synthesizing well-defined polymer backbones composed of sterically-encumbered, rigid, aryl-aryl linkages,^{[18][19]} their limited solubility in polar solvents,^{[8][18]} and ill-defined molecular structures as a result of the post-sulfonation technique commonly employed. These challenges lead to a random distribution of ionic groups on the multitude of available phenyl rings,^{[20][21][22]} as well as the uncertainty of the ratio of *meta:para*

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linkages between phenyl rings along the polymer backbone.^{[18][23][24]}

Recently, we reported the synthesis of a well-defined, branched, sulfonated polyphenylene homopolymer (sPPP-H⁺) using pre-sulfonated monomers.^[24] Membranes cast from this polymer exhibited high proton conductivity and *ex situ* stability to oxidative degradation (as determined by ¹H NMR). When employed as a membrane and/or ionomer in the catalyst layer of a fuel cell, sPPP-H⁺ supported a power density comparable or exceeding that of Nafion[®], the archetypal PFSA ionomer. However, while sPPP-H⁺ membranes remain intact in H₂O at RT, they swelled excessively at higher temperatures, thus limiting research to *in situ* durability.

In this paper, we explore the syntheses of novel sulfonated phenylated polyphenylenes using Diels-Alder (D-A) polymerization reactions with emphasis on molecular design to enhance the positive attributes of sPPP-H⁺. This is accomplished by incorporation of spacer units, biphenyl and naphthyl, in the polymer backbone. Optimization of conditions for synthesis of the polymers is aided by synthetic studies of oligophenylene model compounds which bear structural similarities to the analogous polymers, but are simpler to characterize.^{[18][23][25]} Biphenyl and naphthyl-linked small molecules SM-B and SM-N were obtained through [4 + 2] D-A cycloaddition between 3c and linkers 2b or 2c, respectively (Scheme 1a). Reaction conditions identical to the intended polymerization conditions were employed in order to confirm the stability of the desired spacer units at the temperatures necessary to facilitate the D-A reaction [17][24]



Scheme 1. Sulfonated branched oligophenylenes and polyphenylenes.

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Use of pre-sulfonated monomers allows for the synthesis of polymers containing four sulfonic acid groups per repeating unit, with precise control over their positioning.^[24] Syntheses were accomplished through [4 + 2] D-A cycloaddition between monomer **1c** and linkers **2b** or **2c** to yield **sPPB-HNEt**³⁺ and **sPPN-HNEt**³⁺, respectively (Scheme 1b). A detailed synthesis of each compound is outlined in the Supporting Information (SI). Gel permeation chromatography (GPC) analyses indicated a M_w of 175,000 Da (M_w/M_n = 1.56) for **sPPB-HNEt**³⁺, and 329,000 Da (M_w/M_n = 2.33) for **sPPN-HNEt**³⁺. Successful polymerizations were confirmed by ¹H NMR spectroscopic analysis, using the triethylammonium cations as internal probes. The expected integration ratios between the methyl protons (36 H), methylene protons (24 H), and the polymer aromatic backbone protons (**sPPB-HNEt**³⁺ 40 H; **sPPN-HNEt**³⁺ 38 H) were observed.

Polymer acidic forms **sPPB-H**⁺ and **sPPN-H**⁺ were cast into membranes from DMSO solutions (5% w/w) and dried at 85 °C overnight. Water uptake and swelling ratios are summarized in Table S37. Unlike sPPP-H⁺, both polymers were insoluble in DI H₂O at 80 °C. **sPPB-H**⁺ displayed considerably lower water uptake and swelling values than **sPPN-H**⁺, but higher than Nafion NR-211.^[26]

Fenton's reagent is commonly employed as a preliminary *ex-situ* accelerated degradation test for studying PEM oxidative stability due to its ability to generate oxygen-containing free radicals in solution.^{[27][28]} After exposure to Fenton's reagent (1 h, 80 °C), membranes displayed no observable mass loss (0.69 ± 0.71% and 0.09 ± 0.62% for **sPPB-H**⁺ and **sPPN-H**⁺ respectively), and no changes in chemical structure (¹H NMR), indicating a markedly high chemical resilience to free radical attack. In contrast, phenylated, sulfonated polyarylene ethers displayed mass losses of up to 20% and eventual dissolution under these conditions.^[29]

Mechanical strength measurements show that **sPPB-H**⁺ has superior tensile strength and Young's modulus to NR-211 (59.6 ± 1.4 MPa and 1331 ± 29 MPa vs. 17.3 ± 0.4 MPa and 270 ± 17 MPa, respectively), but lower elongation at break (17.5 ± 1.3% vs. 148.3 ± 3.6%, respectively) when measured in dry state. Similar performances were noted for both **sPPN-H**⁺ and **sPPP-H**⁺ (Table and Figure S48). Fully hydrated membranes showed decreases in tensile strength and Young's modulus, with minor increases in elongation at break (except in the case of **sPPN-H**⁺). In both conditions, membranes were notably robust, flexible, and not brittle, and data compare well to previously published mechanical strength measurements of post-sulfonated phenylated polyphenylenes.^[20]

Titration experiments show that **sPPB-H**⁺ and **sPPN-H**⁺ possess IECs of 3.19 ± 0.05 meq. g⁻¹ and 3.28 ± 0.06 meq. g⁻¹, respectively, compared to theoretical values of 3.46 meq. g⁻¹ and 3.54 meq. g⁻¹, respectively. These IECs are slightly lower than observed for sPPP-H⁺ membranes (3.47 meq. g⁻¹ experimental, 3.70 meq. g⁻¹ theoretical) due to the increase in equivalent weight caused by incorporation of the biphenyl and naphthyl moeities.

Proton conductivity measurements were performed using electrochemical impedance spectroscopy (EIS) under relative humidities (RH) ranging from 30% to 95%, at both 30 °C and 80 °C (Fig. 1). Maximum values of 222 mS cm⁻¹ and 268 mS cm⁻¹

¹ were observed at 95% RH for **sPPN-H**⁺ at 30 °C and 80 °C, respectively. These values are significantly higher than previously reported sulfonated polyphenylenes[20][24][30][31][32] and the 79 mS cm⁻¹ (30 °C) and 113 mS cm⁻¹ (80 °C) values obtained for Nafion NR-211 under identical conditions. sPPB-H+ exhibits proton conductivities of 129 mS cm⁻¹ and 172 mS cm⁻¹ at 30 °C and 80 °C respectively, likewise larger than previously reported sPPP-H⁺ and NR-211. Conductivities decline, as expected, under lower RH,^{[26][33]} due to decreasing membrane water content.^[5] The high proton conductivities of **sPPN-H**⁺ is likely due to its markedly high water uptake which may allow for a greater connectivity of aqueous domains throughout the material.^{[34][35]} Comparison of the acid concentrations ([SO₃H]): 1.17, 1.43, and 1.55 mmolsO3H/cm³membrane for sPPN-H⁺, sPPB-**H**⁺, and NR-211;^[26] and their proton mobility values (μ_{H} +): 2.0, 0.9, and 0.5 × 10⁻³ cm² V⁻¹ s⁻¹ at 30 °C, further supports this assertion (Table S39).^{[26][36]} That is, although the membranes possess lower acid concentrations than NR-211, their proton mobilities are much higher (especially for the case of sPPN-H⁺).

Figure 1. (a) Proton conductivity of polymer membranes at 30 and 80 °C and; (b) the respective log plot.



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Onto 33 ± 2 μ m **sPPB-H**⁺ and 80 ± 4 μ m **sPPN-H**⁺ membranes, catalyst layers containing PFSA ionomer and 0.4 mg Pt·cm⁻² were deposited by ultrasonic spray coating using a Sono-Tek ExactaCoat SC.[37] No delamination was observed before or after fuel cell operation. These were mounted as fuel cells and conditioned in situ, displaying highly repetitive operation for 25 hours of RH cycling (Fig. S41). At 80 °C with zero backpressure, sPPB-H⁺ and sPPN-H⁺ membraneelectrode-assemblies (MEA) displayed peak power densities of 1237 and 927 mW cm⁻², which are 56% and 17% greater than that obtained using N212 reference MEAs (Fig. 2). Using H₂/air, these MEAs displayed peak power densities of 587 and 445 mW·cm⁻², which are 29% larger and similar, respectively, to N212 (Fig. S43). Using H₂/O₂ and H₂/air, favourable comparisons to N211 were found accounting for differences in membrane thicknesses and gas diffusion layer (GDL) optimization (Figs. S43 & S44). In both cases, the in situ membrane resistances (insets), measured during operation by the iR-drop method and verified with high-frequency resistance measurements, were significantly lower than the N212 MEA reference, which is atypical for hydrocarbon membranes.^[38] In situ conductivities, accounting for differences in membrane thicknesses, were 170 ± 21 and 261 ± 22 mS cm⁻¹, for sPPB-H⁺or sPPN-H⁺-based MEAs, which are 111 and 223% larger than N212 at 80 °C, respectively (Fig. S42b).

Figure 2. In situ polarization (left axis, solid), power density (right axis, open), under H₂/O₂. Conditions were 80 °C, 100% RH, 0.5/1.0 slpm anode/cathode gas flows, zero backpressure.



An *in situ* chemical stability accelerated stress test (AST) consisting of a high-temperature, low-RH potential hold at opencircuit voltage (OCV) was performed, comparing **sPPB-H**⁺ with a N211 reference (Fig. 3). Using H₂/air, initial OCVs of **sPPB-H**⁺/N211 were 0.965/0.942 V. Losses at 1, 10, 50, and 100 h were 2/66, 29/181, 55/231, and 111/271 mV, respectively (Table S45). In addition, the H₂ gas crossover for **sPPB-H**⁺ was substantially lower than N211, e.g. 0.5 vs 3.8 mA/cm² at 42 h (Fig. S45). As shown in Fig. 3, the N211 cell showed signs of failure after 100 h, with H₂ crossover currents approaching 100 mA/cm², while the **sPPB-H**⁺ cell exhibited 12 mA/cm² crossover current after 100 h accelerated degradation. An OCV of 0.71 was maintained for the **sPPB-H**⁺ cell after 400 h, whereas the N211 cell fell below 0.7 V after 100 h accelerated degradation, suggesting that the **sPPB-H**⁺ membrane cell exhibited a 4x lifetime compared to N211. Nafion 211 cells completely failed at 153 h, whereas the **sPPB-H**⁺ cell provided polarization curves (Fig. S46) after 400 h, exhibiting a final OCV of 0.71 V and only a 31% decrease in *in situ* conductivity, which is still 21% greater than a N211 fully-conditioned cell at beginning-of-life (Fig. S47).

Figure 3. Accelerated combined chemical/mechanical stress test via an open circuit voltage hold at 30% RH, 90 °C, H₂/Air, zero backpressure. The spikes represent times where the OCV stress test was interrupted to obtain polarization curves and gas cross over current densities.



In summary, the syntheses of two new sulfonated oligophenylenes **SM-N** and **SM-B** were demonstrated, leading to the synthesis of their respective sulfonated polyphenylenes **sPPB-HNEt**₃⁺ and **sPPN-HNEt**₃⁺. The pre-sulfonation technique affords full retention of sulfonic moieties following D-A polymerization, and polymers obtained possess high molecular weights. Exchange to active acidic forms afforded **sPPB-H**⁺ and **sPPN-H**⁺, which were cast into membranes for further characterization, and displayed excellent tensile strength, Young's moduli, and modest elongation at break. EIS analysis revealed exceptional proton conductivities, even under reduced RH. Both polymers displayed remarkable fuel cell performance under non-optimized conditions, with **sPPB-H**⁺ maintaining a high conductivity even after 400 h of accelerated stress testing.

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