Highly Stable, Low Gas Crossover, 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 molecularly designed sulfonated phenylated polyphenylenes as proton-conducting media in electrochemical technologies.

Hydrocarbon-based proton exchange membranes (PEMs) and ionomers, intended for electrochemical applications (fuel cells, electrolyzers, and water treatment) are actively sought after as alternatives to traditional perfluorosulfonic acid (PFSA) ionomers due to their ease of synthesis, low cost, low gas crossover, high $T_p$ and fewer environmental concerns. 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) poly(arylene ether ketone)poly(arylene sulfone) poly(amide)poly(benzimidazole) and poly(para-phenylene). 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). Recent attention has therefore focused on the rational design of hydrocarbon ionomers with enhanced chemical stability. Sulfonated phenylated polyphenylenes (sPPPs) have been of particular interest as PEMs due to the inherent chemical and mechanical stability of a fully aromatic backbone. 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 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 as well as the uncertainty of the ratio of meta/para linkages between phenyl rings along the polymer backbone.

Recently, we reported the synthesis of a well-defined, branched, sulfonated polyphenylene homopolymer (sPPP-H) using pre-sulfonated monomers. Membranes cast from this polymer exhibited high proton conductivity and ex situ stability to oxidative degradation (as determined by $^1$H 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 $H_2O$ 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. Biphenyl and naphthyl-linked small molecules SM-B and SM-N were obtained through D–A cycloaddition between 3e 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.

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. Syntheses were accomplished through D–A cycloaddition between monomer 1e 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 175000 Da ($M_w/M_r = 1.56$) for sPPB-HNEt$_3^+$ and 329000 Da ($M_w/M_r = 2.33$) for sPPN-HNEt$_3^+$. Successor polymerizations were confirmed by $^1$H NMR spectroscopic analysis, using the triethylammonium cation as a reference.
The expected integration ratios between the methyl protons (36H), methylene protons (24H), and the polymer aromatic backbone protons (sPPB-HNEt₃⁺; sPPN-HNEt₃⁺; sPPP-HNEt₃⁺) 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.

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 moieties.

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 (Figure 1). Maximum values of 222 mS cm⁻¹ and 268 mS cm⁻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[20,24,30–32] 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]) of 1:17, 1:43, and 1:55 mmol(SO₃H)/cm²(membrane) for sPPN-H⁺, sPPB-H⁺, and NR-211,[26] and their proton mobility values (μH⁺): 2.0, 0.9, and 0.5 × 10⁻³ cm²V⁻¹s⁻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⁺).

Onto 33 ± 2 µm sPPB-H⁺ and 80 ± 4 µm 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 (Figure S41). At 80°C with zero backpressure, sPPB-H⁺ and sPPN-H⁺ membrane-electrode assemblies (MEA) displayed peak power densities of 1237 and 927 mWcm⁻², which are 56% and 17% greater than that obtained using N212 reference MEAs (Figure 2). Using H₂/air, these MEAs displayed peak power densities of 587 and 445 mWcm⁻², which are 29% larger and similar, respectively, to N212 (Figure 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 (Figures S43 and 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 (Figure S42b).

An in situ chemical stability accelerated stress test (AST) consisting of a high-temperature, low-RH potential hold at open-circuit voltage (OCV) was performed, comparing sPPB-H⁺ with a N211 reference (Figure 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, for example, 0.5 vs. 3.8 mA cm⁻² at 42 h (Figure S45). As shown in Figure 3, the N211 cell showed signs of failure after 100 h, with H₂ crossover currents approaching 100 mA cm⁻², while the sPPB-H⁺ cell exhibited 12 mA cm⁻² 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 4× lifetime compared to N211. Nafion 211 cells completely failed at 153 h, whereas the sPPB-H⁺ cell provided polarization curves (Figure 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 (Figure S47).

In summary, the syntheses of two new sulfonated oligophenylene SM-N and SM-B were demonstrated, leading to the synthesis of their respective sulfonated polyphenylenes sPPB-HNEt₂ and sPPN-HNEt₂. The pre-sulfonation technique affords full retention of sulfonic moietyies 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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Conflict of interest

The authors declare no conflict of interest.

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