Anion Exchange and Bipolar Membranes for Electrochemical Energy Conversion and Storage

Zhongyang Wang
Washington University in St. Louis

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Dissertation Examination Committee:
Vijay Ramani, Chair
Peng Bai
Pratim Biswas
Julio D'Arcy
Palghat Ramachandran

Anion Exchange and Bipolar Membranes for Electrochemical Energy Conversion and Storage
by
Zhongyang Wang

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The Graduate School
of Washington University in
partial fulfillment of the
requirements for the degree
of Doctor of Philosophy

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<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>AEM</td>
<td>Anion exchange membrane</td>
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<tr>
<td>SEBS</td>
<td>Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene</td>
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<tr>
<td>DBFC</td>
<td>Direct sodium borohydride fuel cell</td>
</tr>
<tr>
<td>RFB</td>
<td>Redox flow battery</td>
</tr>
<tr>
<td>PMBI</td>
<td>pH-gradient-enabled microscale bipolar interface</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane electrode assembly</td>
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<td>Vanadium-cerium redox flow battery</td>
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<td>Description</td>
</tr>
<tr>
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</tr>
<tr>
<td>PEMWE</td>
<td>Proton exchange membrane water electrolyzer</td>
</tr>
<tr>
<td>BOR</td>
<td>Borohydride oxidation reaction</td>
</tr>
<tr>
<td>HOR</td>
<td>Hydrogen oxidation reaction</td>
</tr>
<tr>
<td>HRR</td>
<td>Hydrogen peroxide reduction reaction</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>OCP</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>CEI</td>
<td>Cation exchange ionomer</td>
</tr>
<tr>
<td>UUV</td>
<td>Unmanned underwater vehicle</td>
</tr>
<tr>
<td>UAV</td>
<td>Unmanned air vehicles</td>
</tr>
<tr>
<td>CE</td>
<td>Current Efficiency</td>
</tr>
<tr>
<td>EE</td>
<td>Energy Efficiency</td>
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<tr>
<td>VE</td>
<td>Voltage Efficiency</td>
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</tbody>
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Acknowledgments

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Zhongyang Wang

Washington University in St. Louis

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Abstract of The Dissertation

Anion Exchange and Bipolar Membranes for Electrochemical Energy Conversion and Storage

by

Zhongyang Wang

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Professor Vijay K. Ramani, Chair

Anion exchange and bipolar membrane fuel cells generate electrical energy directly from chemical fuels and have attracted considerable interests as alternate power sources for large market applications, such as transportation (hydrogen fuel cells) and unmanned vehicles (sodium borohydride fuel cells). Anion exchange membrane (AEM), generally composed of a polymer with covalently tethered ionic groups, is the central component of the fuel cell serving as the electrolyte, conducting hydroxide ions from cathode to anode, where fast ionic conduction is directly related to power output. However, AEMs currently used in fuel cells (H₂ fuel cells and sodium borohydride fuel cells) exhibit ion poor transport properties at operation conditions of fuel cells, such as low hydroxide ion conductivities at 80 °C. Another concern with the use of AEMs in fuel cells is their stabilities in strong alkaline environment. AEMs suffer Hoffman elimination, where the cation is cleaved and a direct nucleophilic (S_N2) reaction where the cation is completely cleaved too.

This dissertation targets on solving these two major obstacles for using AEMs as electrolytes in alkaline electrochemical energy storage and conversion. To solve the first problem, a triblock copolymer-based polymer (polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene, SEBS) has been developed to synthesize AEMs with high ion conductivities by engineering a
phase-separated morphology. To address the second problem, novel cation groups such as imidazolium-based cation and phosphonium-based cation have been incorporated in AEMs. Also, by attaching a six-carbon alkyl spacer between polymer backbone and cation group, alkaline stability of such AEM has been investigated.

Once the degradation mechanism of AEMs is well understood and AEMs with high ion conductivities have been developed, this dissertation focuses on developing such AEMs electrolyte for different electrochemical systems such as direct sodium borohydride fuel cells (DBFCs) and redox flow batteries (RFBs).

Besides the concern of ionic conductivities and alkaline stabilities of AEMs in alkaline environment, another obstacle for the development of DBFC is the crossover of fuels and oxidants. We demonstrate a pH-gradient-enabled microscale bipolar interface (PMBI) to effectively separate the anolyte and catholyte of the DBFC. The PMBI configuration enabled significantly enhanced performance in a DBFC as compared to either an all-anion-exchange or an all-cation-exchange configuration (330 mA/cm² at 1.5 V and 630 mW_peak/cm² at 1.0 V). The PMBI-type electrodes provide a new and fascinating design to engineer fuel-cell membrane electrode assemblies (MEAs). The bipolar-interface configuration also holds significant applicability in the field of water electrolysis, where the membrane could separate an acidic H₂-evolution cathode (a very fast reaction) from an alkaline O₂-evolution anode (possible on non-Pt-group metals) in a system wherein the benefits of the best electrodes of present acidic/alkaline water electrolyzers are combined.

RFBs are promising candidates for large-scale energy storage systems, since the capacity, power and energy density parameters can be designed independently, which facilitates a convenient way
of modification even after installation. AEMs play an important role as separators in some of RFBs where a degree of reactant isolation is required between the anolyte and catholyte compartments. A primary goal for membrane development in RFBs is to limit the diffusion of active species, while maintaining high oxidative stability in related species. A vanadium-cerium redox flow battery (V-Ce RFB) employing SEBS-based AEM as the separator yields an energy efficiency of 86% at a current density of 50 mA/cm² with a 10% drop in capacity over 20 charge/discharge cycles. In contrast, a V-Ce RFB using Nafion®212 as the separator has an energy efficiency of 80% and a 40% drop in capacity over 20 charge/discharge cycles. The observed capacity fade is primarily due to cation intermixing between the anodic and cathodic compartments – much better permselectivity has been obtained with the AEM separator. After 60 charge-discharge cycles (350 hours of operation), the ion exchange capacity and ionic conductivity of the AEM drops by about 20%. There has been no observed change in mechanical properties. The oxidative stability of the AEM has been evaluated ex situ by immersion in 1.5 M VO₂⁺ + 3 M H₂SO₄ for 500 hours - the ionic conductivity remained constant over this timeframe.
Chapter 1: Introduction

The results of this chapter are partially adapted from the published article Wang, Z., Sankarasubramanian, S., Ramani, V. (2018). Advances in anion exchange membranes for electrochemical energy conversion. Current Opinion in Electrochemistry. 12: 240-245.

Supplementary tables are available in Appendix I
1.1 Background and motivation

There are two types of ion exchange membranes: cation exchange membrane (CEM) and anion exchange membrane (AEM). CEMs are proton conductive polymer electrolyte that allow protons to transport through tethered negatively charged (anionic) groups. AEMs are polymer electrolytes that conduct anions such as OH\(^-\), as AEMs contain positively charged (cationic) groups bond covalently to a polymer backbone.

Fuel cells are widely regarded as an environmental-friendly energy conversion platform for the 21st century. Unlike proton-exchange membrane fuel cells (PEMFCs), alkaline exchange membrane fuel cells (AEMFCs) that use anion exchange membranes AEMs as electrolytes have drawn tremendous research attention. Compared with acidic fuel cells, they have enhanced oxygen reduction reaction kinetics and use non-precious metal catalysts. In recent years, there has been extensive research toward the development of AEMs for AEMFCs, redox flow batteries (RFBs), and solid alkaline water electrolyzers.

Rapid advances in materials design and device fabrication have allowed for the demonstration of record high performance in gas-fed and liquid-fed fuel cells incorporating AEMs. The current state-of-the-art AEMs display high conductivities, increasing temperature stability (now regularly operating at 80 °C) and mechanical strength that has allowed for high water uptake and flux without sacrificing structural integrity. On the device front, novel combinations of membrane and binder, optimized using increasingly powerful in-operando probes have led researchers to achieve a clear understanding of the rate and lifetime limiting processes.

The concept of a “Hydrogen economy” [1] — H\(_2\) or H\(_2\)-derived fuels produced from renewables serving as the fuel mainstay — provides a comprehensive route towards a carbon-neutral energy
system. This drive towards increasing renewables adoption, and the technological build-out of allied energy conversion solutions, such as fuel cells, is increasingly an economical inevitability [2], since the levelized costs of terrestrial solar and wind installations are much lower than conventional coal, nuclear or oil-based power plants. A key component in the integrated hydrogen economy are fuel cells that use H₂ or H₂-derived fuels (NH₃ [3], NaBH₄ [4], N₂H₄ [5], HCCOH [6] etc.). A subset of these technologies, especially those operating at an alkaline pH using AEMs have received increasing attention. Given the wide variety of fuel and oxidant combinations that can be used, this dissertation will examine the larger trends in AEM development using the gas-fed H₂/O₂ AEMFC (shown in Figure 1.1.) and the liquid-fed NaBH₄/H₂O₂ direct borohydride fuel cell (DBFC) (shown in Figure 1.4.) as model systems. Both systems have shown remarkable growth in peak power densities and operating potentials over the past decade (summarized in Appendix I, Table A1.1 and A1.2). The increasing interest is directly attributed to the enticing prospect of using platinum group metal (PGM) free electrocatalyst for carrying out H₂ oxidation and O₂ reduction reactions in AEMFCs while the DBFC has a thermodynamic potential of 2.2V, high energy density (9.3 kWh kg⁻¹) and specific capacity (5.67 kAh kg⁻¹) [7, 8]. These recent advances have resulted in the invalidation of the narrative that AEMFCs are significantly inferior to PEMFCs in terms of power. For example, Wang et al. demonstrated an AEMFC using non-PGM catalyst cathode exceed 1 W cm⁻² peak power density [9] while Varcoe et al. showed an AEMFC with peak power density of more than 2 W cm⁻² using a membrane with 500+ hours of alkaline stability at 80 °C [10]. Nevertheless, significant areas for improvement remain. AEMs need to achieve Nafion® like stability, alternatives to gamma radiation grafting of highly toxic compounds like vinylbenzene chloride (VBC) is urgently required to transition to eventual mass
production and the narrative of the key role of water management [11] needs to be examined in case of non-PGM catalysts.

![Schematic illustration of an AEMFC](image)

Figure 1.1. Schematic illustration of a AEMFC

1.2 Key milestones in the development of alkaline fuel cells

A remarkable increase in the peak power density of AEMFCs have been shown over the last decade, allowing them to presently exhibit performance in the same order of magnitude as PEMFCs. The operating temperatures of these cells has also steadily increased to 80 °C now. These trends are summarized in Figure 1.2 [10, 12-20]. Remarkably, when examining the separators used in these systems (listed in Appendix I, Table A1.1) we find that these representatively high performance AEMFCs all use trimethylamine (TMA) as the functional group attached to the polymer backbone across a range of temperatures from 60-80 °C. Recent reports [10, 17-20], which invariably use PtRu/C catalysts at the anode and Pt/C at the cathode, have exhibited further year-to-year
improvement in performance. This tendency indicates that any future electrocatalytic improvements would be marginal (except for cost savings) and that the major new improvements have been driven by improvements in the AEM. It is this area that calls for future research focus. The backbones used have been fluorinated (eg: fluorinated ethylene propylene (FEP)), partially fluorinated (eg: poly(ethylene-co-tetrafluoroethylene) (ETFE)) or non-flourinated (eg: Low density polyethylene (LDPE)), which have displayed benchmark performance as seen in Appendix I, Table A1.1. Further, the major issue is that the already sluggish oxygen reduction reaction (ORR) at the cathode can be further limited by the insufficient supply of water by back diffusion from the anode [11, 19]. The key to the drastic improvement in peak power density from 2016 to 2017 has been the optimization of the radiation grafted ETFE-based benzyltrimethylammonium-functionalized radiation-grafted AEMs to enhance ion-exchange capacity (and hence water uptake) [18]. In addition, the use of powder anion exchange ionomer (AEI) allows for better ion transport to the reaction site on the catalysts [21]. Alternatively, the use of a thin (<30 μm) LDPE based membrane also helped with water transport and led to improved peak power densities [10]. This theme of improved water transport to the cathode is expected to facilitate further improvements in AEMFC performance in the future as long as it does not lead to cathode flooding [11, 19]. The use of AEMs with even greater IEC (perhaps leading to a need for reinforcement to prevent swelling related mechanical failure) and of co-polymer backbones that allow for Nafion® like phase separation (hence improving ionic and water transport) is one avenue to maintain the pace of performance gains witnessed over the past two years. Ideally, the next step change in AEMFC performance should come while forgoing the need for poorly scalable radiation-based processes or the use of acutely toxic chemicals such as VBC.
The issues in liquid fuel cells tend to be associated with electrocatalytic. This is exemplified by the constant search for better catalysts for DBFCs [22-24]. The major requirement of AEMs in this application is to prevent cross-over and, in case of DBFCs with bipolar interfaces, to retain a sharp pH gradient between the acidic and alkaline regions. It is observed that the placement and engineering of the bipolar interface in these systems are the most crucial aspects to obtain high performance [7]. The major contribution of a highly selective AEM coupled with a cation exchange membrane (CEM) is in improving the operating potential and hence power density. The results of these architectural changes on the overall performance are shown in Appendix I, Table A1.2.

1.3 Cation chemistries and their alkaline stabilities

The chemistries of cation head-groups that have been affixed to polymer backbones include N-based, P-based, S-based, and metal-based groups. The alkaline stability of each cationic group depends on different factors affecting the susceptibility of the cation to be attached by strong nucleophiles such as hydroxide. When the head-group is attached to different polymer backbones,
the alkaline stability could also differ due to electron donation or withdrawal effects. Aromatic polymer backbones are less electron donating than aliphatic polymer backbones, favoring attacks by hydroxide ions [25].

1.3.1 Nitrogen-based cationic head groups

Ammonium cations are the most commonly used group for making AEMs due to their low molecular weights and relatively good stability. Benzyl-trimethylammonium [26] has been used as benchmark to evaluate the alkaline stability of cationic head-groups. Its chemical structure is shown in Figure 1.3A. Parrondo et al. attached the benzyl-trimethylammonium (TMA⁺) onto PPO to make an AEM (PPO-TMA). PPO-TMA was then immersed in 1 M KOH at 60 °C for 30 days. This ex-situ alkaline stability test condition was regarded as a good mimic for real fuel cell operation environment according to Arges et al. [27]. After ex-situ alkaline stability test, there was 18% degradation of the AEM’s initial IEC [28]. Long-alkyl-chain quaternary ammonium is another N-based cationic head-group (see Figure 1.3B.). Hibbs et al. proved that this kind of ammonium was more stable in alkaline condition than the benchmark cationic chemistry. He synthesized AEMs by attaching long-alkyl chain quaternary ammonium onto poly phenylene (PP). He found that when long-alkyl-chain quaternary ammonium based AEM was immersed into 4 M KOH at 60 °C for 14 days, only 5% of its initial IEC was lost, whereas an benzyl-trimethylammonium-based AEM suffered 21% loss of its initial IEC under the same condition [29]. Arges et al. attached quaternary 1-azaoniumbicyclo [2.2.2] octane (ABCO⁺) (see Figure 1.3C.) onto the PPO backbone to make PPO-ABCO, which was next immersed in 1 M KOH at 60 °C for 30 days. They found that there was ca. 72% loss of its initial IEC after this alkaline stability test [30]. Arges et al. also investigated the alkaline stability of the 1,4-dimethylpiperazinium (DMP⁺) (see Figure 1.3D.) cationic head-group. They attached DMP⁺ onto polysulfone (PSF) to
make a PSF-DMP AEM. PSF-DMP was immersed into 1M KOH at 60 °C for 30 days. They found that 35% cation sites of PSF-DMP suffered IEC lost. PSF-DMP was less alkaline stable than benchmark chemistry (PSF-TMA) [31]. Morandi et al. attached 1,4-diazabicyclo[2.2.2]octane (DABCO) (see Figure 1.3E.) to PPO to make a PPO-DABCO AEM. They also attached N,N,N’,N’-tetramethylethylenediamine (TMEDA) to PPO to make a PPO-TMEDA (which has alkaline stability similar to the benchmark head-group chemistry) as reference. The membrane samples were immersed into 1M KOH at 90°C for 10 days. PPO-DABCO lost ca. 28% of its initial IEC and PPO-TMEDA lost ca. 18% of its initial IEC [32]. The DABCO cationic head-group is not as stable as the benchmark head-group. Wang et al. synthesized a series of imidazolium-based AEMs. They attached 1,2-dimethylimidazole (1,2DMI) (see Figure 1.3F.) to PPO to make PPO-1,2DMI, which was immersed in 1M KOH at 60 °C for 13.5 hours. PPO-1,2DMI remained 75% cationic sites after alkaline treatment [33]. Although imidazolium cation initially attracted researchers’ attention mainly for their high hydroxide ion conductivity [34], their applications in alkaline fuel cells and other alkaline electrochemical devices have been limited by their low alkaline stability. It is well known that pyridinium (see Figure 1.3G.) exhibits low stability in alkaline media, due to hydroxide attack in the ortho position followed by irreversible oxidation to pyridone and consequent loss of positive charges, which are needed for the transport of hydroxide anions [35, 36]. Kim et al. synthesized pentamethylguanidinium functionalized, perfluorinated hydroxide conducting ionomers. (see Figure 1.3H.) The alkaline stability of the ionomers largely depended on adjacent groups connected to the cation. Sulfone guanidinium functionalized ionomer degraded almost 100% after immersion into 0.5 M NaOH at 80 °C for 24 hours, while phenylguanidinium did not degrade under the same condition for 72 hours [37].
1.3.2. Phosphorous-based cationic head groups

Gu et al. functionalized polysulfone with the benzyl-tris(2,4,6-trimethoxyphenyl) phosphonium (TTMP⁺) cation (see Figure 1. 3I.) to make AEMs. They clearly showed that TTMP⁺ cations result in highly alkaline-stable AEMs, which did not experience any loss of ionic conductivity after immersion in 1 M KOH at room temperature for 30 days [38-40]. TTMP⁺ as P-based cationic head-group was more alkaline-stable than the benchmark chemistry. TTMP⁺ is a bulky cation that can prevent hydroxide ion attacks on phosphorus atoms. If we can increase the IEC and ion conductivity of TTMP-based AEM, TTMP⁺ cations can be good candidates to make alkaline-stable AEMs. Kong and co-workers chemically attached proazaphosphatranium (see Figure 1. 3J.) cations under microwave treatment to the sulfonic groups of Nafion-F to make a novel AEM. This P-N cationic head-group was confirmed by solid-state nuclear magnetic resonance techniques [41]. The alkaline stability of this novel P-N system was not evaluated. Noonan et al. attached tetrakis (dialkylamino) phosphonium group (see Figure 1. 3K.) onto a polyethylene backbone. The AEM was exposed to 1 M KOH at 80 °C. A small initial loss of hydroxide ion conductivity (from 22 to 18 mS/cm) was observed after 3 days, but no further loss in conductivity was evident up to 22 days. They suggested that the alkaline stability of the phosphonium-functionalized AEM in 1M KOH at 80 °C makes it an excellent candidate for higher-temperature alkaline membrane fuel cell devices [42]. The IEC of Noonan’s AEM was 0.67 mmol OH⁻/g Cl⁻. Although some phosphonium-based AEMs have shown great alkaline stability, they are limited by the requirement of high ion conductivity and IEC.

1.3.3. Sulfur-based cationic head groups

Zhang et al. attached a sulfonium cation (see Figure 1.3L.) onto polysulfone. The AEM remained intact after an immersion in 1 M KOH at 60 °C for 10 days, as it is confirmed by ¹H NMR spectrum.
They claimed that there was no obvious loss of conductivity for this AEM after immersion in 1M KOH for 30 days at room temperature, indicating a good long-term stability [43]. The IEC for this sulfonium-based AEM was 0.69, with a hydroxide ion conductivity of 15.4 mS/cm at 20 °C. Higher IEC values and greater hydroxide ion conductivity are desirable for sulfonium-based AEMs. The AEM showed great alkaline stability at room temperature for 30 days, and it may be a good candidate for alkaline fuel cell at room temperature, but at higher operation temperatures such as 60 °C, further studies need to be done.

1.3.4. Metal-based cationic head groups

Disabb-Miller et al. introduced bis(terpyridine) Ru(II)-based AEM (see Figure 1.3M.), using ring-opening metathesis polymerization techniques with dicyclopentadiene cross-linking moieties. The use of the metal Ru(II) complex in an AEM was targeted toward increased anion conductivity by allowing for two counter ions to be involved in ion transport, instead of the single counter ion typically associated with tethered cations such as benzyl-trimethylammonium. The highest AEM conductivity they obtained was 7.9 mS/cm for the 1.6 mmol/g IEC in chloride form at 30 °C [44]. The alkaline stability of the metal (Ru)-based AEM was not evaluated by the researchers.
Figure 1.3. Cationic head-group chemistries used in the literature to make AEMs.

1.4 Degradation mechanism of cation functional groups

The mechanisms of AEM degradation under alkaline conditions are related to the different degradation modes of the tethered cation groups. For example, quaternary ammonium can degrade
through the following known mechanisms: 1) Hoffman elimination, where the quaternary cation is cleaved, leaving tertiary amine and resulting in the formation of an alkene at the carbon in the polymer backbone where the ammonium was bonded; 2) a direct nucleophilic (S_N2) reaction where the cation is completely cleaved too, resulting in the formation of a tertiary amine and an alcohol at the carbon where the ammonium was bonded; and 3) an additional S_N2 reaction where the organic moiety adjacent to the inorganic atom (usually a methyl or alkyl group) is cleaved, resulting in the formation of a tertiary amine and an alcohol [45-48]. There are less frequently observed degradation pathways that involve the formation of ylide intermediates (commonly encountered in phosphonium and sulfonium cations), known as Sommelet–Hauser rearrangement and Stevens rearrangement [49, 50]. All these mechanisms involve the presence of a strong base and cause the formation of tertiary amines (or other groups, depending on the cation used) with the subsequent loss of ion exchange capacity and ionic conductivity [30, 31, 51, 52]. In summary, the primary reasons for degradation are nucleophilic substitutions [30, 53] and β-elimination [54] through reaction with hydroxide ions. The degradation mechanisms are shown in Figure 1.3.
1.5 Screening stable functionalization sites using model compounds

The demonstration of AEMFCs with practical power densities leads to the question of scalability which is poor for radiation grafted ionomers that enable high power density operation. Two facile alternatives to gamma radiation grafting methods to functionalize polymers are to use chloromethylation or bromination. For example, aromatic backbones such as polysulfone (PS) can be functionalized by chloromethylation followed by reaction with TMA [31]. Similarly, aromatic polymer backbones with benzyl group such as poly(phenylene oxide) (PPO) can be brominated.
followed by reaction with TMA [55]. Unfortunately, quaternary ammonium (QA) groups fixed onto backbones in this way are prone to nucleophilic attack from OH⁻ ions due to the electro-withdrawing nature of the aromatic backbone. Additionally, the delocalized π-electrons of the aromatic ring could stabilize free radicals formed during fuel cell operation, resulting in the degradation of the AEM. Rational choice of functional group and site can be made by extending the study of Marino et al. They investigated the alkaline stability of quaternary ammonium cations using model compounds [54] with the QA attached to electron-withdrawing and electro-donating substituents (Table 1.1.). The key insight from Table 1 is that the electron withdrawing groups in the backbone lead to lower half-life while electron-donating groups enhance it as a function of the degree of electrophilicity or nucleophilicity of the attachment site. Thus, stability of future AEMs can be improved by designing the backbone to contain strongly electron-donating groups.

Table 1.1. Half-life of quaternary ammonium at T= 160 °C in 6 M NaOH with electro-withdrawing and electro-donating substituents compared to a TMA benchmark. The data was summarized from Marino et al. [54]. Abbreviation of the four molecules are as follows: tetramethylammonium (TMA); 3-methoxyl-benzyl trimethylammonium (MBTM); benzyltrimethylammonium (BTM); 3-nitrobenzyltrimethylammonium (NBTM).

<table>
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<td>TMA</td>
<td>61.9</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="MBTM structure" /></td>
<td>MBTM</td>
<td>16.6</td>
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</table>
1.6 Phase segregated AEMs

To improve the hydroxide ion conductivities of AEMs, a common strategy is to improve the effective mobility of hydroxide ions rather than to increase the IEC (to avoid excessive water uptakes and dimensional swelling on hydration). The mobility of OH\(^-\) in dilute KOH solution is actually rather high and is only inferior to that of H\(^+\) but much superior to that of other ions. However, in AEMs, the motion of OH\(^-\) can be retarded by the polymer framework where the effective mobility of OH\(^-\) is often much lower than that in dilute solutions. The conduction of OH\(^-\) ions relies on the presence of water so the structure of hydrophilic domains in a polymer is the predominant factor for ion conduction. It is believed that the high ion conductivities of Nafion\(^{\circledR}\) are attributed to its phase segregation morphology. Specifically, the presence of both hydrophobic fluorocarbon polymer backbone and hydrophilic side chains drives the formation of a hydrophilic/hydrophobic phase separation structure, where ion-containing domains overlap and form interconnected ionic channels. Though, the IEC of Nafion\(^{\circledR}\) is only 0.92 mmol/g, the localised proton concentration in the ionic channels is much higher. Since, the conduction of hydroxide ions
operates in a similar mechanism. AEMs with phase segregated morphology are expected to have high ion conductivities [56].

Figure 1.4A. shows the commonly used cation group tethered directly onto polymer backbone. This structure can hardly form phase segregated morphology. Phase segregated morphologies generally exist in block (Figure 1.4B., 1.4D. & 1.4E.) and graft copolymers (Figure 1.4F.), which results from the enthalpy associated with the demixing of incompatible segments. Figure 1.4C. shows the a new method to achieve highly efficient phase segregation in a polysulfone AEM by directly attaching long hydrophobic side chains [57].

Figure 1.5. General strategies to develop AEMs with phase segregated morphology.
1.7 Anion exchange materials for sodium borohydride/hydrogen peroxide fuel cells

One of the main obstacles to developing DBFCs is the issue of crossover of the alkaline fuel and acidic oxidant. Traditional CEM separators for DBFC [58] leads to $H^+$ crossover from cathode to anode. However, replacing the CEM with AEMs [59] would maintain the alkali environment at the anode but result in $H_2O_2$ decomposition at the cathode due to crossover of $OH^-$. This led to the proposal of a bipolar interface (Figure 1.4.) to stabilize the local pH environment at the anode and cathode [7, 60]. The broad design principles identified in the case of AEMFCs is applicable here. The selection of the alkaline binder forming part of the bipolar junction is of vital importance to access high power density. The need for effective hydration is illustrated here as well by the observation that the peak power density of ca. 110 mW/cm$^2$ obtained by Arges et al. utilizing PPO-TMA (20% water uptake at 50 °C) was almost tripled by Wang et al. who use more a hydroscopic alkaline binder (120% water uptake at 30 °C) [61, 62]. Analogous to the AEMFC, water is a participant in the overall cell reaction in a DBFC. Water needs to be split at the interface during DBFC operation and the more hydroscopic alkaline binder helps to absorb more water as source for hydroxide ions and protons.
Figure 1.6. General scheme of bipolar interface structure and cell mechanism for direct sodium borohydride/ hydrogen peroxide fuel cell.

1.7.1 Derivation of junction potential at bipolar interface

At the interface of an ideal CEM and AEM, mobile protons in the CEM and mobile hydroxide in the AEM can be combined to form water. Protons in the CEM will continue to react with hydroxide in the AEM until the electrochemical potentials in the two phases become equal. The difference in activity of the protons is counterbalanced by the potential balance in the two phases. The neutralization of the protons and hydroxide at the interface of the AEM and CEM leaves that region at a relatively neutral pH. An electric field, \( E \), is generated by the fixed charges on each side of the interface, resulting in a potential difference between the two materials. The gradient in the potential, \( \phi(x) \), is opposite to the field, \( E(x) \) is given by:

\[
E(x) = -\frac{d\phi(x)}{dx}
\]  

(1)

A quantitative relationship for the electric field and activity of mobile ions can be obtained by expanding the above equation:
\[ J_{H^+} = 0 = q[\mu_{H^+}a_{H^+}E(x) - D_{H^+}\left(\frac{da_{H^+}}{dx}\right)] \]  

(2)

Where \( q \) is the elementary charge, \( \mu_{H^+} \) is the proton mobility, \( a_{H^+} \) is the activity of the protons, and \( D_{H^+} \) is the proton diffusivity. The above equation can be rearranged along with Einstein relationship \( \mu_{H^+}/D_{H^+} = q/kT \), where \( k \) is the Boltzmann constant and \( T \) is temperature, yielding the following equation:

\[ -\left(\frac{q}{kT}\right)\left(\frac{d\phi(x)}{dx}\right) = \left(\frac{1}{a_{H^+}}\right)\left(\frac{da_{H^+}}{dx}\right) \]

(3)

where \( \phi(x) \) is the potential within the membrane as a function of the distance \( x \) going from CEM to the AEM. Integration of the above equation will yield the equation for water junction:

\[ E_j = \Phi^{AEM} - \Phi^{CEM} = \frac{RT}{F} \ln \left(\frac{a_{H^+}^{CEM}}{a_{H^+}^{AEM}}\right) \]

(4)

where \( E_j \) is the contact potential between the AEM (\( \Phi^{AEM} \)) and CEM (\( \Phi^{CEM} \)) and \( R \) is the ideal gas constant. It is assumed that hydroxide and protons are in equilibrium everywhere and \( K_w = a_{H^+}a_{OH^-} \), which yields

\[ E_j = \Phi^{AEM} - \Phi^{PEM} = \frac{RT}{F} \ln \left(\frac{a_{H^+}^{PEM}}{a_{H^+}^{AEM}}\right) - \frac{RT}{F} \ln(K_w) \]

(5)

If the activity of the protons in the PEM and hydroxide within the AEM were both at unit activity, then the contact or interface potential would be 0.83 V. The derivation was based on the work of Kohl et al [60].

**1.8 Anion exchange materials for redox flow batteries**

The drive towards increased renewables adoption and the technological build-out of allied energy conversion solutions like redox flow batteries (RFBs) is increasingly an economical inevitability
with the levelized costs of terrestrial solar and wind installations being much lower than conventional coal, nuclear or oil-based power plants. A key component in this envisioned integrated hydrogen economy are RFBs that use different redox couples: All-vanadium,[63-66] all-uranium [67], iron-vanadium [68, 69], iron-chromium [70, 71], zinc-nickel [72], zinc-cerium [73-75], and zinc-bromine [76, 77]. Among these redox couples, the all-vanadium redox flow battery (VRFB) (shown in Figure 1.7.) has been considered the most reliable RFB system due to its long-life and mild operating temperature range [78]. Moreover, intermixing of negative and positive electrolyte does not cause irreversible damage in the VRFB [79]. The drawbacks of VRFBs include their low standard cell voltage (1.26V) and the relatively low solubility of vanadium salts (typically 1.5 M in common acids, such as sulfuric acid), which limit their specific capacity and energy density. Besides, hydrocarbon-based membrane separators suffered from oxidative degradation caused by the vanadium (V) cation. This required the use of fluorocarbon-based membranes as separators. The expensive vanadium salts and the high cost of the fluorocarbon-based separators have limited the commercialization of VRFBs. The detailed study of a specific type RFB system will be discussed in the following section.
1.9 Dissertation outline

There are four following chapters, each of which addresses one critical problem in the topical of alkaline stability of AEMs and application of anion exchange and bipolar membranes in electrochemical energy storage and conversion. Each chapter consists 6 subsections: *abstract*, *introduction*, *methods*, *results and discussion*, *conclusion*, and the end-of-chapter *references*.

The most commonly used AEMs reported in the literature contain quaternary ammonium groups, primarily in the form of benzyl trimethylammonium cations [7, 21, 30, 52, 80-98]. However, it had been shown that such quaternary ammonium-based AEMs are sensitive towards Hofmann
elimination [30, 99] and direct nucleophilic elimination reactions [53, 100] that result in loss of IEC and ionic conductivity. Chapter 2 investigates the alkaline stability of alternative cations such as novel imidazolium cation groups. The objectives of this chapter were two-fold. First, the role of flexible alkyl spacers in enhancing the alkaline stability of imidazolium-based AEMs was clarified. Second, the effect of grafting alkyl chains at the C-2 and N-3 positions of imidazolium cations on the degradation rate and mechanism (upon exposure to alkali) of the resultant imidazolium-based-AEMs was investigated.

Chapter 3 targets the synthesis of polystyrene-\textit{block}-poly(ethylene-\textit{ran}-butylene)-\textit{block}-polystyrene (SEBS)-based AEMs with hydroxide ion conductivity of more than 100 mS/cm at 70 °C. The objectives of this chapter were two-fold. First, the fuel cell performance using SEBS-based membranes and solubilized AEM binders were investigated. Second, \textit{in situ} stability of different AEM binders in an operating AEM fuel cell were compared and analyzed. To this end, chloromethylated SEBS with a high degree of functionalization (DF) was prepared and quaternized by reaction with trimethylamine to obtain SEBS-based AEMs. Trimethylamine and tris(2,4,6-trimethoxyphenyl) phosphine were also reacted with brominated PPO (BrPPO). Besides, trimethylamine was reacted with the brominated PPO containing a six-carbon pendant chain to obtain the corresponding AEMs.

Chapter 4 demonstrates a PMBI that facilitates significantly different local pH environments at the anode and cathode of a DBFC. The overarching objectives of the current work were two-fold. First, we experimentally prepared microscale bipolar interfaces and examined their ability to control the local pH gradient at the electrocatalytic reaction sites. Second, we translated these microscale bipolar interfaces to DBFC devices and engineered the interfacial pH gradient to obtain a high-voltage device able to deliver practical current densities at cell voltages above 1.2 V. The
resultant PMBI-based DBFC yielded a current density of 330 mA/cm$^2$ at 1.5 V and a peak power density of 630 mW/cm$^2$ at 1 V.

Chapter 5 explores alternative redox species/couples for RFB application other than VRFB. The vanadium-cerium redox flow battery (V-Ce RFB) has relative high cell voltage (Ce$^{4+}$/Ce$^{3+}$ has standard potential of 1.44 V vs. SHE compared with V$^{5+}$/V$^{4+}$ at 1 V vs. SHE), good reversibility and acceptable energy density [101]. SEBS-based AEMs with high ionic conductivity was used to efficiently separate the decoupled anolyte and catholyte solutions containing different elemental species so that the (irreversible) intermixing is minimized. The stability of the AEMs in conditions resembling those encountered in the RFB (acidic, with selected metal cations present) was investigated.

1.10 References


Chapter 2: Alkaline stability of poly(phenylene oxide) based anion exchange membranes containing imidazolium cations


Supplementary figures and tables are available in Appendix II
Abstract

Two modified imidazole bases (1-heptyl-2-methyl-imidazole and 1-dodecyl-2-methyl-imidazole) were synthesized, each with a long alkyl chain (7 or 12 carbon) attached to the N-3 position. Anion exchange membranes (AEMs) were prepared with imidazolium cations derived from these bases that were either grafted directly onto the benzyl position of poly (phenylene oxide) (PPO) or affixed to the PPO using a hexyl spacer chain. First, we reacted 1-methylimidazole with brominated PPO and with PPO with a hexyl spacer chain. By comparing the alkaline stability of the resultant AEMs, we demonstrated that a hexyl spacer chain could improve AEM alkaline stability substantially. Second, by comparing the alkaline stability of PPO-based AEMs obtained by the reaction of brominated PPO with 1-methylimidazole and 1,2-dimethylimidazole, we showed that C-2-substituted (with a methyl group) imidazolium-based AEMs were much more stable in alkali than C-2-unsubstituted imidazolium-based AEMs. Finally, by investigating the alkaline stability of AEMs synthesized by reaction of brominated PPO with 1,2-dimethylimidazole and modified imidazole bases (with 7 or 12 alkyl carbon chain at the N-3 position), we demonstrated that the increase in length of a long alkyl chain affixed to the N-3 position decreases the alkaline stability of the resultant imidazolium-based AEMs.
2.1 Introduction

There is a growing interest in using anion exchange membranes (AEMs) as separators in alkaline membrane fuel cells (AMFCs) [1, 2] and in other energy conversion and storage systems such as redox flow batteries (RFBs) [3-5], alkaline water electrolyzers (AWEs) [6, 7] and reverse electrodialysis (RED) cells [8].

The most commonly used AEMs reported in the literature contain quaternary ammonium groups, primarily in the form of benzyl trimethylammonium cations [6, 9-30]. However, it had been shown that quaternary ammonium-based AEMs are sensitive towards Hofmann elimination[10, 31] and direct nucleophilic elimination reactions [32, 33] that result in loss of ion exchange capacity (IEC) and ionic conductivity. To resolve the stability problem inherent to quaternary-ammonium-group-containing AEMs, several alternative cations, including imidazolium,[31, 34, 35] benzimidazolium [36], guanidinium [37], phosphonium [38-40] and metal cations [41] have been proposed and investigated. Imidazolium-based AEMs have drawn researchers’ interests mainly because of their high hydroxide-ion conductivities [42]. However, it has been reported that imidazolium-based AEMs degrade under alkaline conditions at temperatures below 80 °C. Ye et al. investigated the degradation mechanism of imidazolium-based AEMs at several relative humidities, temperatures and pH. They found that imidazolium-based AEMs were chemically stable at low temperatures, but relatively unstable at higher temperatures in alkaline conditions (degradation commences at 80 °C when [KOH]>1M). They postulated the following degradation mechanism: Ring-opening of the imidazolium ring was triggered by the nucleophilic attack of OH− on the imidazolium ring at the C-2 position (alpha carbon with respect to both nitrogen atoms). The degradation products were carboxylates and alkoxide salts, and the imidazolium ring was cleaved [31].
Wang et al. investigated the activation free energy for the hydroxide-induced nucleophilic substitution reaction on alpha-carbon-methyl-substituted imidazolium cations (trimethylimidazolium) and alpha-carbon-methyl-unsubstituted imidazolium cations (dimethylimidazolium) using DFT. They found that the activation free energy barrier (57.1 kJ/mol) for the nucleophilic reaction of the trimethylimidazolium cation with hydroxide ion exceeded the corresponding energy barrier for the alpha-carbon-methyl-unsubstituted dimethylimidazolium cations by about 43 percent. Their results suggested that the alpha-carbon-methyl-substituted imidazolium cations were more stable under alkaline conditions than imidazolium cations containing hydrogen in the alpha position. This was attributed to hyper conjugation between the methyl group at the alpha-carbon position and the imidazole ring, and due to the steric effect of the methyl group [28].

Lin et al. grafted a methyl group onto the C-2 position of imidazole (alpha carbon with respect to both nitrogen atoms) to improve the alkaline stability of the imidazolium cation. They reported 48% degradation of C-2 unsubstituted 3-ethyl-1-methylimidazolium bromine exposed to 1 M KOH for 60 hours, while the C-2 substituted 3-ethyl-1,2-dimethylimidazolium bromine did not degrade even in 2M KOH after exposure for 168 hours [34]. These experimental findings supported the modeling results of Wang et al. [28].

Marino et al. tested the half-life of imidazolium salts in 6 M sodium hydroxide, and they reported that the half-life of the C-2 unsubstituted 1-methyl-3-octyl-imidazolium was too short to measure at 60 °C, and that the half-life of the C-2 substituted 1,2,3-trimethylimidazolium was also too short to measure at 160°C [43]. So, the question of whether grafting a methyl group to the C-2 position of the imidazole ring would improve the alkaline stability of the resultant cation remains controversial.
Gu et al. investigated the alkaline stability of C-2 substituted (methyl group) imidazolium cations with various groups attached to the N-3 atom (nitrogen atom that is located farthest from the polymer backbone). They reported 36.4% degradation of 1,2,3-trimethylimidazolium iodide exposed to 2 M KOH solution at 80 °C for 432 hours, while the corresponding degradation extent of 1,2-dimethyl-3-butylimidazolium bromine was 3.2% [35]. This report suggested that attaching a long alkyl chain to the N-3 position would improve the alkaline stability of imidazolium cations. These prior results make it reasonable to postulate that imidazolium-based AEMs modified by grafting alkyl chains to the C-2 and N-3 positions have the potential to exhibit higher alkaline stability than traditional quaternary-ammonium-based AEMs.

Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) has been extensively studied and shown to be a mechanically and chemically stable backbone for the synthesis of alkaline stable AEMs [44] [36] [10] [14]. Hibbs [45] has shown that poly(phenylene)-based AEMs with quaternary ammonium cations affixed to the benzene rings in the backbone using a six-carbon alkyl chain spacer were considerably more stable than those prepared with benzyl trimethylammonium cations attached directly to the backbone. When these two types of AEMs were immersed in nitrogen-degassed 4M KOH at 60°C for 14 days, only a minimal (ca. 5%) loss in IEC was observed in the former case while a 21% loss in IEC was observed in the latter case. This result suggested that the introduction of alkyl spacers separating the cation from the backbone enhanced the alkaline stability of AEMs based on polyphenylene backbones.

Dang et al. [46] functionalized a PPO backbone with quaternary ammonium groups via flexible alkyl spacers and compared this AEM with to one prepared by reacting PPO directly with quaternary ammonium groups. They reported the quaternary ammonium protons in the 1H NMR spectrum stayed unchanged when the AEM with spacer was immersed in 1 M NaOH for for 192
hours. However, in the case of the AEM with quaternary ammonium group attached directly to PPO, the proton on quaternary ammonium degraded by 84% after 192 hours in 1 M NaOH. Parrondo et al. [47] investigated AEMs prepared with hexyl trimethylammonium cations, separated from the PPO backbone by a hexyl pendant chain. They reported that AEMs prepared with the pendant chains exhibited a 33% loss in IEC after 30 days in 1 M KOH at 60 °C. The degradation rate was very similar for AEMs prepared without pendant chains. This discrepancy in results suggests that the degradation of AEMs prepared with spacers separating the backbone from the cation involves complex interplays between the backbone, the cations affixed and the experimental conditions employed.

The objectives of the current work were: 1) to clarify the role of flexible alkyl spacers in enhancing the alkaline stability of imidazolium-based AEMs; 2) to investigate the effect of grafting alkyl chains at the C-2 and N-3 positions of imidazolium cations on the degradation rate and mechanism (upon exposure to alkali) of the resultant imidazolium-based-AEMs,

To this end, AEMs were prepared by reacting several imidazole bases (prepared with methyl and alkyl groups attached to C-2 and N-3 position in imidazole ring) directly with brominated PPO (BrPPO; brominated at the benzyl position of PPO) or with brominated PPO containing the bromide leaving group at the end of a hexyl pendant chain affixed to the PPO backbone (BrPPO-C6Br). The resultant imidazolium-based AEMs were studied to evaluate and compare the alkaline stability of several variants of AEMs: a) those prepared with and without a hexyl pendant chain separating the backbone and cation group, b) those prepared with and without methyl groups grafted onto the C-2 position, and c) those prepared with and without alkyl pendant chains of different lengths grafted onto the N-3 position of the imidazolium group. We functionalized the six-carbon spacer onto PPO using a three steps synthesis process: 1) Friedel–Crafts acylation using
6-bromo-1-hexanoyl chloride; 2) reduction of the ketone in the benzyl carbon attached to the aromatic ring, to improve the alkaline stability; and 3) quaternization by reaction with 1-methylimidazolole or with modified imidazole bases with methyl and/or alkyl groups grafted on C-2 and/or N-3 positions. The alkaline stability was evaluated with time.

2.2 Methods

2.2.1 Materials

PPO (Mn=20000, Polydispersity=2.5) was purchased from Polysciences Inc. 1-methylimidazolole (99%, ACROS Organics™), Chlorobenzene, methanol (99.9%), chloroform (99.8%), were purchased from Fisher Scientific. 2-methylimidazolole (99%), 1,2-dimethylimidazolole (98%), 1-bromoheptane (99%), 1-bromododecane (99%), N-bromosuccinimide (99%), azobisisobutyronitrile (98%), chloroform-d (99.96%), dimethyl sulfoxide-d6 (99.96%), dimethylformamide-d7 (99.5%), 1-methyl-2-pyrrolidinone (99.5%), 6-bromohexanoyl chloride (97%), aluminum chloride (99.99%), 1,2-dichloroethane (99.8%), triethylsilane (99.9%), KOH (90%) and trifluoroacetic acid (99%) were purchased from Sigma-Aldrich.

2.2.2 Synthesis of 1-heptyl-2-methyl-imidazole (2MI-C7) and 1-dodecyl-2-methyl-imidazole (2MI-C12)

A mixture of 2-methylimidazolole (2g) and of 1-bromoheptane (3.82 mL) was dissolved in 20 mL of 1-methyl-2-pyrrolidinone (NMP) and stirred at 60°C for 24 h (see Figure 2.1. for details of the reaction). The product was recovered after evaporation of the solvent and unreacted reagents in an oven at 70 °C overnight. ¹H NMR spectroscopy and 2-D correlation spectroscopy (COSY) were used to verify that the reaction yielded the desired product, and to test the purity of the product (see Appendix II, Figures A2.1. & A2.2.).
A mixture of 2-methylimidazole (2g) and 1-bromoheptane (5.86 mL) was dissolved in 20 mL of NMP and stirred at 60°C for 24 h (see Figure 2.1. for details of the reaction). The product was recovered by removing the solvent in an oven at 70°C. $^1$H NMR and COSY NMR spectroscopy were used to confirm that the reaction occurred as expected and to test the purity of the product (see Appendix II, Figures A2.3. & A2.4.).

Figure 2.1. Scheme for the synthesis of the bases: 1-heptyl-2-methyl-imidazole (2MI-C7) and 1-dodecyl-2-methyl-imidazole (2MI-C12).

### 2.2.3 Synthesis of brominated PPO (BrPPO)

A mixture of PPO (20g) and N-bromosuccinimide (20g) was dissolved in chlorobenzene (300 mL). After complete dissolution, 0.4g of azobisisobutyronitrile (free radical initiator) was added, and the mixture was heated to 108°C and kept under stirring (in inert atmosphere) for 12 h. The brominated polymer thus obtained was precipitated in methanol and purified by re-dissolution in chlorobenzene and precipitation in methanol. The polymer was filtered, washed with abundant
methanol and methanol/water (1:1 Vol.) and dried in a vacuum oven at 60 °C for 24 hours. Figure 2.2. shows the reaction scheme for the synthesis of brominated PPO. The degree of functionalization (DF, number of bromines per polymer repeat unit) was 0.36 mol (see \(^1\)H NMR spectrum of brominated PPO in Appendix II, Figure A2.5.).

![Reaction Scheme for the Synthesis of Brominated PPO](image)

Figure 2.2. Scheme for synthesis of imidazolium-based AEM by attaching the corresponding bases to the benzyl position of PPO (P1, P12, PC7 and PC12).
2.2.4 Synthesis of imidazolium-based AEMs: P1, P12, PC7 and PC12

**P1:** BrPPO (0.5g) and 1MI (70 μL) were dissolved in 9 mL of NMP, stirred at 60 °C for 24 h, cast onto a glass plate (3.5” x 3.5”) and the solvent dried in an oven at 70 °C for 12 h. (See reaction scheme is in Figure 2.2. and resulting ¹H NMR spectrum in Appendix II, Figure A2.6.).

**P12:** BrPPO (0.5g) and 1,2DMI (88μL) were dissolved in 9mL of NMP, stirred at 60°C for 24 h, cast onto a glass plate (3.5” x 3.5”) and the solvent dried in an oven at 70°C for 12 h (see reaction scheme is in Figure 2.2. and resulting ¹H NMR spectrum in Appendix II, Figure A2.7.).

**PC7:** BrPPO (0.5g) and 2MI-C7 (0.18g) were dissolved in 9 mL of NMP, stirred at 95°C for 48 h, cast onto a 3.5” x 3.5” glass plate and the solvent evaporated in an oven at 70°C for 12h. (See reaction scheme in Figure 2.2. and ¹H NMR spectrum in Appendix II, Figure A2.8.).

**PC12:** BrPPO (0.5g) and 2MI-C12 (0.25g) were dissolved in 9 mL of NMP, stirred at 100°C for 48 h, cast onto a 3.5” x 3.5” glass plate and heated in an oven at 70°C to dry the solvent. (Reaction scheme shown in Figure 2.2. and ¹H NMR spectrum of resulting AEM shown in Appendix II, Figure A2.9.).

2.2.5 Addition of a six carbon pendant chain to poly (phenylene oxide): PPO-KC6Br

The addition of an alkyl pendant chain to PPO was carried out following a slight modification of the method described by Hibbs[45]. PPO (10g) was dissolved in 500 mL of chlorobenzene in a round bottom flask. Once PPO was completely dissolved, the flask was placed in an ice bath and allowed to equilibrate for 30 mins. Subsequently, 19.1 mL of 6-bromohexanoyl chloride and 5 g of aluminum (III) chloride (Lewis acid catalyst) were added, the ice bath was removed and the
mixture was allowed to react overnight. The resultant brominated polymer was precipitated in 2.5 L methanol, and purified by re-dissolution in chloroform and re-precipitation in methanol. The yield for the acylation reaction was approximately 25% and the degree of functionalization (DF) of the polymer was 0.31. The DF was determined from the $^1$H NMR peak area (see $^1$H NMR spectrum in Appendix II, Figure A.2.10.).

2.2.6 Reduction of the ketone group in PPO-KC6Br (PPO-C6Br)

PPO-KC6Br (5g) was dissolved in 400 mL of 1,2-dichloroethane. Once completely dissolved, trifluoroacetic acid (290 mL) and triethylsilane (30 mL) were added, the reaction mixture heated under stirring to 100 °C and kept reacting under reflux conditions overnight. Subsequently, the polymer solution was washed with 500 mL of 1 M KOH until neutral pH and poured into 2L of deionized water and heated until the organic solvent evaporated. The solid precipitate was dried in a vacuum oven at 60 °C and purified by re-dissolution in chloroform and re-precipitation in methanol. The $^1$H NMR spectrum of the resultant polymer confirming the reduction of the ketone group is shown in Appendix II, Figure A2.11. Further details of the synthesis and characterization of the polymer can be found in our previous paper [47].

2.2.7 Synthesis of imidazolium-based AEMs with a six-carbon alkyl spacer:

PX1, PX12, PXC7 & PXC12

$PX1$: PPO-C6Br (0.5g) and 1MI (70μL) were dissolved in 9 mL of NMP and stirred at 60 °C for 24 h, the solution was cast on a glass plate (3.5” x 3.5”) and the solvent evaporated in an oven at 70 °C for 12h. (See Figures 2.3. and Appendix II, Figure A2.12. to see the synthesis scheme and $^1$H NMR spectrum, respectively).
PX12: PPO-C6Br (0.5g) and 1,2DMI (88μL) were dissolved in 9 mL of NMP and stirred at 60°C for 24 h. Then, the solution was cast on a glass plate (3.5” x 3.5”) and the solvent evaporated in an oven at 70°C for 12h. (See Figures 2.3, and Appendix II, Figure A2.13. to see the synthesis scheme and 1H NMR spectrum, respectively).

PX7: PPO-C6Br (0.5g) and 2MI-C7 (0.17g) were dissolved in 9 mL of NMP and allowed to react at 130°C for 48 h. To get the thin-film membrane, the solution was cast onto a glass plate (3.5” x 3.5”) and the solvent was evaporated in an oven at 70°C for 12 h. (See Figures 2.3. and Appendix II, Figure A2.14.).

PX12: PPO-C6Br (0.5g) and 2MI-C12 (0.23g) were dissolved in 9 mL of NMP, and heated at 110°C for 48 h. The membrane was obtained by casting the polymer solution as described above (Figures 2.3. and Appendix II, Figure A2.15.).
Figure 2.3. Scheme for the synthesis of imidazolium-based AEMs by attaching the corresponding bases to the end of an alkyl chain pendant attached to the PPO polymer backbone (PX1, PX12, PXC7 and PXC12).
2.2.8 Characterization of the AEMs

The following NMR spectroscopy experiments were performed on a Bruker Avance 360 MHz NMR spectrometer: 1) $^1$H NMR spectra (collected at 360 MHz) and 2) correlation spectroscopy (COSY). Additional details regarding the NMR experiments are presented in Appendix II and in our previous papers [22, 47, 48].

Anion exchange capacity was determined using Volhard titration. The AEMs (dry weight of approximately 0.1 g) were immersed in 20 mL of 1 M sodium nitrate for 48 h. The amount of chloride ions exchanged was determined by back titration using 0.1 M potassium thiocyanate, after addition of 5 mL of 0.1 M silver nitrate. A control sample containing only 20 mL of 1M sodium nitrate was also titrated as described above. Iron (III) nitrate was used as endpoint indicator. The anion exchange capacity (for the chloride counter ion) was calculated using the following equation:

$$ IEC = 0.1x \frac{(V_C-V)}{W} $$

(2.1)

Where $IEC$ is the anion exchange capacity (mol/g), $V_C$ is the volume (mL) of 0.1 M potassium thiocyanate necessary to reach the equivalence point with the control sample, $V$ the volume (mL) of thiocyanate required to reach the equivalence point with the AEM sample and $W$ the dry weight (g) of the AEM sample. Additional details of the application of the method can be found in our previous papers [3, 6, 10, 14, 47].

2.3 Results and Discussion

Figure 2.1. shows the scheme for the synthesis of modified imidazolium cation groups: 1-heptyl-2-methyl-imidazole (2MI-C7) and 1-dodecyl-2-methyl-imidazole (2MI-C12). The formation of 2MI-C7 was confirmed by the $^1$H-NMR and 2D NMR (Correlation Spectroscopy; COSY) spectra
as shown in Appendix II, Figures A2.1. and A2.2 The $^1$H NMR spectrum of 1-bromoheptane (in CDCl$_3$, 350MHz) revealed the presence of protons at chemical shifts of ca. $0.9$ ppm (3H, triplet), $1.4$ ppm (8H, overlapping of several peaks), $1.8$ ppm (2H, multiplet) and $3.4$ ppm (2H, triplet). The $^1$H NMR spectrum of 2-methylimidazole revealed protons at chemical shifts of ca. $2.3$ ppm (3H, singlet) and $6.8$ ppm (2H, singlet) [49]. The protons initially at $3.4$ ppm (in the spectrum of 1-bromoheptane) shifted, after reaction with 2-methylimidazole, to ca. $4.2$ ppm. The disappearance of the proton peak at $3.4$ ppm confirmed that the reaction of 2-methylimidazole to 2MI-C7 was complete (see Appendix II, Figure A2.1.).

$^1$H-$^1$H COSY NMR spectroscopy (Appendix II, Figure A2.2) showed a coupling between protons “4” and “3”, but there were no couplings between protons “4” and protons “5” or “6”, which were in the aromatic ring and were separated from protons “4” by a nitrogen atom. Please refer to the proton labels and chemical structure in Appendix II, Figure A2.2. Multiple proton-proton couplings in the aliphatic chain “1-4” were also observed. $^1$H NMR and COSY spectra thereby confirmed the formation of the desired product (2MI-C7).

The $^1$H NMR spectrum of 1-bromododecane (CDCl$_3$, 350MHz) showed protons at chemical shifts of ca. $0.9$ ppm (3H, triplet), $1.4$ ppm (18H, overlapping of several peaks), $1.8$ ppm (2H, multiplet) and $3.4$ ppm (2H, triplet) ppm. As in the previous instance, the protons in 1-bromododecane that initially featured at a chemical shift of $3.4$ ppm were altered after the reaction with 2-methylimidazole to a chemical shift of $4.2$ ppm. The peak at $3.4$ ppm that was initially present in the reactant disappeared, confirming that the reaction of 2-methylimidazole to 2MI-C12 was complete (see Appendix II, Figure A2.3.). The corresponding COSY spectrum (Appendix II, Figure A2.4.) showed couplings between the protons in the aliphatic chain: “4” and “3”, “3” and “2”, and “2” and “1”. No couplings of these protons were observed with any of the protons in the
imidazole ring (the nitrogen atom present in-between impeded any possible couplings). The \(^1\)H NMR and COSY spectra thereby confirmed the formation of the desired product (2MI-C12).

AEMs were synthesized by reacting the BrPPO with 1-methylimidazole (1MI), 1,2-dimethylimidazole (1,2DMI), 1-heptyl-2-methyl-imidazole (2MI-C7) and 1-dodecyl-2-methyl-imidazole (2MI-C12). When 1MI was attached on the benzyl position of PPO, the imidazolium-based AEM (P1) was obtained. Following a similar scheme, imidazolium-based AEMs, P12, PC7 and PC12 were obtained. All these AEMs had the cations affixed directly to the benzyl position. Figure 2.2. shows the scheme for the synthesis of these imidazolium-based AEMs (P1, P12, PC7 and PC12). Note: The N-1 position in the imidazole base and the N-3 position in the imidazolium cation attached to the polymeric backbone are equivalent. The different numbers result from the naming conventions. In the imidazole base, the numbering starts from the nitrogen to which the alkyl group is attached (i.e. heptyl; N-1). The base therefore reacts at the N-3 position under this system. Once the imizalolium cation is being formed, the numbering starts from the nitrogen attached to the backbone, which become the new N-1. BrPPO had a bromomethyl group (benzyl position) and these protons (peak “3”) appear at a chemical shift of 4.33 ppm (Appendix II, Figure A2.5.). The degree of functionalization (DF, mol of bromomethyl groups per polymer repeat unit) obtained by comparison of the peak areas of protons “3” to the protons present in the aromatic rings of the backbone was 0.36. Details of the calculations employed to arrive at this value can be found in our previous papers.[10, 47] The shift of the protons present initially in the bromomethyl group (peak “3”, initially at 4.33 ppm) to higher frequencies (5.30 ppm) was attributed to the proximate presence of the positively charged cation and demonstrated the formation of the product (P1, see Appendix II, Figure A2.6.). A small shift in the protons of type “6”, from \textit{ca}. 7 ppm to 7.65 ppm was also observed during the reaction with brominated PPO. A similar shift in the
protons present in the aromatic ring of imidazole and those present in the bromomethyl groups was observed upon reaction of the other three imidazole bases (1,2DMI, 2MI-C7 and 2MI-C12) and BrPPO (see Appendix II, Figure A2.7., Figure A2.8. & Figure A2.9.).

Friedel–Crafts acylation of 6-bromohexanoyl chloride was employed to add a six-carbon spacer to PPO, allowing the cation to be separated from the backbone in an attempt to minimize the possible electronic effects of the backbone/cation on the alkaline stability of the AEM. The following AEMs were synthesized using this modified platform: PX1, PX12, PXC7 and PXC12.

Figure 2.3. shows the synthesis scheme for imidazolium-based AEMs prepared with the spacer chain (PX1, PX12, PXC7 and PXC12). The grafting of the six-carbon pendant chain to the PPO backbone (to yield PPO-KC6Br) was confirmed through $^1$H NMR spectroscopy (see Appendix II, Figure A2.10.). Peak “5” (3.0 ppm) corresponds to the protons attached to the carbon adjacent to the ketone group. Additional assessment of the presence of the ketone group in the benzyl position was performed using $^{13}$C NMR spectroscopy in our previous paper [47]. The peak at 207 ppm corresponds to the carbon in the ketone group. The $^1$H NMR peak at 3.4 ppm (peak “9”) corresponds to the protons in the bromomethyl group at the end of the pendant chain. The brominated polymer (PPO-KC6Br) had a degree of bromination (DF) of 0.31 mol of bromine per polymer repeat unit. This DF was selected to prepare AEMs with suitable IEC (of at least 0.7-1.0 mmol (chloride)/g) after addition of the bulky imidazolium bases used in this work.

Hibbs [45] pointed out that the ketone group in PPO-KC6Br promotes rapid AEM degradation in alkaline solutions. To increase the stability of our AEMs, the ketone group in PPO-KC6Br was reduced with triethylsilane in the presence of trifluoroacetic acid in 1,2-dichloroethane (Appendix II, Figure A2.11. shows the $^1$H NMR spectrum of the reduced polymer, PPO-C6Br). The protons
in the aromatic rings functionalized with the pendant chain shifted from 6.1 ppm (peak “2’”) to ca.
6.0 ppm (peak “2”) after reduction of the ketone group. Both peaks were present in the NMR
spectrum of the reduced product and their areas were used to calculate the yield of the ketone
reduction reaction (Formula: Area 2/ (Area 2 + Area 2’)). The yield for the ketone reduction
reaction was between 95 to 98%.

The ¹H NMR spectrum of the product obtained from the reaction between 1-methylimidazole and
PPO-C6Br is shown in Appendix II, Figure A2.12. The protons of the bromomethyl group (at 3.40
ppm) shifted to 4.19 ppm (peak “10”) after reaction with the imidazole base. The protons in the
aromatic ring of imidazole (“11”) shifted from ca. 7.1 ppm to 7.82 ppm after reaction with PPO-
C6Br, yielding PX1. Similar changes in NMR spectra were observed for PX12 (Appendix II,
Figure A2.13.), PXC7 (Appendix II, Figure A2.14.) and PXC12 (Appendix II, Figure A2.15.), and
these observations confirmed the successful synthesis of the three AEMs.

The IECs of the different AEMs synthesized in this work are shown in Appendix II, Table 2.1.
The theoretical IEC values were calculated from the DF of the corresponding brominated polymers
(Formula: IEC (mmol/g) =1000 x DF/ Equivalent Weight (g/mol)) [47]. The theoretical IEC values
for P1, P12, PC7 and PC12 were 1.69 mmol/g, 2.15mmole/g, 1.45mmol/g and 1.31mmol/g,
respectively. The theoretical IEC values decreased when larger bases were used as a result of the
increasing molecular weight of the polymer repeat unit.

The experimental IEC values for all AEMs were obtained by the Volhard titration method. The
details of the method can be found in our previous paper [10]. The IEC for P1 was very close to
the theoretical IEC, confirming that the reaction yield was almost 100%. For P12, PC7 and PC12,
the yields for the corresponding reactions were 95%, 54% and 70%, respectively (see Appendix
II, Table 2.1.). The long alkyl chain attached to the N-3 position of the imidazole ring made the resultant base bulkier than 1-methylimidazole, and, consequently, more difficult to react with the PPO-C6Br. Similarly, the yields for the reactions between the bases (1MI, 1,2DMI, 2MI-C7 and 2MI-C12) and PPO-C6Br were 93%, 97%, 57% and 72%, respectively. The reasons for the low conversions with 2MI-C7 and 2MI-C12 were the same as described earlier for BrPPO.

Our motivation in studying the alkaline stability of the above AEMs was three-fold. Firstly, we wanted to verify if the finding of Hibbs [45] that the presence of a long alkyl spacer between the PPO backbone and the quaternary ammonium group would improve the alkaline stability of AEM to a great extent would hold for imidazole-based cations in conjunction with the PPO backbone. To verify this finding, we reacted the same imidazolium cation such as 1MI with BrPPO and PPO-C6Br. Then, we compared the alkaline stability of these two AEMs. The second finding that we wanted to verify was that of Lin and coworkers [34], who proposed that C-2 substituted (with a methyl group) imidazolium-based AEMs were much more stable in alkali when compared with C-2 unsubstituted imidazolium-based AEMs. To verify this finding, we compared the alkaline stability of AEMs made using C-2 substituted imidazole (1,2DMI) and C2 unsubstituted imidazole (1MI). In the third instance, we wanted to verify and extend the work of Ye et al.[31], who reported that N-3 substituted (by adding a long chain alkyl group) imidazolium-based alkaline anion exchange polymerized ionic liquid (poly(1-[(2-methacryl-oyloxy)ethyl]-3-butylimidazolium hydroxide) is more stable in alkali than N-3 unsubstituted imidazolium-based AEM. We wanted to further investigate if increasing the length of long chain alkyl group in the N-3 position would further enhance the alkaline stability of the resultant AEM. By reacting the bases (1,2DMI, 2MI-C7 and 2MI-C12) with BrPPO, we studied the role played by the long chain alkyl group in the N-3 position on alkaline stability.
Figure 2.4. shows the results of our AEM alkaline stability evaluation experiments. From the experiment results in Figure 2.4., we could demonstrate three trends. First, the IEC fractions retained after 810 minutes exposure to 1M KOH at 60 °C were 27% and 70%, for P1 and PX1, respectively. The AEMs prepared with a spacer chain still degraded under these conditions, but the presence of the six-carbon spacer grafted between the PPO backbone and the 1MI cation, substantially improved the stability. This result verified the finding of Hibbs [45] that an alkyl spacer between the BrPPO and cation group would sterically shield the beta-hydrogens and thereby increase stability. Besides, when there was a nonmethyl substitution on the nitrogen atom, there was an increased susceptibility to S_N2 attack. Second, as shown in Figure 2.4., the IEC fractions retained after 810 minutes of exposure to 1M KOH for P1 and P12 were 27% and 74%, respectively. The C-2 carbon of 1-methylimidazolium is the most likely place to be attacked by the hydroxide ion [28]. When a C-2 methyl group was grafted, the alkaline stability of the resultant imidazolium cation increased as a consequence of enhanced steric hindrance towards OH^- ion attack at the C-2 position of the imidazolium ring. Third, the IEC fractions retained for PX12, PXC7 and PXC12 were 88%, 17% and 11%, respectively. This result demonstrated both that the N3 substituent lead to worse alkaline stability, and that increasing the length of N-3 alkyl chain did not improve the alkaline stability. Sean et al. [50] reacted trimethylamine and N,N-dimethylhexylamine with chloromethylated polystyrene to make two types AEMs. The AEM of N,N-dimethylhexylamine attached to the polystyrene degraded faster under alkaline conditions than trimethylamine attached to the polystyrene. Our alkaline stability test for N-3 substituted with long alkyl chain was consistent with the finding of Sean and co-workers. Even with an alkyl spacer between polymer backbone and imidazolium cation, the long alkyl chain in the N-3 position of imidazolium cation significantly decreased the alkaline stability of the AEM. So the long alkyl
chain at the N-3 position of the imidazolium cation decreased both the IEC and the stability of imidazolium-based AEMs.

Figure 2.4. Alkaline stability of imidazolium-based AEMs in 1 M KOH at 60 °C. The solutions were degassed with nitrogen to prevent any carbonate formation.

Figure 2.5. shows the $^1$H NMR spectra of PC7 before and after exposure to 1M KOH (at 60°C) for 6 hours. After immersion in alkali, we observed the appearance of a new peak [6’*] at a chemical shift of 3.93 ppm (see red rectangular frame in Spectrum1 in Figure 2.5.). Ye et al. [31] have observed that imidazolium-based anion exchange ionic liquids treated with alkali experienced hydroxide ion attack at the C-2 carbon, resulting in a ring-opening reaction. The protons labeled as 6 and 6’ (Spectrum 2 in Figure 2.5.) corresponding to the aromatic protons in the imidazolium ring will disappear in the case of a ring opening reaction. The protons will be in an aliphatic chain
in the final product \([6^* \text{ and } 6'^*]\) and will have considerably lower chemical shifts (\textit{ca.} 4 ppm). We have observed all these changes in our spectra, confirming that the ring opening reaction occurred in PC7 upon exposure to alkali. We have also observed that the peak area for the protons in the methylene bridge (peak 8, linking the backbone to the base) decreased after exposure to alkali. This observation also confirmed the loss of cationic sites and reaffirmed the ring opening reaction in the imidazolium group.

Figure 2.5. \(^1\)H NMR spectra of PC7 anion exchange membranes before (1) and after immersion in 1M KOH at 60\(^\circ\)C for 6 hours (2). The solutions were degassed with nitrogen to prevent carbonate formation.

Figure 2.6. shows the \(^1\)H NMR spectrum for PXC12, before and after exposure to 1 M KOH at 60 \(^\circ\)C for 6 hours. A new peak (peak 11\(^{\text{**}}\) at \textit{ca.} 4 ppm, in red rectangular frame in the figure) was
observed after this AEM was exposed to alkali. The presence of this new peak and the decrease in the area of peak 10 confirmed that there was degradation of the AEM. A ring-opening degradation mechanism of imidazolium cation was posited.

Figure 2.6. $^1$H NMR spectra of PXC12 anion exchange membranes before (1) and after immersion in 1M KOH at 60$^\circ$C for 6 hours (2). The solutions were degassed with nitrogen to prevent carbonate formation.

Figure 2.7. shows the proposed degradation mechanism based on the $^1$H-NMR spectrum (Figure 2.6.). The degradation process was triggered by the nucleophilic attack of hydroxide ion at the C-2 position of the cation. A covalent bond was formed between the hydroxide ion and the C-2 carbon (alpha carbon with respect to both nitrogen atoms). Subsequently, there was a ring-opening...
reaction that resulted in loss of cation sites. The covalent bond between C-2 and N-1 or N-3 was then broken, and, after a rearrangement reaction, formyl groups (-CHO) were formed (steps 2 and 3).

Figure 2.7. Mechanism proposed for the alkaline degradation AEMs containing imidazolium cations (R stands for the polymer backbone, with or without the alkyl spacer). The mechanism is based on the work of Ye et al. [31].

2.4 Conclusion

A series of imidazole bases (1MI, 1,2DMI, 2MI-C7 and 2MI-C12) were employed in the synthesis of AEMs based on PPO backbones. The cations were: 1) directly grafted onto the benzyl position of PPO and 2) attached at the end of a hexyl spacer chain previously grafted onto the PPO backbone
using Friedel-Crafts acylation. The latter approach was attempted to minimize the electronic effects between the backbone and cation. The AEMs with cations in the benzyl position were synthesized by reaction of the brominated polymers with 1MI, 1,2DMI, 2MI-C7 and 2MI-C12 to yield the following AEMs: P1, P12, PC7 and PC12.

The AEMs with the six-carbon spacer were synthesized by Friedel-Crafts acylation of 6-bromo-1-hexanoyl chloride on PPO, followed by reduction of the ketone and reaction with the imidazole bases. The reaction with 1MI, 1,2DMI, 2MI-C7 and 2MI-C12 resulted in the following AEMs: PX1, PX12, PXC7 and PXC12. 1H NMR and 2D correlation spectroscopy (COSY) confirmed the successful synthesis of the modified imidazole bases and of the AEMs. The IECs of the AEMs synthesized were measured using Volhard titration. The IEC for P1 and P12 was 1.66 ±0.02 mmol/g and 2.04 ±0.02 mmol/g, very close to the theoretical IEC; the IEC was significantly lower for PC7 and PC12 (0.78 and 0.92 mmol/g) because the bulkier imidazolium bases were less reactive towards the brominated polymer. A similar trend was observed for the AEMs prepared with the pendant chain.

The alkaline stability of imidazolium-based AEMs (with and without pendant chains) was evaluated using two independent measurements to assure the conclusions were definitive. We measured the change in IEC after immersion in 1M KOH at 60 °C for up to 810 mins. By comparing the fraction of retained IEC of P1 and PX1 (27% and 70%), we confirmed that grafting a long alkyl chain as a spacer between PPO backbone and imidazolium cation could increase the alkaline stability to great extent. By comparing the the fraction of retained IEC of P1 and P12 (27% and 74%), we demonstrated that grafting a methyl group at the C-2 site could increase alkaline stability of the imidazolium-based AEMs. By comparing the the fraction of retained IEC of PX12, PXC7 and PXC12 (88%, 17% and 11%), we discovered that substitution of long alkyl chains at
the N-3 position would not only decrease the IEC of imidazolium-based AEMs but also lower the alkaline stability of imidazolium-based AEMs.

We also used 1-D NMR spectroscopy to probe the AEM structure to unearth any signs of AEM degradation after exposure to alkali. The predominant degradation process was posited the opening of the imidazole ring. Although more studies are needed to confirm the findings, it is suggested that substituting all the hydrogen atoms on the imidazolium ring will improve the alkaline stability of imidazolium-based AEMs, provided that an appropriate backbone and cation-grafting strategy (use of spacers) is employed.

2.5 References


Chapter 3: Anion exchange membranes based on polystyrene-\textit{block}-poly(ethylene-\textit{ran}-butylene)-\textit{block}-polystyrene triblock copolymers: cation stability and fuel cell performance


Supplementary figures and tables are available in Appendix III
Abstract

A series of polystyrene-\textit{block}\-poly(ethylene-\textit{ran}\-butylene)-\textit{block}\-polystyrene (SEBS)\-based anion exchange membranes (AEMs) were synthesized via chloromethylation of SEBS followed by quaternization with trimethylamine (TMA). SEBS\-based AEMs functionalized with TMA$^+$ cations exhibited a hydroxide ion conductivity of 136 mS/cm at 70$^\circ$C. This membrane exhibited a phase-separated morphology with wide and interconnected ionic channels as observed by atomic force microscopy. Poly (phenylene oxide) (PPO)\-based AEMs with quaternary benzyl-trimethylammonium (TMA$^+$) and quaternary benzyl-tris(2,4,6-trimethoxyphenyl) phosphonium (TTMPP$^+$) and PPO\-based AEMs with hexyl pendant chains were also synthesized and evaluated as binders in AMFC electrodes. PPO\-based AEMs functionalized with TTMPP$^+$ demonstrated the best \textit{ex situ} alkaline stability, losing only 9\% of their ion-exchange-capacity after 30 days in 1M KOH (at 60 $^\circ$C). The best \textit{in situ} stability was achieved by SEBS\-based MEAs (as membrane and as binder in the electrodes); The peak power density dropped approx. 35\% after holding the cell at a constant voltage of 0.55V for 12 hours. Fuel cell performance with SEBS\-based AEMs resulted in peak power densities of 300 mW/cm$^2$ at 70 $^\circ$C. The optimum performance was obtained with MEAs made with SEBS\-based AEMs and PPO\-based ionomers containing a hexyl pendant chain.
3.1 Introduction

Anion exchange membranes (AEMs) are a promising technology for alkaline membrane fuel cells (AMFCs) [1-6], redox flow batteries (RFBs) [7-13], alkaline water electrolyzers (AWEs) [14-16] and reverse electrodialysis (RED) cells [17, 18]. The AEMs commonly reported in peer reviewed papers mostly contain quaternary ammonium fixed cation groups, mainly in the form of benzyl trimethylammonium cations [14, 19-40]. However, it has been shown that quaternary ammonium-based AEMs are sensitive towards Hofmann elimination [20, 41] and direct nucleophilic elimination reactions [42, 43] that result in loss of ion exchange capacity (IEC) and ionic conductivity. To resolve the stability problem inherent to quaternary-ammonium-group-containing AEMs, several alternative cations, including imidazolium [41, 44, 45], benzimidazolium [3, 45, 46], guanidinium [15, 47, 48], phosphonium [8, 9, 49] and metal cations [50, 51] have been proposed and investigated. Phosphonium-based AEMs were investigated by Gu et al. [52] Gu et al. attached benzyl-tris(2,4,6-trimethoxyphenyl) phosphonium (TTMPP$^+$) onto polysulfone backbone to make AEMs, and found them to be alkaline stable; There was no ionic conductivity fade after immersion in 1M KOH for 30 days at room temperature. The bulky phosphonium-based AEMs remained stable in alkali because of the steric hindrance effect that protects the core phosphorus atom and the α-cabons against hydroxide ion attack. There is no possibility of β-elimination reaction because of the lack of hydrogen atoms in β-carbons. However, very few researchers have investigated in situ stability of bulky phosphorus-based AEMs. It is essential to correlate the ex situ stability results obtained in immersion alkaline stability tests with in situ stability in a functional H$_2$/O$_2$ fuel cell.

Hibbs [53] has shown that poly(phenylene)-based AEMs with alkyl-substituted quaternary ammonium cations using a six-carbon alkyl chain spacer were considerably more stable than those
prepared with benzyl trimethylammonium cations attached directly to the backbone. When these two types of AEMs were immersed in nitrogen-degassed 4 M KOH at 60°C for 14 days, only a minimal (ca. 5%) loss in IEC was observed in the former case while a 21% loss in IEC was observed in the latter case. This result suggested that the introduction of alkyl spacers separating the cation from the backbone enhanced the alkaline stability of AEMs based on polyphenylene backbones. Parrondo et al. [54] investigated AEMs prepared with hexyl trimethylammonium cations, separated from the Poly (phenylene oxide) (PPO) backbone by a hexyl pendant chain. They reported that AEMs prepared with the pendant chains exhibited a 33% loss in IEC after 30 days in 1M KOH at 60 °C. The degradation rate was very similar for AEMs prepared without any pendant chains. This discrepancy suggests that the degradation of AEMs prepared with spacers separating the backbone from the cation involves complex interplays between the backbone, the cations affixed and the experimental conditions employed. Further in situ stability tests are necessary to verify the role that long alkyl spacer chains play in the alkaline stability of AEMs.

Ion-containing block copolymers exhibit phase separation between hydrophilic and hydrophobic phases, and this has resulted in materials with excellent ionic conductivity [55-58]. Styrene block-copolymers (such as polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene, SEBS) are among these materials, and have attracted considerable attention recently due to their high thermal and chemical stability and tunable mechanical properties [59]. Mohanty et al. employed borylation and Suzuki coupling reactions to functionalize SEBS to obtain AEMs with ion exchange capacities (IECs) of ca. 2.2 mmol/g and chloride ionic conductivity of 13 mS/cm at 30 °C [60]. However, the chloromethylation of SEBS did not always yield high degrees of functionalization (DF) and sometimes resulted in gelation [54, 56].
The ultimate strength and the elongation at break are very important in applications where the membranes are to be assembled in electrochemical cell, wherein they are subjected to stresses that could result in deformation and mechanical failure. It is interesting to note that the mechanical properties of tri-block copolymers (e.g. SEBS) can be tuned by changing the proportion of styrene, which provides rigidity, to ethylene-butylene copolymers, which provides elasticity [61]. According to our previous study, SEBS-based AEMs were mechanically stable under both strongly acidic and basic environments for up to 1 month. However, the functional group carrying the fixed cation suffered degradation in these harsh chemical environments [10]. Thus, the chemical stability of the functional groups affixed to the polymer backbone is more relevant to the degradation of SEBS-based AEM than the mechanical stability of the polymer membrane.

PPO has been extensively studied and shown to be a mechanically and chemically stable backbone for the synthesis of alkaline stable AEMs [62]. PPO-based AEMs suffered degradation during fuel cell operation primarily because of the degradation of cation group [20]. With regard to the mechanical integrity of the membranes, we have found that the PPO-based AEM does not dissolve under fuel cell conditions in the presence of water. A mixture of isopropanol (or methanol) and water is required to produce a solvent strong enough to dissolve the PPO-TMA AEMs.

Besides, PPO-based AEMs are highly soluble in organic solvents such as isopropanol/water, which make them perfect candidates as binders for the fabrication of membrane electrode assemblies (MEAs).

Given this background, the overarching objectives of this work were: 1) to synthesize SEBS-based AEMs with high ionic conductivity, to minimize ohmic losses during fuel cell operation; 2) to investigate the fuel cell performance using SEBS-based membranes and solubilized AEM binders;
3) to investigate the in situ stability of different AEM binders in an operating AEM fuel cell. To
this end, chloromethylated SEBS with a high DF was prepared and quaternized by reaction with
trimethylamine to obtain SEBS-based AEMs. Trimethylamine and tris(2,4,6-trimethoxyphenyl)
phosphine were also reacted with brominated PPO (BrPPO). Besides, trimethylamine was reacted
with the brominated PPO containing a six-carbon pendant chain to obtain the corresponding
AEMs. SEBS-based AEMs and PPO-based AEMs were characterized by measuring their IEC,
ionic conductivity, water uptake, mechanical properties (ultimate tensile strength and elongation
at break) and their phase morphology using atomic force microscopy (AFM). The in situ (during
fuel cell operation) and ex situ alkaline stability tests were employed to assess the feasibility of
using SEBS-based and PPO-based AEMs in AMFCs

3.2 Method

3.2.1 Materials

N-bromosuccinimide (99%), azobisisobutyronitrile (98%), dimethyl sulfoxide-d6 (99.96%),
dimethylformamide-d7 (99.5%), 6-bromohexanoyl chloride (97%), aluminum chloride (99.99%),
1,2-dichloroethane (99.8%), triethylsilane (99.9%), KOH (90%) trifluoroacetic acid (99%),
chlorobenzene (99.5%), tin(IV) chloride (99.995%), chlorotrimethylsilane (99%), chloroform
(99.5%), methanol (99.9%), paraformaldehyde (99.5%), silver nitrate (0.1N), potassium
thiocyanate (0.1N), sodium nitrate (99%), chloroform-d (99.96%), 1-methyl-2-pyrrolidinone
(99.7%), trimethylamine solution (31%-35% weight percent in ethanol) and sulfuric acid
(99.999%), were purchased from Sigma Aldrich. SEBS (35:65 molar ratio of styrene to rubber)
was sourced from Kraton Performance Polymers Inc. SEBS (M_n=118000, 30:70 molar ratio of
styrene to rubber) was obtained from Sigma Aldrich. PPO (Mn=20000, Polydispersity=2.5) was purchased from Polysciences Inc.

**3.2.2 Synthesis of chloromethylated SEBS (CMSEBS)**

SEBS (5 g) was dissolved in chlorobenzene (250 mL). Paraformadehyde (16.7 g) was added into the mixture and the temperature was set to 55 °C. Chlorotrimethylsilane (70.5 mL) and tin (IV) chloride (1.3 mL) were added to mixture, and the reaction temperature was raised to 80 °C. The mixture was reacted for with 7 days. After the product, was precipitated in methanol (1.3 L), recovered by filtration, and washed with abundant methanol. The product was purified by re-dissolving in chloroform/chlorobenzene (4:1) and re-precipitating in methanol. The purification process was repeated two times. Chloromethylation of SEBS (30:70 molar ratio of styrene to rubber) and SEBS (35:65 molar ratio of styrene to rubber) resulted in chloromethylated SEBS polymers CMSEBS30 and CMSEBS35 with degrees of chloromethylation (DF; mol of chloromethyl groups per mol of polymer repeat unit) of 0.16 and 0.22, respectively (see Appendix III, Figures A3.2. & A3.3.).

**3.2.3 Synthesis of SEBS-based AEMs (SEBS30-TMA and SEBS35-TMA)**

*SEBS30-TMA*: CMSEBS30 (0.5 g) was dissolved in chlorobenzene (9 mL). The mixture was cast onto a 3.5 inch × 3.5 inch glass plate and the solvent was evaporated in an oven at 60 °C. The membrane was peeled off and placed in a round-bottom flask containing 1.17 mL of trimethylamine (TMA) and 30 mL of 1-methyl-2-pyrrolidinone (NMP). The reaction was conducted at 30 °C for two days.

*SEBS35-TMA*: CMSEBS35 (0.5 g) was dissolved in chlorobenzene (9 mL). The mixture was cast onto a 3.5 inch × 3.5 inch glass plate and the solvent was evaporated in an oven at 60 °C for 12
hours. The membrane was peeled off and placed in a round-bottom flask containing 1.57 mL of trimethylamine (TMA) and 30 ml of 1-methyl-2-pyrrolidinone (NMP). The reaction was conducted at 30 °C for two days.

3.2.4 Synthesis of brominated PPO (BrPPO)

A mixture of PPO (20 g) and N-bromosuccinimide (20 g) was dissolved in chlorobenzene (300 mL). After complete dissolution, 0.4 g of azobisisobutyronitrile (free radical initiator) was added, and the mixture was heated to 108 °C and kept under stirring (in inert atmosphere) for 12 h. The brominated polymer thus obtained was precipitated in methanol and purified by re-dissolution in chlorobenzene and precipitation in methanol. The polymer was filtered, washed with abundant methanol and methanol/water (1:1 Vol.) and dried in a vacuum oven at 60 °C for 24 hours.

3.2.5 Synthesis of PPO-based AEMs (PPO-TMA and PPO-TTMPP)

**PPO-TMA:** BrPPO (0.5 g) and TMA (0.71 mL) were dissolved in 9 mL of NMP, stirred at 30 °C for 24 hours, cast onto a glass plate (3.5” x 3.5”) and dried the solvent in an oven at 70 °C for 12 hours.

**PPO-TTMPP:** BrPPO (0.5 g) and tris(2,4,6-trimethoxyphenyl) phosphine (0.53 g) were dissolved in 9 mL of NMP, stirred at 80 °C for 48 hours, cast onto a glass plate (3.5” x 3.5”) and dried the solvent in an oven at 70 °C for 12 h.

3.2.6 Addition of a six-carbon pendant chain to poly (phenylene oxide): PPO-KC6Br

The procedure of synthesis of PPO-KC6Br can be found in previous experimental section (2.2.5)
3.2.7 Reduction of the ketone group in PPO-KC6Br (PPO-C6Br)

PPO-KC6Br (5 g) was dissolved in 400 mL of 1,2-dichloroethane. Once completely dissolved, trifluoroacetic acid (290 mL) and triethylsilane (30 mL) were added, the reaction mixture heated under stirring to 100 °C, and kept reacting under reflux conditions overnight. Subsequently, the polymer solution was washed with 500 mL of 1M KOH until neutral pH, and poured into 2 L of deionized water and heated until the organic solvent evaporated. The solid precipitate was dried in a vacuum oven at 60 °C and purified by re-dissolution in chloroform and re-precipitation in methanol. The 1H NMR spectrum of the resultant polymer confirming the reduction of the ketone group is shown in Appendix III, Figure A3.9. Further details of the synthesis and characterization of the polymer can be found in our previous paper [54].

3.2.8 Synthesis of PPO-based AEMs with a six-carbon alkyl spacer: PPO-C6-TMA

PPO-C6-TMA: PPO-C6Br (0.5 g) and TMA (0.65 mL) were dissolved in 9 mL of NMP, stirred at 30 °C for 24 hours, cast onto a glass plate (3.5” x 3.5”) and dried the solvent in an oven at 70 °C for 12 hours.

3.2.9 Ion exchange capacity, ionic conductivity and water uptake

Ion exchange capacity: The procedure of ion exchange capacity characterization can be found in previous experimental section (2.2.8)

Ionic conductivity: In-plane ionic conductivity measurements were carried out in a 4-point conductivity cell (BT-110, Scribner Associates) using electrochemical impedance spectroscopy (EIS) to measure the resistance. A 1 cm × 3 cm membrane was placed in the PTFE conductivity cell in contact with the 4 platinum electrodes and immersed in a temperature controlled DI water
A Gamry series G750 potentiostat was used to measure the impedance in the frequency range 100kHz to 0.1 Hz. The high frequency resistance was estimated from the Bode plots (corresponding to a phase angle of zero). The membrane conductivity was calculated using equation [1]:

$$\sigma = \frac{L}{R \cdot t \cdot w}$$ \[1\]

where, $$\sigma$$ was the in-plane membrane conductivity (mS cm\(^{-1}\)); $$R$$ was the in-plane membrane resistance (mOhm); $$t$$ was the membrane thickness (fully hydrated) (cm); $$w$$ was the membrane width (fully hydrated) (cm); $$L$$ was the distance between the two inner electrodes (cm).

**water uptake:** Vacuum dried AEM samples (< 1 inHg at 60 °C for at least 12 hours), typically in the chloride form, are weighed (approx. weight of 0.1 g), then immersed in DI water and kept in an oven at 30 °C for at least 24 hours. The samples are quickly swabbed to remove surface water and then immediately placed into previously tared Ziploc® bags to measure their weight. Water uptake is determined as follows:

$$WU = \frac{W_{t_{\text{hydrated}}} - W_{t_{\text{dry}}}}{W_{t_{\text{dry}}}} \cdot 100\%$$ \[2\]

Here, $$WU$$ is the water uptake (%), $$W_{t_{\text{hydrated}}}$$ is the weight of the fully-hydrated membrane (g), and $$W_{t_{\text{dry}}}$$ is the weight of the dry membrane (g). The dimensions (thickness, length and width) of the dry and fully hydrated membrane are also measured and used to estimate the swelling ratio.

### 3.2.10 NMR characterization of the polymers

The procedure of NMR characterization can be found in previous experimental section (2.2.8)
3.2.11 FTIR spectroscopy

The presence of functional groups was qualitatively confirmed by using FTIR spectroscopy. FTIR was performed using membrane films in a Bruker Tensor 27 instrument. The data was collected continuously in the range 4000 to 400 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\). All the samples were dried in a vacuum oven (at 60 °C for 12 hours) before the measurement to minimize the presence of water. Appropriate background corrections were also performed.

3.2.12 Atomic force microscopy

The membranes morphology was investigated by tapping mode with a Bruker Dimensions ICO atomic force microscope (AFM). A PFQNE-AL probe (Bruker) with a cantilever spring constant of 0.8 N m\(^{-1}\), and a tip radius of 5 nm was employed in the experiments. Imaging was performed using at ambient temperature and relative humidity. The AFM samples were prepared by casting an AEM solution on a platinum plate to form a very thin film. All the AEMs evaluated in the present work were tested in the chloride form.

3.2.13 Ex situ alkaline stability

For all ex situ alkaline stability tests, dry AEM samples of uniform thickness are cut into several pieces, weighed, and placed in N\(_2\)-degassed 1 M KOH solution in sealed poly-propylene containers. The containers are kept at a constant temperature of 60 °C inside an oven for 1 month. After 1 month, the AEM samples are washed with abundant DI water to remove residual KOH, and dried in an oven at 60 °C overnight prior to determine IEC. The procedure to determine IEC has been shown in previous sections. There is no established ex situ standard test to evaluate the alkaline stability of AEMs. We perform all our laboratory tests under the same conditions (1 M
KOH, 60 °C) to have a better comparison of the alkaline stability of the AEMs synthesized in our laboratories.

### 3.2.14 Fuel cell performance testing

Carbon-supported Pt catalyst (46 wt % Pt/C Tanaka K. K.) was used for the cathode and anode. For the catalyst ink, four different types of ionomers (SEBS35-TMA, PPO-TMA, PPO-TTMPP and PPO-C6-TMA) were employed. The required amounts of PPO-based ionomers (PPO-TMA, PPO-TTMPP and PPO-C6-TMA) to get electrodes with ionomer loadings of 30 wt% in chloride form were dissolved in 6.5 mL of isopropanol/water mixture (1:1 weight ratio), added to 0.2 g Pt/C catalyst (wetted with a few drops of DI water), and ultrasonicated in a horn sonicator (QSonica Q700 sonicator) for 7 minutes. To make SEBS-TMA binders, first, the required amount of CMSEBS was dissolved in 6.5 mL of chlorobenzene, mixed with 0.2 g Pt/C catalyst, and sonicated for 7 minutes. The inks were applied onto a gas diffusion layer (GDL; 25BCH from SGL Carbon) with the aid of an airbrush (Badger model 150). In the case of CMSEBS electrodes, the GDL was immersed into a mixed solution of NMP (30 mL) and TMA (3mL) at 30 °C for 2 days to functionalize the CMSEBS and obtain the AEM material. The nominal catalyst loadings for the anode and cathode were 0.5 mgPt/cm².

Fuel cell performance was evaluated at 70 °C in 5 cm² geometric-active-area single cell (Fuel Cell Technologies, Inc.), with no back pressure being applied, and a relative humidity of the inlet gases of 98%. Stoichiometric flow rates were 2 for hydrogen and 3 for oxidants (Pure oxygen, Air, Helox, and 4% O₂ balance N₂) with minimum flows of 0.2 L min⁻¹ for all gases. A constant voltage of 0.55 V was applied for 30 minutes to condition the MEAs before acquisition of the polarization curves; This step was performed to remove the residual bicarbonate/carbonate ions contained in the AEM and binder resultant from the exposure to air. Polarization curves were acquired (Scribner
Associates model 850e fuel cell test station) by scanning the current from 0.02 A to 15 A (15 points per decade). The system was held at each current density for 2 min, and the acquisition stopped when the voltage dropped below 0.05 V.

3.2.15 In Situ stability test

In situ stability tests were performed in an operating fuel cell by holding a constant voltage of 0.55 V for 12 hours. The polarization curves were acquired before and after continuous operation (H₂/O₂) for 12 hours. The initial and final polarization curves were compared to ascertain the MEA stability.

3.3 Results and Discussion

3.3.1 Synthesis and characterization of AEMs

We have employed a facile backbone-functionalization method to introduce the quaternary ammonium groups in the SEBS backbone. The chloroform commonly employed as solvent during the chloromethylation reaction [63] was replaced by chlorobenzene, allowing the reaction to be carried out at higher temperatures (80 °C) thereby increasing the reaction rates and final functionalization degrees. This procedure allowed us to obtain AEMs (after quaternization of the chloromethylated polymer) with IECs of up to 1.93 mmol/g, resulting in hydroxide ion conductivities of approx. 78 mS/cm (30 °C). Figure 3.1. shows the scheme followed for the synthesis of the SEBS-based AEMs. Appendix III, Figure A3.1. shows the 1H NMR spectrum of SEBS and Appendix III, Figure A3.2. shows 1H NMR spectrum of chloromethylated SEBS (with a 30:70 molar ratio of styrene to rubber, CMSEBS30). A new peak “e” at a chemical shift of ca. 4.5 ppm, corresponding to the protons in the chloromethyl group, can be seen in Appendix III, Figure A3.2. (2H, multiplet). The presence of peak “e” confirmed the chloromethylation of
SEBS30. The DF was estimated to be 0.16 mol of chloromethyl groups /mol of polymer repeat unit. Appendix III, Figure A3.3. shows the $^1$H NMR of the chloromethylated SEBS polymer with a 35:65 molar ratio of styrene to rubber (CMSEBS35). The DF for this polymer was calculated to be 0.22 mol/mol. CMSEBS30 and CMSEBS35 were reacted with TMA to obtain the following AEMs: SEBS30-TMA, SEBS35-TMA (reaction scheme in Figure 3.1.). Since SEBS-based AEM could not be dissolved in common deuterated solvents, it was not possible to characterize the reaction products using NMR spectroscopy. Instead, FTIR was employed to confirm the generation of affixed quaternary ammonium groups by quaternization of the chloromethylated SEBS. Appendix III, Figure A3.4. shows the FTIR spectra of SEBS30-TMA and CMSEBS30. A FTIR peak appearing at ca. 1030 cm$^{-1}$ was assigned to the C-N bond stretching, confirming the formation of SEBS30-TMA AEM. Similar results were observed for SEBS35-TMA [64]. Moreover, IEC determination confirmed the quaternization of CMSEBS and the completion of the reaction. The theoretical IECs calculated (from the relative areas of $^1$H NMR peaks “e”, “b” and “d”) for SEBS30-TMA and SEBS35-TMA were 1.52 mmol/g, and 1.99 mmol/g, respectively. Quaternization reaction yield for SEBS30-TMA and SEBS35-TMA were 89% and 97%, respectively. Additional characterization to determine hydroxide ionic conductivity, water uptake, and ultimate tensile strength and elongation at break were performed (Table 3.1).
**Figure 3.1. Scheme for the synthesis of SEBS-based AEMs (SEBS-TMA)**

**Table 3.1. Properties of the SEBS-based and PPO-based AEMs synthesized in this work.**

<table>
<thead>
<tr>
<th></th>
<th>SEBS30-TMA</th>
<th>SEBS35-TMA</th>
<th>PPO-TMA</th>
<th>PPO-TTMPP</th>
<th>PPO-C6-TMA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental IEC</strong></td>
<td>1.35±0.02</td>
<td>1.93±0.02</td>
<td>1.76±0.02</td>
<td>1.1±0.1</td>
<td>1.83±0.01</td>
</tr>
<tr>
<td><strong>Theoretical IEC</strong></td>
<td>1.52</td>
<td>1.99</td>
<td>1.91</td>
<td>1.40</td>
<td>1.90</td>
</tr>
<tr>
<td><strong>Hydroxide ion</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>conductivity @ 70°C,</strong></td>
<td>112±15</td>
<td>136±13</td>
<td>74±6</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td><strong>mS/cm</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ultimate tensile stress</strong></td>
<td>3.1±0.6</td>
<td>3.8±0.2</td>
<td>6.3±0.3</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td><strong>(MPa)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Elongation at break</strong></td>
<td>536±7</td>
<td>499±1</td>
<td>1.9±0.8</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td><strong>(%)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Water uptake (%)</strong></td>
<td>52.0</td>
<td>121.5</td>
<td>37</td>
<td>8</td>
<td>32</td>
</tr>
</tbody>
</table>

Notes. The tensile tests were done at 25°C and 100% relative humidity. Water uptake was performed at 30 °C. PPO-C6-TMA and PPO-TTMPP were too brittle to measure the ionic conductivity and tensile tests.
When the molar ratio of polystyrene in SEBS increased, the polymer backbone becomes more rigid. When the molar ratio of rubber to styrene is being increased, the polymer backbone becomes more elastic. It was therefore possible to tune the mechanical properties of the AEM to make them more suitable for the applications under consideration. We have found from tensile testing that SEBS-based AEMs (SEBS30-TMA and SEBS35-TMA) had a very elastic nature (elongations at break of 500% of their initial lengths). However, the ultimate tensile strengths were relatively low (3-4 MPa) when compared with other AEM materials resired in the literature. We deem these AEMs to be sufficiently strong to be assembled and operated for long periods of time in any electrochemical cell.

PPO-based AEMs were synthesized by reacting the BrPPO with TMA and TTMPP. When TMA was attached onto the benzyl position of PPO, the PPO-based AEM (PPO-TMA) was obtained. Following a similar scheme, PPO-TTMPP was obtained by reaction of the brominated polymer with TTMPP. Figure 3.2. shows the reaction schemes for the synthesis of these PPO-based AEMs. BrPPO had a bromomethyl group (benzyl position) and these protons (peak “3”) appear at a chemical shift of 4.33ppm (Appendix III, Figure A3.5.). The degree of functionalization (DF, mol of bromomethyl groups per polymer repeat unit) obtained by comparison of the peak areas of protons “3” to the protons present in the aromatic rings of the backbone was 0.36. Details of the calculations employed to arrive at this value can be found in our previous papers [20, 54]. The shift of the protons present initially in the bromomethyl group (peak “3”, initially at 4.33 ppm) to higher frequencies (4.50 ppm) was attributed to the proximate presence of the positively charged cation and demonstrated the formation of the product (PPO-TMA and PPO-TTMPP, see Appendix III, Figure A3.6. &A3.7.). The theoretical IECs calculated (from the relative areas of $^1$H NMR) for PPO-TMA and PPO-TTMPP were 1.91 mmol/g, and 1.40 mmol/g, respectively. The experimental
IEC tested by Volhard titration for PPO-TMA and PPO-TTMPP were 1.76 mmol/g, and 1.10 mmol/g. Quaternization reaction yields for PPO-TMA and PPO-TTMPP were 92% and 79%, respectively.

Figure 3.2. A) Scheme for the synthesis of PPO-based AEMs (PPO-TMA and PPO-TTMPP); B) Scheme for the synthesis of PPO-based AEMs with a six-carbon spacer (PPO-C6-TMA).

Friedel–Crafts acylation of 6-bromohexanoyl chloride was employed to add a six-carbon spacer to PPO, allowing the cation to be separated from the backbone to minimize any possible electronic effects of the backbone/cation on the alkaline stability of the AEM. The PPO-based AEM (PPO-C6-TMA) was synthesized using this modified platform. Figure 3.2B shows the reaction scheme for the synthesis of PPO-based AEM (PPO-C6-TMA) prepared with the spacer chain. The grafting of the six-carbon pendant chain to the PPO backbone (to yield PPO-KC6Br) was confirmed through $^1$H NMR spectroscopy (see Appendix III, Figure A3.8.). Peak “5” (3.0 ppm) corresponds to the protons attached to the carbon adjacent to the ketone group. Additional assessment of the
presence of the ketone group in the benzyl position was performed using $^{13}$C NMR spectroscopy in our previous paper [54]. The $^1$H NMR peak at 3.4 ppm (peak “9”) corresponds to the protons in the bromomethyl group at the end of the pendant chain. The brominated polymer (PPO-KC6Br) had a degree of bromination (DF) of 0.31 mol of bromine per polymer repeat unit.

Hibbs [53] pointed out that the ketone group in PPO-KC6Br promotes rapid AEM degradation in alkaline solutions. To increase the stability of our AEMs, the ketone group in PPO-KC6Br was reduced with triethylsilane in the presence of trifluoroacetic acid in 1,2-dichloroethane (Appendix III, Figure A3.9. shows the $^1$H NMR spectrum of the reduced polymer, PPO-C6Br). The protons (peak “2”) in the aromatic rings functionalized with the pendant chain shifted from 6.1 ppm to 6.03 ppm after reduction of the ketone group. Both peaks were present in the NMR spectrum of the reduced product and their areas were used to calculate the yield of the ketone reduction reaction (Area 2/ (Area 2 + Area 2')). The yield for the ketone reduction reaction was between 95 to 98%.

The $^1$H NMR spectrum of the product obtained from the reaction between TMA and PPO-C6Br is shown in Appendix III, Figure A3.10. The protons on quaternary ammonium group (peak “m”) confirmed the successful synthesis of the AEM. The theoretical IEC calculated by $^1$H NMR was 1.9 mmol/g. The experimental IEC determined by Volhard titration for the same polymer was 1.83 mmol/g. The quaternization reaction yield was 96%.

A four-probe (in-plane) conductivity cell was used to determine the AEM ionic conductivity (Figure 3.3.). As reported in our previous paper [10], the chloride conductivity of SEBS35-TMA was higher than that of the benchmark AEM (Tokuyama A201) at all tested temperatures (30-70 °C). The hydroxide conductivity of SEBS35-TMA was measured in this work. At 70 °C, the hydroxide ion conductivity of SEBS35-TMA was 136 mS/cm whereas it was 133 mS/cm for the benchmark AEM. Even though PPO-TMA had a higher IEC (1.76 mmol/g) than SEBS30-TMA
(1.35 mmol/g), the hydroxide ion conductivity (70 °C) of SEBS30-TMA was 112 mS/cm compared to 75 mS/cm for PPO-TMA. Pan et al. constructed an ionic pathway for polysulfone-based AEMs (aQAPS-S₈; IEC = 1.0 mmol/g) and achieved a hydroxide ion conductivity of 90 mS/cm at 70°C. By properly constructing ion-aggregating structures, a hydroxide ion pathway can be built, such that hydroxide ion conduction in aQAPS-S₈ (AEM) can be as efficient as proton conduction in Nafion® at fuel cell operation temperatures [65]. Si et al. synthesized a PEEK-based AEM containing gemini-cation (two quaternary ammonium were attached to the same side chain) (IEC=2.02 mmol/g) and showed an hydroxide conductivity of 44.8 mS/cm at 75 °C [66]. Ponce-Gonzalez et al synthesized ETFE-g-poly(vinylbenzyl-N-methylpiperidinium)-based AEM (IEC=1.64mmol/g) and achieved a hydroxide ion conductivity of 138 mS/cm at 90 °C. They claimed a benchmark performance for the benzyltrimethylammonium head-group type AEM [67]. Thus, based on all the above discussion and results from other authors, we can conclude that the hydroxide ion conductivity of SEBS35-TMA is consistent with the range reported by others, and sufficient for applications in alkaline fuel cells and electrolyzers.
AEMs based on block copolymers can provide a better pathway to access higher conductivities when compared with aromatic-backbone-based polymers. This is consequence of the block copolymer’s ability to yield a phase-separated morphology with wide and interconnected ionic channels that favor ion transport. AFM phase images (500 nm × 500 nm) were obtained to study the morphology of the AEMs. The elastic modulus (obtained using Derjaguin-Muller-Toporov model, DMT) of SEBS30-TMA, PPO-TMA, PPO-C6-TMA and PPO-TTMPP AEMs in chloride ion form was measured at room temperature and ambient humidity (Figure 3.4.). SEBS30-TMA exhibited a very prominent phase separation (see Figure 3.4A.). Darker regions corresponded to areas where the elastic modulus was smaller than in the brighter areas. The darker areas were assigned to the soft hydrophilic parts of the block copolymer composed of quaternary ammonium
groups affixed to the styrene units. The brighter areas corresponded to the hydrophobic parts of polymer backbone (polyethylene, polybutylene and unfunctionalized polystyrene) [68]. The hydrophilic domains formed ion conductive nano-channels for ion transport [69]. For SEBS30-TMA, the sizes of the ionic domains vary from 57 nm to 95 nm as can be seen in Figure 3.4A. The larger size and connectivity of the ionic domains contributed to the ionic conductivity and water uptake. Liu et al. synthesized a series of partially fluorinated copolymers, and investigated the relationship between the size of the ionic channels and the polymer water uptake. They found that the polymers with larger ionic domains exhibited more water uptake. For an average ionic domain size of 22.5 nm, the water uptake of the partial fluorinated copolymer was 50.8% [70]. The water uptake of SEBS30-TMA was 52% (Table 3.1.), which correlated well with the relatively large ionic domains found experimentally (57 nm to 95 nm). These findings agree reasonably well with the result of Liu et al. Phase separation phenomena were not found in any PPO-based AEMs: PPO-TMA (Figure 3.4B.), PPO-C6-TMA (Figure 3.4C.) and PPO-TMPP (Figure 3.4D.).
Figure 3.4. DMT modulus AFM images of A) SEBS30-TMA, B) PPO-TMA, C) PPO-C6-TMA and D) PPO-TTMPP AEMs in chloride ionic form.

Figure 3.5 shows AFM tapping mode measurements: elastic modulus (Figure 3.5A.), adhesion (Figure 3.5B.), deformation (Figure 3.5C.) and topographic height (Figure 3.5D.) for SEBS30-TMA in chloride ionic form at room temperature and ambient humidity. As discussed above, dark areas in elastic modulus (Figure 3.5A.) correspond to soft and hydrophilic domains. The hydrophilic domains exhibited less adhesive forces as seen by the matching between the darker regions in Figure 3.5A. (lower elastic modulus) and the darker regions in Figure 3.5B. (lower adhesion forces). The brighter regions in Figure 3.5C. (larger deformations) match well to the dark regions in Figure 3.5A., as expected, because the regions with lower elastic modulus deform more when a certain force is applied to the polymer surface. During the membrane casting process, heat was applied to evaporate the organic solvent. The hydrophilic domains, which had lower modulus,
shrunk more than hydrophobic domains in polymer, resulting in height differences between the two separated phases as seen in Figure 3.5D.

Figure 3.5. A) Elastic modulus (DMT), B) Adhesion force, C) Deformation, and D) topographical height of SEBS30-TMA AEM in chloride ionic form.

3.3.2 Ex situ alkaline stability of AEMs

*Ex situ* alkaline stability tests (Figure 3.6.) were performed by immersion of AEMs in 1M KOH at 60 °C for 30 days. SEBS30-TMA lost 28% of the initial IEC after 30 days, whereas PPO-TMA showed better alkaline stability, and lost only 18% of the initial IEC. However, after the alkaline stability test, PPO-TMA suffered mechanical failure and broke into pieces. The mechanical properties (elongation at break and ultimate tensile strength) of SEBS30-TMA after the alkaline stability tests remained the same as in the pristine polymer (SEBS30-TMA). PPO-C6-TMA showed the worst alkaline stability (lost 34% of the initial IEC). These findings contradict Hibbs conclusions that attaching a six-carbon spacer between the polymer backbone and the quaternary
ammonium increases the alkaline stability. Further *in situ* stability tests in a working AMFC are needed to reach more definitive conclusions. PPO-TTMPP showed the best *ex situ* alkaline stability with a loss of 10% of the initial IEC.

![Figure 3.6](image)

Figure 3.6. *Ex situ* alkaline stability (1M KOH and 60 °C) for SEBS30-TMA, PPO-TMA, PPO-C6-TMA and PPO-TTMPP.

### 3.3.3 Fuel cell performance and *in situ* stability tests

Fuel cell polarization curves for MEAs fabricated with SEBS30-TMA membrane and electrodes containing SEBS35-TMA, PPO-TMA, PPO-C6-TMA and PPO-TTMPP as AEM binders are shown in Figures 3.7A-D. Hydrogen was used as fuel and pure oxygen, CO₂-free air, Helox (same concentration of oxygen as in air but balanced with helium), and 4% oxygen balance nitrogen were employed as oxidants. Herein, we used SEBS30-TMA as membrane separator mainly because of its excellent mechanical stability in alkaline environment and good ionic conductivities. SEBS35-TMA, PPO-TMA, PPO-C6-TMA and PPO-TTMPP binders were employed to investigate their effect in fuel cell performance and stability. The 30wt% AEM binder was optimized for this study.
When the SEBS30-TMA was used as membrane and 20wt% SEBS35-TMA ionomer was used as binder, power density obtained was 40 mW/cm$^2$ at 0.55 V. When the SEBS30-TMA was used as membrane and 40 wt% SEBS35-TMA ionomer was used as binder, power density obtained was 47 mW/cm$^2$ at 0.55V. Compared with the power density (82 mW/cm$^2$) we got from 30 wt% SEBS35-TMA binder, we believed that the binder loading was optimized for this study. We did not perform similar experiments for the other binders. Because of their similar nature with SEBS30-TMA binder, we expect similar results. The best fuel cell performance (Figure 3.7C.) was obtained by using PPO-C6-TMA as electrode binder (30wt%); A peak power density of 300 mW/cm$^2$ was achieved at 0.46 V by using hydrogen as fuel and oxygen as oxidant. MEAs containing SEBS35-TMA (Figure 3.7A.), PPO-TMA (Figure 3.7B.) and PPO-TTMPP (Figure 3.7D.) as electrode binders (all at a concentration of 30wt%) exhibited peak power densities of 95 mW/cm$^2$, 276 mW/cm$^2$ and 46 mW/cm$^2$, respectively. The area specific resistance for MEA made with PPO-C6-TMA as binder and SEBS35-TMA as separator was the lowest (170 ohm-cm$^2$). The ASR of MEA made with SEBS35-TMA as binder and SEBS30-TMA as separator was 275 ohm-cm$^2$. The ASR of MEA made with PPO-TMA as binder and SEBS30-TMA as separator was 200 ohm-cm$^2$. The ASR of MEA made with PPO-TTMPP as binder and SEBS30-TMA as separator was 500 ohm-cm$^2$. We believe the ASR (which indirectly denoted the stability of the membrane-electrode interface) contributed to the trends seen in performance. SEBS35-TMA AEMs had excellent ionic conductivity, however, showed poor fuel cell performance when employed as electrode binders. Since SEBS-based AEMs cannot be dissolved in any organic solvents, the MEAs containing SEBS35-TMA as binder were made by dissolving the chloromethylated polymer (CMSEBS35) in chlorobenzene, mixing with the Pt/C catalyst to make the ink, and finally applying the ink onto the GDL. Afterwards, the GDL was immersed in a TMA solution in NMP.
to quaternize the polymer and obtain the AEM material. By using this method, it is probable the catalyst is being covered by a larger extent by the binder, impeding the access of the oxygen to the catalyst active sites. Wang et al. achieved 1.0 W/cm² peak power density at 0.45 V by employing 0.4 mgPtRu/cm² as anode catalyst and 0.4 mgPt/cm² as cathode catalyst with a polysulfone-based AEM separator (IEC=1.0 mmol/g). The O₂ and H₂ were both fed at flow rates of 0.4 L/min with gauge back pressure of 0.1MPa [71]. Chen et al. obtained a peak power density of 0.6 W/cm² at 0.35 V with anode and cathode catalyst loadings of 0.4mgPt/cm² and a polysulfone-based AEM separator with an IEC of 0.98 mmol/g. The O₂ and H₂ were fed at flow rates of 0.25 L/min with gauge back pressure of 0.1MPa [72]. Kaspar et al. achieved a peak power density of 737 mW/cm² at 0.4 V by operating the fuel cell at a relatively high temperature of 80°C with the anode and cathode containing 0.4mgPt/cm² catalyst. A Tokuyama A901 AEM was employed as the separator. The flow rates of O₂ and H₂ were 0.2 L/min and the back pressure was 250 kPa (gauge pressure) [73]. There are several factors such as catalyst type and catalyst loadings, flow rates, cell temperature, gas back pressure, and test protocol (especially the hold time per point) that can affect the performance of the fuel cell. This makes it very difficult to make meaningful comparisons with prior work. The fuel cell performance obtained with Helox was same as CO₂-free air for all four binders. Impedance spectroscopy (SEBS35-TMA as binder shown in Appendix III, Figure A3.11.) did not show any differences between Helox and CO₂-free air fuel cell operation. From these observations, it was inferred that the transport of oxygen at the cathode was not limited by gas phase transport phenomena (bulk/Knudsen diffusion through the pore-structure of the electrode). This finding agrees with the results shown by Arges et al. [20]. The transport of oxygen was instead limited by condensed-phase transport phenomena, i.e., transport of oxygen through the AEM binder covering the catalyst, or through liquid water in the electrode. The minimum values of
impedance were found when PPO-C6-TMA was used as binder (H2/O2, 800 mV, Appendix III, Figure A3.12.). The minimum values of the impedance for PPO-C6-TMA as binder corresponded as expected with the best fuel cell performance obtained with PPO-C6-TMA as binder.

Figure 3.7. H2/O2, H2/Air, H2/Helox, and H2/4%O2 fuel cell polarization curves for MEAs comprising A) SEBS30-TMA as membrane and SEBS35-TMA as binder; B) SEBS30-TMA as membrane and PPO-TMA as binder; C) SEBS30-TMA as membrane and PPO-C6-TMA as binder; and D) SEBS30-TMA as membrane and PPO-TTMPP as binder. Catalyst loading is 0.5 mgPt/cm2 (46wt% Pt on carbon) for both anode and cathode. The AEM binder concentration in the electrodes was 30wt%.

In situ stability tests were performed in a working fuel cell by holding a constant voltage of 0.55V for 12 hours. The polarization curves were acquired before and after continuous operation (H2/O2) for 12 hours. The comparison of the initial and final polarization curve after the 12 hours voltage hold are shown in Figures 3.8A-D. After the in situ stability test, the peak power densities of the
MEAs with SEBS35-TMA and PPO-TMA binder remained at ca. 65% of their initial value (Figure 3.8A&B.). Peak power densities of MEAs containing PPO-C6-TMO and PPO-TTMPP binders remained ca. 14% (Figure 3.8C.) and 36% (Figure 3.8D.) of their initial values. SEBS35-TMA and PPO-TMA had the best in situ stabilities, however, they were not among the most stable during ex situ alkaline stability tests. Moreover, PPO-TTMPP and PPO-C6-TMA were relatively stable during ex situ alkaline stability tests but showed poor stability during in situ stability testing. PPO-TTMPP and PPO-C6-TMA binders were brittle solids, that may exhibit poor contact with SEBS30-TMA AEMs, thereby compromising MEA performance over the long run. ASR was measured by the current interrupt method and monitored during the 12 hour in situ stability test. For the PPO-TMA binder the ASR remained unchanged (at approx. 200 mohm-cm\(^2\)) during the 12 hours confirming that the contact interface between SEBS30-TMA and the electrodes made with PPO-TMA remained unchanged (Appendix III, Figure A3.13.). For the PPO-C6-TMA binder the same test revealed a dramatic increase of cell resistance, from 170 mohm-cm\(^2\) to 550 mohm-cm\(^2\) (Appendix III, Figure A3.14.), which can only be attributed to deterioration of the interface between the electrode and the separator in the MEA. Note that the current interrupt method will not reveal changes in resistance within the electrode layer – it only reveals the separator resistance and the interfacial resistance [74]. Since the same membrane separator was used in both cases, it is clear that the interface was degrading, due to the incompatibility in the interface between the membrane and the electrode, in the latter case.

The stability of MEAs during fuel cell operation depends not only on the alkaline stability of the AEMs and binders, as assessed by the ex situ alkaline stability testing, but also rely on a good compatibility and stability of the contact interface between the electrode, containing the binder and AEM.
3.4 Conclusion

A series of SEBS-based AEMs were synthesized via chloromethylation of SEBS followed by quaternization reaction with TMA. Reaction conditions allowed the synthesis of AEMs with sufficient ionic conductivities (hydroxide ion conductivity of 136 mS/cm at 70 °C) and IECs (ca. 2 mmol/g). For comparison, the Tokuyama A201 benchmark AEM had a hydroxide ion conductivity of 133 mS/cm and an IEC of 1.6 mmol/g, under same conditions. Phase separation was confirmed by AFM for SEBS-based AEMs. The hydrophilic segments formed ion conductive domains with sizes ranging from 57 nm to 95 nm.
A series PPO-based AEM binders were prepared and characterized to evaluate their alkaline stability and fuel cell performance: PPO-TMA, PPO-TTMPP and PPO-C6-TMA. *Ex situ* alkaline stability tests showed that PPO-TTMPP had the best stability, losing only 10% of its initial IEC after 30 days in 1 M KOH (60 °C). In contrast, SEBS30-TMA lost 28% of the initial IEC after 30 days under same experimental conditions. However, the mechanical properties of SEBS30-TMA after the alkaline stability tests remained the same as in the pristine polymer.

The best *in situ* stability (MEA hold at 0.55 V for 12 hours) were obtained for MEAs fabricated with SEBS30-TMA membrane and SEBS35-TMA and PPO-TMA binders. The peak power densities remained at ca. 65% of their original values after 12 hours of continuous operation. The contact between the binder and AEM plays an important role during *in situ* stability testing. The best fuel cell performance was attained by using PPO-C6-TMA as binder (SEBS30-TMA as AEM separator) with a peak power density of 300 mW/cm² (hydrogen/oxygen operation).

### 3.5 References


Chapter 4: Efficient pH-Gradient-Enabled Microscale Bipolar Interfaces in Direct Borohydride Fuel Cells


Supplementary figures and tables are available in Appendix IV
Abstract

The disparate pH requirements for borohydride oxidation and peroxide reduction in direct borohydride fuel cells (DBFCs) currently hinders their performance and efficiency. Here we develop a pH-gradient-enabled microscale bipolar interface (PMBI) that facilitates significantly different local pH environments at the anode and cathode of a DBFC. Using a recessed planar electrode (RPE) in conjunction with TEM, we show that the PMBI maintained a sharp local pH gradient (0.82 pH units/nm on average) at the electrocatalytic reaction site. The PMBI configuration enabled significantly enhanced performance in a DBFC as compared to either an all-anion-exchange or an all-cation-exchange configuration (330 mA/cm² at 1.5 V and 630 mW/peak/cm² at 1.0 V). The high power densities obtained at voltages well above 1 V, achieved by virtue of the effective separation of anolyte and catholyte locally at the electrocatalytically active sites by the PMBI, can significantly reduce fuel cell stack size for autonomous propulsion applications.
4.1 Introduction

Electrochemical energy conversion devices usually operate at uniform pH or over a narrow pH range. For example, anion exchange membrane fuel cells (AEMFCs) [1] and anion exchange membrane water electrolyzers (AEMWEs) [2] both operate at high pH, while proton exchange membrane fuel cells (PEMFCs) [3] and proton exchange membrane water electrolyzers (PEMWEs) [4] both operate at low pH. The uniform pH environment of these devices frequently hampers the facility of one of the half-cell reactions. In PEMFCs/PEMWEs, where both the anode and cathode operate at acidic pH, the H₂ oxidation/evolution reaction is quite facile while the O₂ reduction/evolution reaction is sluggish. In AEMFCs/AEMWEs, the converse is true. Moreover, the chemical stability of some reactants depends strongly on the pH. For example, NaBH₄ is only stable at high pH and disproportionates in acidic and neutral solutions. H₂O₂, conversely, disproportionates at high pH but is stable at low pH. Therefore, a NaBH₄/H₂O₂ fuel cell (DBFC) using H₂O₂ as oxidant can only be operated effectively by maintaining sharply different pH environments at the anode and cathode [5]. Given this, we postulate that if electrochemical devices can be designed with an interfacial pH gradient that enables decoupled pH at the two electrodes, it would be possible to enhance half-cell reaction kinetics, expand the selection of electrocatalysts (especially non-noble-metal electrocatalysts) that can be used, and broaden the selection of (combinations of) fuels and oxidants that can be employed.

Unlu et al. demonstrated a hybrid anion exchange membrane (AEM)/cation exchange membrane (CEM) bipolar configuration for H₂/O₂ fuel cells and direct methanol fuel cells (DMFCs) [6]. The H₂/O₂ fuel cell with an AEM/CEM bipolar configuration yielded a current density of a few tens of mA/cm², which was low compared to state-of-the-art PEMFCs and AEMFCs. They attributed the lower performance to non-optimized fabrication methods for the bipolar electrode assembly and
to the large membrane thickness (174 μm). To improve performance, they employed a modified bipolar interface, wherein the AEM component was integrated within a high-pH anion conducting electrode and directly coupled to a Nafion® membrane. By using this modified bipolar interface, the ionic resistance contribution of the AEM was avoided and the bipolar junction resided closer to the electrode, allowing for higher transport rates. This device yielded enhanced performance with a peak power density of 62 mW/cm² in H₂/O₂ mode, though this was still significantly lower than a state-of-the-art PEMFCs. Devices prepared with this modified design provided a key advantage compared with traditional PEMFCs, namely self-humidification by water generated at the bipolar interface that enabled operation under dry conditions [6]. The concept of the bipolar interface described above offers interesting possibilities if the overall performance of the device employing the interface can be improved.

DBFCs have received considerable attention due to their high power density, and high open circuit and operating voltages [7]. The high (theoretical) energy density (9.3 kWh kg⁻¹) and specific capacity (5.67 kAh kg⁻¹) of NaBH₄ offer considerable advantages over competing technologies [8], although the practical energy density will be lowered upon accounting for the added weight of KOH solution required to stabilise NaBH₄. Liquid H₂O₂ is a safe and energy dense oxidant for low temperature DBFCs. The standard thermodynamic cell voltage of a DBFC is 2.18 V when liquid H₂O₂ is employed as oxidant, a significant enhancement over the 1.23 V obtained with a traditional H₂/O₂ cell (standard half-cell and overall reactions are provided in the Supplementary Discussion section).

DBFCs have been primarily demonstrated using either a CEM [9-11] or an AEM [12-14] separator. Arges et. al. synthesized poly(phenylene oxide)-based AEMs (PPO-TMA⁺) and employed it for the fabrication of a bipolar interface membrane electrode assembly (BIMEA) for
a DBFC operated with liquid H$_2$O$_2$ [15]. Two additional configurations were also evaluated including a DBFC with an all-AEM configuration and a DBFC with an all-CEM configuration. Under the same experimental conditions, peak power densities of 110 mW/cm$^2$, 82 mW/cm$^2$ and 80 mW/cm$^2$ were obtained for the DBFC with the BIMEA, AEM and CEM configurations, respectively. While these results were promising, further studies were deemed necessary to understand the functional principles of the bipolar interface, specifically the role of the pH gradient across the interface, and to enhance the power density obtained.

The choice of electrocatalyst is critical in the evaluation of DBFC performance. Pt/C was chosen as a standard catalyst for H$_2$O$_2$ reduction at the cathode. The choice of a NaBH$_4$ oxidation catalyst required significant thought given the complexities associated with this reaction. As detailed in the Appendix IV, we drew upon the extensive work of other researchers [10, 15-27] to arrive at the choice of Pd/C on Ni foam as the electrocatalyst of choice.

Given this background, the overarching objectives of the current work were two-fold. First, we experimentally prepared microscale bipolar interfaces and examined their ability to control the local pH gradient at the electrocatalytic reaction sites. Second, we translated these microscale bipolar interfaces to DBFC devices and engineered the interfacial pH gradient to obtain a high-voltage device able to deliver practical current densities at cell voltages above 1.2 V. The resultant PMBI-based DBFC yielded a current density of 330 mA/cm$^2$ at 1.5 V and a peak power density of 630 mW/cm$^2$ at 1 V.

### 4.2 Method

#### 4.2.1 Materials

Chlorotrimethylsilane (99%), KOH (90%), chlorobenzene (99.5%), tin(IV) chloride (99.995%),
chloroform (99.5%), methanol (99.9%), paraformaldehyde (99.5%), silver nitrate (0.1N), potassium thiocyanate (0.1N), sodium nitrate (99%), chloroform-d (99.96%), 1-methyl-2-pyrrolidinone (NMP, 99.7%), trimethylamine solution (TMA; 31 wt.%-35 wt.% in ethanol) and sulfuric acid (95%), hydrogen peroxide solution (30 wt.% in H₂O), Nafion® perfluorinated resin solution (5 wt.% in lower aliphatic alcohols and water) were purchased from Sigma Aldrich. polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS; 55:45 molar ratio of styrene to rubber) was sourced from Kraton®. Ni foam was purchased from MTI Corporation. 46.5% Pt on Vulcan was purchased from TANAKA K. K. 40% Pd on Vulcan was purchased from Premetek Corporation. GDL 24AA (diffusion media) was purchased from Ion Power.

4.2.2 Synthesis of chloromethylated SEBS (CMSEBS)

SEBS (5g) was dissolved in chlorobenzene (250 mL). Paraformaldehyde (16.7 g) was added into the mixture and the temperature was set to 55 °C. The mixture was reacted for with 7 days. The product was precipitated in methanol (1.3 L), recovered by filtration, and washed with abundant methanol. The product was purified by re-dissolving in chloroform/chlorobenzene (4:1) and re-precipitating in methanol. The purification process was repeated two times. Chloromethylation of SEBS (55:45 molar ratio of styrene to rubber) resulted in chloromethylated SEBS polymers CMSEBS55 with degrees of chloromethylation (DF; mol of chloromethyl groups per mol of polymer repeat unit) of 0.31 (see Appendix IV, Figure A4.6.).

4.2.3 Synthesis of SEBS-based AEIs (SEBS55-TMA)

SEBS55-TMA: CMSEBS55 (0.5 g) was dissolved in chlorobenzene (9 mL). The mixture was cast onto a 3.5 in × 3.5 in glass plate and the solvent was evaporated in an oven at 60 °C. The membrane was peeled off and placed in a round-bottom flask containing 3 mL of trimethylamine (TMA) and
30 mL of NMP. The reaction was conducted at 30 °C for two days.

4.2.4 Ion exchange capacity and ionic conductivity

The experimental procedure of measuring ion exchange capacity and ionic conductivity can be found in previous section (3.2.9)

4.2.5 NMR and FTIR spectroscopy characterization of the polymers

The experimental procedure of measuring ion exchange capacity and ionic conductivity can be found in previous sections (3.2.10 & 3.2.11)

4.2.6 Atomic force microscopy

The experimental procedure of measuring ion exchange capacity and ionic conductivity can be found in previous section (3.2.12)

4.2.7 Permselectivity and transport numbers

Membrane permselectivity and transport numbers were measured using the membrane potential method in a lab-made diffusion cell (Appendix IV, Figure A4.10.). The CEM was clamped between two well-stirred compartments containing different concentrations of the same salt (0.1 M and 1 M NaCl). Two identical silver chloride reference electrodes were used to measure the potential difference (E_m (mV)) between the two solutions arising from the different mobilities of chloride and sodium ions through the membrane. The membrane potential was used to calculate the membrane permselectivity (selectivity of the cation exchange membrane towards cations) and the transport numbers (in this case for chloride and sodium). The following equation was used to calculate anion and cation transport numbers and membrane permselectivity:
\[ E_m = \left( \frac{RT}{zF} \right) \left[ t_+ \ln \left( \frac{a_{Na^+ \text{concentrated}}}{a_{Na^+ \text{dilute}}} \right) - t_- \ln \left( \frac{a_{Cl^- \text{concentrated}}}{a_{Cl^- \text{dilute}}} \right) \right] \quad (1) \]

Where \( t_+ \) and \( t_- \) are the transport numbers for the cation (Na\(^+\)) and the anion (Cl\(^-\)) respectively, \( a_{Na^+} \) and \( a_{Cl^-} \) are the activities of the electrolyte (NaCl) at in the concentrated and diluted compartments separated by the membrane, \( z \) is charge of the species, \( T \) is the absolute temperature, \( R \) is the gas constant and \( F \) is the Faraday constant. The coefficient \( t_+ - t_- \) is commonly referred as the membrane permselectivity and represents the difference between the transport numbers for cations and anions [28].

### 4.2.8 Evaluation of PMBI at the electrocatalyst site using RPE

The impact of the bipolar interface on the local pH conditions at the electrochemical reaction site has been hypothesized in several reports [6, 15] but a direct demonstration of this effect is lacking. Herein, the efficacy of the microscale bipolar interface in maintaining a pH gradient was studied using RPE experiments. The RPE experiments were designed to mimic the electrochemical environment and current distribution of the anode half-cell. The OCP was measured at different bulk pH values and it was observed that the predominant reaction at the anode was unchanged with changing bulk pH when the microscale bipolar interface was employed. This provided direct evidence of the effectiveness of the microscale bipolar interface configuration in maintaining a high pH gradient across the bipolar junction and in preventing catholyte contact with the anode active sites. The RPE system was designed to simulate the conditions at the DBFC anode. The recessed nature of the disk ensured that the current distribution was uniform over the disk surface and the PTFE shroud ensured that slurry did not stick to the shroud walls leading to undesirable edge thickening. Thus, a uniform, planar catalyst layer with isogalvanic current distribution lines orthogonal to the surface over the entire active area was ensured [29]. The discs were precision
machined out of a Ni rod (Goodfellow, 5 mm dia., 99.99+% purity) to simulate the Ni support used in the DBFC and fitted into a PTFE U-Cup (Pine Instruments) such that it was recessed by ~1mm as depicted in Figure 4.1. The Ni disk was covered by a thin catalyst film using standard drop casting techniques and catalyst inks that matched the compositions used in the DBFC anode. The first catalyst ink was made of a suspension of 0.4 g Pd/C (40 wt % Pd/C from Premetek Corporation, P30A400) catalyst in a solution of 0.17 g chloromethylated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (CMSEBS55; 55:45 molar ratio of styrene to rubber) in 9.75 ml of chlorobenzene. The catalyst ink mixture was sonicated for 7 minutes and then drop-cast onto the Ni disk, followed by drying to yield the thin-film electrode. The electrode was immersed into a mixed solution of 1-methyl-2-pyrrolidinone (NMP) (30 ml) and trimethylamine (TMA; 31%-35% weight percent in ethanol) (3 ml) at 30 ºC for two days to functionalize the CMSEBS55 and yield the AEI (SEBS55-TMA). The second catalyst ink was made of a suspension of 0.4 g Pd/C catalyst in a solution of 3.42 g Nafion® perfluorinated resin solution in 6 ml of isopropanol/water mixture (1:1 weight ratio), with an identical method of thin-film electrode preparation. The electrolyte bulk consisted of NaBH₄ solution in KOH. The solution composition was varied to change the pH value in the bulk and the OCP was monitored over time. The following solution compositions were used to test the OCP: 1) 0.5 M KOH + 0.1 M NaBH₄; 2) 0.1 M KOH + 0.1 M NaBH₄; 3) 0.01 M KOH + 0.1 M NaBH₄; 4) DI water + 0.1 M NaBH₄; 5) 0.05 M H₂SO₄ + 0.1 M NaBH₄. By changing the bulk electrolyte pH values in the RPE system, the control of the pH gradient across the binder in the thin-film electrode could be observed by monitoring OCP of BOR. All the measurements were carried out in a standard three electrode system with a Pt counter electrode and a calomel reference electrode. To convert the potential monitored from saturated calomel electrode to standard hydrogen electrode, 0.241 V was added to
the potential obtained using the saturated calomel electrode. The pH was recorded using an Accumet® portable laboratory pH meter. The calculation of BOR limiting current can be found in Appendix IV, Figure A4.11.

Figure 4.1. Scheme for the recessed planar electrode (RPE) system designed to simulate a pH-gradient-enabled microscale bipolar junction. The pH sensitive sodium borohydride electrooxidation reaction is chosen as a test case. a, sodium borohydride electrooxidation reaction mechanism. b, cross-section of the RPE. c, ion transport in RPE with anion exchange ionomer binder. d, ion transport in RPE with cation exchange ionomer binder.

4.2.9 Preparation and characterization of PMBI

Carbon-supported Pd catalyst (40 wt % Pt/C) was used at the anode (BOR electrode). A suspension of 0.4 g Pd/C catalyst in a solution of 0.17 g CMSEBS55 in 9.75 ml of chlorobenzene was sonicated for 7 minutes. The resultant ink was sprayed on a porous nickel foam electrode (1.6 mm
thickness from MTI Corporation) with an airbrush (Badger model 150). The electrode was immersed into a mixture of NMP (30 mL) and TMA solution (3 mL) at 30 °C for two days to functionalize the CMSEBS55 and yield the AEI (SEBS55-TMA).

Carbon-supported Pt catalyst (46 wt % Pt/C from Tanaka K. K.) was used at the cathode (HRR catalyst). A suspension of 0.4 g Pt/C catalyst in a solution of 3.42 g Nafion® perfluorinated resin solution in 6 ml of isopropanol/water mixture (1:1 weight ratio) was sonicated for 7 minutes. The resultant ink was sprayed on a porous carbon paper (GDL 24AA diffusion media from Ion Power) with an airbrush (Badger model 150). The nominal catalyst loadings at the anode and the cathode for the 5-cm² active area cell was 1 mg<sub>catalyst</sub>/cm². The nominal catalyst loadings at the anode and the cathode for the 25-cm² active area cell was 3 mg<sub>catalyst</sub>/cm².

The Pd/C deposited on Ni foam and Pt/C deposited on the GDL 24AA were characterized using a SEM (FEI Nova 230) equipped with an EDX analyzer. The beam energy used was 10 kV, the chamber pressure was 9×10⁻³ Pa and the chamber temperature was 23 °C. Additional characterization of the PMBI can be found in Appendix IV, Figures A4.6., A4.7., A4.8., and Table A4.1. The SEM cross section view of electrode can be found in Appendix IV, Figure A4.9.

4.2.10 Direct borohydride fuel cell performance tests

DBFC devices with the PMBI configuration were scaled to a 25-cm² active cell area. Fuel cell performance was evaluated at 70 °C in a corrosion-resistant single-cell device (Fuel Cell Technologies, Inc.). To construct the DBFC with the all-CEM configuration, Nafion® solution (equivalent weight, 1100) was used as the binder for both anode and cathode. Nafion®117 was used as the membrane separator. To construct the DBFC with the all-AEM configuration, the SEBS-based AEI described earlier was used as binder for both the anode and cathode. A SEBS-
based AEM (SEBS30-TMA) was used as the membrane separator for this configuration. The characterization of SEBS30-TMA can be found in our previous reports [1]. To construct the DBFC with the PMBI interface, the SEBS55-TMA AEI was used as the anode binder and Nafion® was used as the cathode binder. Nafion®117 was used as the membrane separator. Prior to fuel cell testing, the anode was immersed into 1 M KOH for 4 hours at room temperature and cathode was immersed into 1 M H₂SO₄ for 4 hours at room temperature.

The pinch (compression) used during assembly of the fuel cell hardware for all fuel cell experiments was 3 mils on each side and the torque used to assemble the cell was 25 lb-in at each bolt. Polarization curves were acquired using a Scribner Associates model 850e fuel cell test station by scanning the current from 0.8 mA cm⁻² to 800 mA cm⁻² (15 points per decade). The system was held at each current density for 2 min, and the acquisition was stopped when the voltage dropped below 0.05 V. For the DBFC tests, the fuel used was 1.5 M NaBH₄ in 3 M KOH and the oxidant used was 15 wt% H₂O₂ in 1.5 M H₂SO₄. The flow rates for both anode and cathode were varied from 0.4 ml min⁻¹ cm⁻² to 4.8 ml min⁻¹ cm⁻². DBFC performance data can be found in Appendix IV, Table A4.1.

4.2.11 Direct borohydride fuel cell stability test

In situ DFBC stability tests were performed in an operating fuel cell by holding the cell at a constant voltage of 1.0 V for 60 minutes. Ex situ accelerated cell stability tests were performed by immersing the anode into a 3M KOH solution at 70 °C for 50 hours and cathode into 1.5 M H₂SO₄ solution at 70 °C for 50 hours. Polarization curves were acquired before and after this ex situ treatment. The initial and final polarization curves were compared to ascertain the MEA component stability under this accelerated test.
4.2.12 Efficiency of DBFCs and PEMFCs

The overall reaction occurring in a DBFC is shown below:

\[
\text{NaBH}_4 + 4\text{H}_2\text{O}_2 \rightarrow \text{NaBO}_2 + 6\text{H}_2\text{O}
\]

Under standard conditions, the thermodynamic efficiency is given by the ratio of Gibbs free energy change to the enthalpy change in the overall cell reaction. \( \Delta G^0 = -796.8 \text{ kJ/mol} \) and \( \Delta H^0 = -788.4 \text{ kJ/mol} \). The thermodynamic efficiency of the DBFC is therefore:

\[
\text{Thermodynamic efficiency} = \frac{\Delta G^0}{\Delta H^0} \times 100\% = 99\% \quad (2)
\]

The overall reaction of the PEMFC is shown below:

\[
\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}
\]

Under standard conditions, the thermodynamic efficiency is given by the ratio of Gibbs free energy change to the enthalpy change in the overall cell reaction. \( \Delta G^0 = -237.1 \text{ kJ/mol} \) and \( \Delta H^0 = -285.8 \text{ kJ/mol} \). The thermodynamic efficiency of the PEMFC is therefore:

\[
\text{Thermodynamic efficiency} = \frac{\Delta G^0}{\Delta H^0} \times 100\% = 83\% \quad (3)
\]

All data has been taken from CRC Handbook of Chemistry and Physics [30]. The voltage efficiency is the ratio of the actual voltage under operating condition to the theoretical cell voltage. At the same operating current density (at 500 mA/cm\(^2\)), the voltage efficiency of our DBFC is \textit{ca.} 55\% and the voltage efficiency of a PEMFC is \textit{ca.} 57\%.
4.3 Results and Discussion

4.3.1 Historic trends in DBFC performance

Table 4.1. summarizes the publications reporting DBFC operation with O₂, Air, and H₂O₂ as oxidants. Notably, even though the theoretical open circuit voltage (OCV) for a DBFC operated with H₂O₂ is 2.18 V, only a few reports show OCVs above 1.8 V [27, 31, 32]. This is primarily because of the crossover of the alkaline fuel and acidic oxidant steams. A high pH is imperative for the DBFC to achieve the high OCV values reported herein, as the borohydride electrooxidation reaction (BOR) (E⁰ = -1.24V vs. SHE) is in competition with the hydrogen oxidation reaction (HOR) (E⁰ = 0V vs. SHE). Thus, the measured and reported OCVs from prior studies were understood to be a mixed potential with contributions from both reactions, with a strong pH dependence.

Table 4.1. Summary of representative literature for DBFC performance with O₂, air or H₂O₂.

<table>
<thead>
<tr>
<th>Anode catalyst</th>
<th>Cathode catalyst</th>
<th>Separator</th>
<th>Oxidant</th>
<th>Operation temperature (°C)</th>
<th>Peak power density (mW cm⁻²)</th>
<th>OCV (V)</th>
<th>Current density at 1.5V (mA cm⁻²)</th>
<th>Year published</th>
<th>Reference</th>
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<td>NA*</td>
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<td>2012 [43]</td>
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<td>Reaction</td>
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<td>Current (mA)</td>
<td>RA (Ω)</td>
<td>Time</td>
<td>Reference</td>
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NA* = no current at 1.5V.

### 4.3.2 Evidence of sharp local pH gradient at the bipolar interface

In this work, the PMBI configuration was selected to control the local pH at the anode electrocatalyst. The PMBI configuration allows the realization of the key idea that a cation exchange separator in intimate contact with an anion exchange binder covered electrocatalyst...
would behave as a microscopic and localized bipolar interface. The effect of the electrode binder composition was examined using the recessed planar electrode (RPE) depicted in Figure 4.1. The clear distinction between the pH values at the electrolyte bulk and the pH values locally at the PMBI covered catalyst surface is key to understanding the functioning of the PMBI. The hypothesis behind using the PMBI was that irrespective of the lowering of the electrolyte bulk pH, the pH at the catalyst surface (i.e. reaction site) would be alkaline due to the H\(^+\) blocking effect of the PMBI.

Initially, bounds were established for the possible open circuit potential (OCP) values with the two ideal cases being either complete HOR or complete BOR. The HOR and BOR OCPs depicted in Figure 4.2. were calculated for different pH values from the standard equilibrium potentials (as detailed in Appendix IV). These OCPs serve as upper and lower bounds respectively for the experimental measurements with different binder configurations and at different pH values.

![Figure 4.2. Evidence for strong and localized pH gradients. Open circuit potential variation with pH for recessed planar electrode system in case of a, cation exchange ionomer binder used at the anode, and b, anion exchange ionomer binder used at the anode. The error bars represent the standard error with n=3.](image-url)
A key point to consider here is that these OCP values are calculated for the local pH at the electrode, not the bulk pH. When a cation exchange ionomer (CEI) binder is used at the anode, it allows for the added H⁺ ions to reach the catalytic sites. Consequently, the local pH values track the bulk pH values and the HOR and BOR theoretical OCPs change as depicted in Figure 4.2a. But when an anion exchange ionomer (AEI) binder is used at the anode, the added H⁺ ions cannot reach the catalytic sites. Thus, the local pH at the anode is constant (ca. 13.5 in our case) and so the HOR and BOR theoretical OCPs do not change despite changes in bulk pH, as seen in Figure 4.2b. Consider a DBFC operating with a CEM separator. Initially, the highly basic anolyte would strongly favor the BOR. Over time, the use of a CEM such as Nafion® as the separator would lead to a drop in the bulk anolyte pH due to the free cross-over of H⁺ from the catholyte. The anode electrocatalyst can be reasonably assumed to be covered by a thin layer of the binder and hence the local conditions at the electrocatalyst surface would be a function of the type of binder used. When a CEI binder is used, the local pH near the electrocatalyst surface is acidic and the OCP will be dominated by contributions from the HOR reaction (with hydrogen produced as a result of borohydride hydrolysis), whose kinetics is enhanced at lower pH [55]. This was experimentally verified by the OCP values obtained with the CEM-based RPE depicted in Figure 4.2a. The CEM binder does not prevent the H⁺ ions from reaching the catalyst particles and so as the bulk pH become more acidic, so does the local pH near the electrode. The measured OCPs for an electrode with a CEM binder showed that the contribution from the BOR to the OCP was minimal and that the anode was behaving similar to the anode in a hydrogen fuel cell.

The OCP values measured on the RPE with the AEI binder were found to be dominated by the contribution from the BOR. This is due to the ability of the AEI binder to be highly selective toward OH⁻ ions. This ensures that even when the bulk electrolyte pH is lowered (for example,
due to cross-over of the H⁺ from the catholyte in a full cell), the local pH is alkaline. Initially, at a pH of 13.5, the OCP was a mixed potential with a >60% contribution from the BOR. This establishes the upper bound of the OCP. As the bulk electrolyte pH changes, the local pH is nearly constant and alkaline (close to the initial value of 13.5). Thus, the OCP is invariant with bulk pH, as seen in Figure 4.2b. The remarkably constant OCP values over a wide range of alkaline pH values unequivocally confirmed that the reaction was not occurring in an environment similar to the electrolyte bulk and provided direct evidence of the formation of a PMBI that permitted a sharp pH gradient across it.

Figure 4.3. shows the structure of the microscale bipolar interface. The AEI covers the surface of the Pd/C catalyst, providing alkaline conditions for the BOR. From the discussion above, the pH value at the surface of electrocatalyst was estimated to be 13.5. Assuming close to zero permeation for the H⁺ and OH⁻ in case of the AEI and the CEM (permselectivity measurements substantiating this assumption can be found in Appendix A4.10.) respectively, the pH inside the microscale bipolar interface should be close to 7.0. Since it is not possible for us to precisely measure the thickness distribution of the bipolar interface, we do recognize that this assumption of close to 7 pH at the interface is somewhat speculative. Variations in the thickness and distribution of the bipolar interface will lead to deviations from this ideal value. The thickness distribution of the AEI covering the surface of the anode was obtained from TEM measurements (Figure 4.4a. &4.4b.). The AEI was not distributed entirely uniformly with the average thickness being 8 nm, in reasonable agreement with values measured with electron tomography for CEM-based electrodes with similar binder loadings (7.2-7.6 nm) [56]. The interfacial pH gradient distribution ranged from 0.5 pH-units/nm to 3.3 pH-units/nm (Figure 4.4c.) with the average being 0.82 pH-units/nm. This value of the pH gradient should translate reasonably to the anode catalyst layer of DBFC, as
the binder loading in the catalyst ink used in the RPE experiment was the same as that used to make the DBFC membrane electrode assembly. These pH-gradient-enabling interfaces were then deployed in DBFCs and the performance of the DBFCs were optimized as described below.

Figure 4.3. **General scheme of the pH-gradient-enabled microscale bipolar interface (PMBI).** The PMBI forms at the junction between the cation exchange membrane (CEM) and the anion exchange ionomer (AEI) binder. The reaction sites on the catalyst particle surface are covered by the AEI binder, which allows for selective transport of hydroxide ions. Thus, the local conditions at the reaction sites are alkaline irrespective of bulk conditions at and beyond the CEM.
Figure 4.4. Characterization of the pH-gradient-enabled microscale bipolar interface (PMBI) a, distribution of thickness of anion exchange ionomer covering Pd/C. b, TEM image of Pd/C covered by anion exchange ionomer (SEBS55-TMA). c, the calculated distribution of pH gradients across the microscale bipolar interface.

4.3.3 Impact of the PMBI on DBFC performance

The impact of the PMBI on DBFC performance was evaluated by examining three different DBFC configurations. Two configurations were designed to exhibit no/minimal pH gradient, including a DBFC with an all-CEM configuration with low-pH electrodes and a low-pH CEM separator and a DBFC with an all-AEM configuration with high-pH electrodes and a high-pH AEM separator. The third configuration consisted of DBFCs with an PMBI configuration that included a high-pH
anode, a low-pH CEM separator and a low-pH cathode, with a sharp pH gradient of 0.82 units/nm across the anode/CEM interface.

The operation of the DBFCs with CEM and AEM separators occurs with the external current being balanced by cation and anion transport, respectively, in the electrolyte while the operation of the DBFC with a PMBI configuration needs further explanation. The CEM separator on one side of the PBMI allows for the facile transport of cations, which will be blocked by the AEI covering the anode (for the sake of this discussion, perfect permselectivity is postulated). Thus, it maybe erroneously assumed that since neither cation nor anion can traverse the path between the anode and cathode, no ionic transport can occur, and the cell cannot operate. This is not the case, as the junction potential at the PBMI corresponds to water splitting at the bipolar junction and the OH\(^{-}\) and H\(^{+}\) produced will travel to the anode and cathode sides respectively and can participate in the BOR and H\(_2\)O\(_2\) reduction reactions (HRR). The thermodynamics of this process has been extensively and elegantly dealt with by Grew et al. [57] and Unlu et al.[6].

Figure 4.5. shows the polarization curves obtained from the DBFC experiments together with the configuration schemes employed. The DBFC with a PMBI configuration yielded the best performance with an OCV of 1.8 V and a peak power density of ca. 300 mW/cm\(^2\) (Figure 4.5c.). The OCV was quite close to the thermodynamic cell voltage for the overall reaction (2.18 V, after accounting for the junction potential). The 400 mV deviation between the experimental OCV and theoretical OCV for the DBFC with PMBI configuration was attributed to the HOR and the oxidation of other intermediates (e.g., BH\(_3\)OH\(^{-}\)), giving rise to a mixed potential. The DBFC with the CEM configuration yielded the lowest OCV (1.3 V, very close to the H\(_2\)/O\(_2\) system, indicating that NaBH\(_4\) hydrolysis occurred first followed by HOR) with a peak power density of ca. 50 mW/cm\(^2\) (Figure 4.5a.). The DBFC with the all-AEM configuration yielded an OCV of 1.7 V
along with a peak power density *ca.* 280 mW/cm² (Figure 4.5b.). The low OCV observed in the DBFC with the all-AEM configuration was attributed to the large amounts of OH⁻ and BH₄⁻ crossing over from the anode to the cathode through the AEM. The acid in the cathode side was neutralized due to this crossover and it was difficult to maintain the acidic conditions necessary to avoid H₂O₂ disproportionation. The performance of the DBFC with the AEM configuration was slightly lower than that of the DBFC with the PMBI configuration, but the alkali crossover in the former presented an important (and intractable) operational drawback. Hence, we concluded that the sharp pH gradient enabled by the PMBI configuration offered the only solution to secure high performance.

*In situ* cell stability tests were performed by holding the DBFC at a constant voltage (1.0 V) for 60 minutes. There was no apparent current decay observed for any of the DBFCs (Figure 4.5d., 4.5e., 4.5f.). Na⁺ (all-CEM) and SO₄²⁻ (all-AEM) ions do migrate through the membrane. However, the flow rate of fuel and oxidant was sufficient to replenish any cross-over species and to flush any resultant side products out of the cell, resulting in stable cell performance. Other possible side-reactions at the PMBI such as the formation of NaBO₂ by chemical reactions and the formation of water due to the reaction of H⁺ and OH⁻ were also considered. The absence of any increase in overall cell resistance (and the absence of any precipitate at the junction upon dis-assembly of the cell) indicated that there was no significant accumulation of NaBO₂ at the PMBI within the timescale of our experiment. Further, any NaBO₂ formed at the interface should be transported to the anolyte and flushed out of the system due to the high concentration gradient that exists. The water splitting reaction at the PMBI is expected to far outweigh any chemical production of water and allow us to maintain the required pH at the anolyte and catholyte sides.
Figure 4.5. **Impact of the interface on device performance.** a, polarization curves for a DBFC with an all-CEM configuration that includes an anode with CEM binder, a CEM separator and a cathode with CEM binder. b, polarization curves for a DBFC with an all-AEM configuration that includes an anode with AEM binder, an AEM separator and a cathode with AEM binder. c, polarization curves for a DBFC with a PBMI configuration that includes an anode with AEM binder, a CEM separator and a cathode with CEM binder. d, cell stability test for a DBFC with an all-CEM configuration. e, cell stability test for a DBFC with an all-AEM configuration. f, cell stability test for a DBFC with a PBMI configuration.

It is possible that the DBFC performance could deteriorate over time due to the poisoning of the catalyst surface by BH$_{X,\text{ads}}$ species. However, the judicious selection of Pd as the electrocatalyst on the anode side mitigates this issue as Pd has been observed to maintain high BOR activity even at high NaBH$_4$ concentrations, unlike Pt and Au catalysts [24]. This leads us to believe that catalyst
poisoning by BH$_{ads}$ species should not be a major issue in our system. *Ex situ* accelerated cell stability tests (Appendix IV, Figures A4.1., A4.2., and A4.3.) showed that MEAs for DBFCs with all configurations were completely stable for at least 50 hours upon exposure to the corresponding electrolyte media.

### 4.3.4 Optimization of DBFC performance and comparison with a PEMFC

To further enhance the performance of the DBFC with the PMBI configuration, different thicknesses of the separator membrane were investigated (see Appendix IV, Figure A4.4.). The PMBI with the Nafion®117 separator yielded the best performance when compared with Nafion®112 and Nafion®115 separators. We attributed this to the lower permeation flux of BH$_4^-$ when using thicker separators. The cell was then scaled up from a 5-cm$^2$ to a 25-cm$^2$ active area and the loading of catalyst was increased to 3 mg$_{metal}$/cm$^2$. Flow rates for both the anolyte and catholyte were varied systematically from 0.8 to 4.8 ml min$^{-1}$ cm$^{-2}$ to optimize the power output (Appendix IV, Figure A4.5.). When the flow rates were enhanced from 0.8 to 4.0 ml min$^{-1}$ cm$^{-2}$, there was a significant improvement in DBFC performance in terms of peak power density (from 225 to 610 mW/cm$^2$). Further increase in the flow rate from 4.0 to 4.8 ml min$^{-1}$ cm$^{-2}$, yielded a limited enhancement in DBFC peak power density (from 610 to 630 mW/cm$^2$). State-of-the-art DBFC performance using the PMBI configuration was obtained when operating with a flow rate of 4.8 ml min$^{-1}$ cm$^2$ (Figure 4.6.), with an OCV of 1.95 V and a peak power density of 630 mW/cm$^2$. An excellent current density of 330 mA/cm$^2$ was obtained at 1.5 V (corresponding to a power density of *ca.* 500 mW/cm$^2$). Whereas a PEMFC (H$_2$/air, unpressurized) [58] yielded a power density of about 410 mW/cm$^2$ at 0.70 V (Figure 4.6.), our DBFC with the PMBI configuration provides a 20% higher power density than this state-of-the-art PEMFC, but at double the operating voltage. The high-voltage operation without compromise on power density will help
reduce the size (and cost) of fuel cell stacks by simplifying stack design considerably. Doubling the cell voltage could conceivably reduce the number of cells by a factor of 2 without compromising overall power output (current scales with cell area, where there is much flexibility), while still enabling seamless integration with motors and other accessories at the rated stack voltage. This is particularly relevant in propulsion systems for autonomous platforms such as unmanned underwater vehicles (UUVs, submersibles) and unmanned air vehicles (UAVs, drones), where stack size and weight are at a premium.

Figure 4.6. **Comparison of DBFC and PEMFC.** Polarization curves for a scaled up (25-cm²) DBFC with pH-gradient-enabled microscale bipolar interface configuration and state-of-the-art PEMFC taken from the literature [58].
The maximum possible (thermodynamic) efficiency for DBFC under standard conditions is 99%, while for PEMFCs the thermodynamic efficiency is 83% at standard conditions (calculations can be found under Appendix IV). However, the faradaic efficiency of the BOR in dilute alkaline solution was measured to be ca. 50% with Ni+Pd/C catalyst due to H₂ evolution [7], while the faradaic efficiency for the HOR in a PEMFC is known to be close to 100%. The development of selective catalysts that promote the BOR and HRR while inhibiting HER and OER (hence improving faradaic efficiency) is therefore a valuable next step in the development of DBFCs. At the same operating current density (at 500 mA/cm²), the voltage efficiency of our DBFC is ca. 55% and the voltage efficiency of a PEMFC is ca. 57%. The catalyst loading for our DBFC at both anode and cathode were 3 mg\text{catalyst/cm}² while the catalyst loading for a state-of-the-art PEMFC is 0.1 mg\text{catalyst/cm}² at the anode and about 0.25 mg\text{catalyst/cm}² at the cathode. Clearly, the primary advantage of the DBFC configuration reported herein over a PEMFC is not an enhanced efficiency, but rather the ability to provide high power densities at high voltage - nearly double the voltage of a state-of-the-art PEMFC, thereby significantly lowering the size of the fuel cell stack.

The OCV of a DBFC with PMBI configuration can be as high as 1.95 V, while the theoretical OCV is 2.18 V. Both are significantly higher than the thermodynamic potential for water splitting. This indicates that side reactions such as water electrolysis are indeed plausible, though not at an extent that causes significant concern in terms of lowered current efficiencies. Pt exhibits sluggish kinetics for the oxygen evolution reaction at the acidic cathode and most catalysts including Pd have an activity for the hydrogen evolution reaction that is usually about two to three orders of magnitude lower in alkaline media than in acidic media [59]. This further minimizes the impact of parasitic losses due to water electrolysis. To completely avoid the issue of parasitic losses due to water electrolysis, the DBFC can be operated at lower voltages such as 1.3-1.5 V and provide high
power densities (ca. 600 mW/cm$^2$) at these relatively high operating voltages. The DBFC demonstrated by us in this work proves the ability of a PMBI to achieve efficient separation of the acidic and basic electrolytes, paving the way for a practical DBFC system incorporating fuel and oxidant recycling.

### 4.4 Conclusion

A DBFC with a PMBI configuration was developed by employing a highly conductive anion exchange ionomer as the anode binder, Nafion$^\circledR$ as the cathode binder and Nafion$^\circledR$117 as the membrane separator. The ability of the PMBI configuration to maintain a sharp pH gradient was experimentally demonstrated by the measurement of OCP change as a function of pH using a RPE setup. The PMBI was shown to enable a pH gradient of 0.82 pH units per nm on average at the electrocatalytic reaction sites. This PBMI configuration was translated to the anode of a DBFC and yielded significantly improved performance as compared to either all-anion-exchange or all-cation-exchange configurations. The PMBI-based DBFC yielded a current density of 330 mA/cm$^2$ at 1.5 V and a peak power density of 630 mW/cm$^2$ at 1 V. The high OCV (1.95 V) and high performance at high voltage were attributed to the effective separation of anolyte and catholyte locally at the electrocatalytically active sites. The high power densities obtained at high voltages can significantly lower fuel cell stack size, which has significant favourable implications in the design of propulsion systems for autonomous vehicles.

### 4.5 References


Chapter 5: Polystyrene-\textit{block}-poly(ethylene-\textit{ran}-butylene)-\textit{block}-polystyrene Triblock Copolymer Separators for a Vanadium-cerium Redox Flow Battery

The results of this chapter have been published in Wang, Z., Parrondo, J., Ramani, V. (2017). 

**Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene Triblock Copolymer**


Supplementary figures and tables are available in Appendix V
Abstract

A series of polystyrene-	extit{block}-poly(ethylene-	extit{ran}-butylene)-	extit{block}-polystyrene (SEBS)-based anion exchange membranes (AEMs) were synthesized via chloromethylation of SEBS followed by quaternization with trimethylamine (TMA). AEMs functionalized with TMA$^+$ cations exhibited high chloride ion conductivity of 33.6 mS/cm at 70ºC. A V-Ce RFB employing the SEBS-based AEM as the separator yielded an energy efficiency of 86% at a current density of 50 mA/cm$^2$ with a 10% drop in capacity over 20 charge/discharge cycles. In contrast, a V-Ce RFB using Nafion®212 as the separator had an energy efficiency of 80% and a 40% drop in capacity over 20 charge/discharge cycles. The observed capacity fade was primarily due to cation intermixing between the anodic and cathodic compartments – much better permselectivity was obtained with the AEM separator. After 60 charge-discharge cycles (350 hours of operation), the ion exchange capacity and ionic conductivity of the AEM dropped by about 20%. There was no observed change in mechanical properties. The oxidative stability of the AEM was evaluated 	extit{ex situ} by immersion in 1.5 M VO$_2^+$ + 3M H$_2$SO$_4$ for 500 hours - the ionic conductivity remained constant over this timeframe. The chemical and mechanical stability and high conductivity of SEBS-based AEMs make them promising separator candidates for electrode-decoupled RFBs.
5.1 Introduction

There is a growing interest in using anion exchange membranes (AEMs) as separators in alkaline membrane fuel cells (AMFCs) [1-3] and in other energy conversion and storage systems such as redox flow batteries (RFBs) [4-6], alkaline water electrolyzers (AWEs) [7-9] and reverse electrodialysis (RED) cells [10].

RFBs are promising candidates for large-scale energy storage systems since the capacity, power and energy density parameters can be designed independently and easily modified even after installation [11, 12]. Original work on the iron/chromium RFB was performed by NASA researchers in 1970s [13]. Over the past few decades, several redox couples have been studied for RFB applications: All-vanadium [1, 14-16], all-uranium [17], iron-vanadium [18, 19], iron-chromium [20, 21], zinc-nickel [22], zinc-cerium [23-25], and zinc-bromine [26, 27]. Among these redox couples, the all-vanadium redox flow battery (VRFB) has been considered the most reliable RFB system due to its long-life and mild operating temperature range [28]. Moreover, intermixing of negative and positive electrolyte does not cause irreversible damage in the VRFB [29]. The drawbacks of VRFBs include their low standard cell voltage (1.26V) and the relatively low solubility of vanadium salts (typically 1.5 M in common acids, such as sulfuric acid), which limit their specific capacity and energy density [4]. Besides, hydrocarbon-based membrane separators suffered from oxidative degradation caused by the vanadium (V) cation. This required the use of fluorocarbon-based membranes as separators. The expensive vanadium salts and the high cost of the fluorocarbon-based separators have limited the commercialization of VRFBs.

Alternative redox species / couples could alleviate some of these issues. By using an AEM-separator, it is possible to operate “electrode-decoupled” RFBs with different redox elements at
the anode and cathode. The vanadium-cerium redox flow battery (V-Ce RFB) has relative high cell voltage (Ce$^{4+}$/Ce$^{3+}$ has standard potential of 1.44 V vs. SHE compared with V$^{5+}$/V$^{4+}$ at 1 V vs. SHE), good reversibility and acceptable energy density [12]. There has been some prior work on V-Ce RFB using AEM separators. Yun et al. developed cardo-poly-(ether ketone)-based AEMs and employed them as separators in a V-Ce RFB. Over 20 charge/discharge cycles, the RFB with the cardo-poly-(ether ketone)-based AEM separator yielded unchanged efficiencies and capacity, while the loss in capacity was about 50% for the benchmark Nafion®212 separator [4].

Studies of ion-containing block copolymers have provided clear evidence that the phase separation between hydrophilic and hydrophobic phases can produce materials with excellent ionic conductivity [30, 31]. Styrene block-copolymers (such as polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene, SEBS) have attracted considerable attention given their high thermal and chemical stability and tunable mechanical properties [32]. Several groups have attempted to synthesize SEBS-based AEMs using a variety of techniques. However, the chloromethylation of SEBS did not yield high degrees of functionalization (DF) and sometimes resulted in gelation when high DF values were attempted [31, 33]. Mohanty et al. used borylation and Suzuki coupling reactions to functionalize SEBS, obtaining AEMs with ion exchange capacities (IECs) of ca. 2.2 mmol/g and a chloride ionic conductivity of 13 mS/cm at 30 °C [34].

The most commonly used cation in AEMs is the benzyl trimethylammonium cation (TMA$^+$) [33, 35-56]. The derivative AEMs are easy to synthesize due to the basicity of trimethylamine, which allows it to react easily with halogenated polymers through the SN$_2$ pathway, resulting in membranes that exhibit relatively large IECs and good ionic conductivities. Other alternatives were also considered but they generally yielded much lower ionic conductivities.
The mechanical properties (ultimate strength and elongation at break) of the separator are very important for applications where the membranes will be assembled in cells with relatively large active areas, wherein they are exposed to stresses that could result in deformation. The mechanical properties of tri-block copolymers (e.g. polystyrene-\textit{block}-poly(ethylene-\textit{ran}-butylene)-\textit{block}-polystyrene (SEBS)) can be tuned by changing the proportion of styrene, which provides rigidity, to ethylene-butylene copolymers, which provides elasticity [57].

Given this background, the overarching objectives of this work were: 1) to synthesize SEBS-based AEMs with high ionic conductivity, to minimize ohmic losses during RFB operation; 2) to efficiently separate the decoupled anolyte and catholyte solutions containing different elemental species so that the (irreversible) intermixing is minimized; 3) to investigate the stability of the AEMs in conditions resembling those encountered in the RFB (acidic, with selected metal cations present).

To this end, chloromethylated SEBS with a high DF were prepared and quaternized by reaction with trimethylamine to obtain SEBS-based AEMs. The SEBS-based AEMs were characterized by measuring their IEC, ionic conductivity, water uptake, mechanical properties (ultimate tensile strength and elongation at break), permselectivity, transport number and swelling ratio. $^{1}$H NMR spectroscopy was used to confirm the chloromethylation of SEBS and estimate the DF. FTIR spectroscopy was employed to confirm the quaternization of chloromethylated SEBS.

A V-Ce RFB using SEBS-based AEMs as separators was operated for several charge/discharge cycles to evaluate the AEM electrochemical stability and its effectiveness as a barrier. The RFB performance and cycling efficiencies were compared with a V-Ce RFB using Nafion$^\text{®}$ 212 as the separator. After 60 charge/discharge cycles, the SEBS-based AEM was disassembled from the cell.
and characterized to evaluate its \textit{in situ} chemical stability. By immersing the membranes into the electrolyte solutions for 500 hours (\textit{ex situ}), the oxidative stability of SEBS-based AEM was independently evaluated.

\section*{5.2 Method}

\subsection*{5.2.1 Materials}

Chlorobenzene (99.5\%), tin(IV) chloride (99.995\%), chlorotrimethylsilane (99\%), chloroform (99.5\%), methanol (99.9\%), paraformaldehyde (99.5\%), silver nitrate (0.1N), potassium thiocyanate (0.1N), sodium nitrate (99\%), chloroform-d (99.96\%), 1-methyl-2-pyrrolidinone (99.7\%), trimethylamine solution (31\%-35\% weight percent in ethanol), sulfuric acid (99.999\%), vanadium (IV) oxide sulfate (97\%) and cerium (IV) sulfate (97\%) were purchased from Sigma Aldrich. SEBS (35:65 molar ratio of styrene to rubber) was sourced from Kraton Performance Polymers Inc. SEBS (M\textsubscript{n}=118000, 30:70 molar ratio of styrene to rubber) was obtained from Sigma Aldrich.

\subsection*{5.2.2 Single-cell RFB testing}

RFB experiments were carried out in an acid-resistant single cell with an active area of 25 cm\textsuperscript{2} (Fuel Cell Technologies, Inc.). The RFB was assembled by sandwiching the SEBS-based AEM (with a thickness equivalent to Nafion\textsuperscript{®}212) between two graphite felt electrodes (SGL Carbon, Sigracell\textsuperscript{®} GFA6) previously activated by heating in an oven at 400 °C for 30 hours [58]. The electrolyte in the negative compartment (150 mL) contained 0.5 M V\textsuperscript{2+} in 1M H\textsubscript{2}SO\textsubscript{4}. The positive compartment (150 mL) contained 0.5 M Ce\textsuperscript{4+} in 1M H\textsubscript{2}SO\textsubscript{4}. The active redox species were V\textsuperscript{3+}/V\textsuperscript{2+} in the negative electrode and Ce\textsuperscript{4+}/Ce\textsuperscript{3+} in the positive electrode. A redox cell test system (model 857, Scribner Associates, Inc.) comprising a fluid control unit and a potentiostat with
impedance spectroscopy capabilities was employed in the experiments. System control and data acquisition were done using the Flow Cell software (Version 1.1, Scribner Associates, Inc.). The RFB was charged and discharged at a constant current density of 50 mA cm$^{-2}$ at room temperature (approx. 21 °C). Both solutions were circulated through the electrodes using peristaltic pumps at a constant flow rate of 100 mL min$^{-1}$. The RFB was considered charged once the cell voltage reached 2 V and discharged when the cell voltage dropped below 0.65 V (cutoff voltages).

The current efficiency (CE), energy efficiency (EE) and voltage efficiency (VE) were calculated using the following equations:

\[
\text{CE} = \frac{Q_d}{Q_c} \times 100\% \quad [1]
\]

\[
\text{EE} = \frac{E_d}{E_c} \times 100\% \quad [2]
\]

\[
\text{VE} = \frac{\text{EE}}{\text{CE}} \times 100\% \quad [3]
\]

where \(Q_d\) and \(Q_c\) were the discharge and charge capacities (Ah/L), and \(E_d\) and \(E_c\) were the energy density (Wh/L) released during the discharge and consumed during charge, respectively.

5.3 Results and Discussion

We have employed a backbone-functionalization method more facile than those previously employed by Mohanty and coworkers [32]. The chloroform commonly employed as solvent during the chloromethylation reaction [59] was replaced by chlorobenzene, allowing the reaction to be carried out at higher temperatures (80 °C) thereby increasing the reaction rate. This procedure allows us to obtain AEMs (after quaternization of the chloromethylated polymer) with an IEC of up to 1.93 mmol/g, resulting in a chloride ion conductivity of 16 mS/cm (at 30 °C). Figure 5.1. shows the scheme followed for the synthesis of the AEM. Appendix V, Figure A5.1. shows the $^1$H
NMR spectrum of SEBS and Appendix V, Figure A5.2. shows $^1$H NMR spectrum of chloromethylated SEBS with a 30:70 molar ratio of styrene to rubber (CMSEBS30). A new peak “e” at a chemical shift of ca. 4.5 ppm, corresponding to the protons in the chloromethyl group, can be seen in Appendix V, Figure A5.2. (2H, multiplet). The presence of the peak “e” confirmed the chloromethylation of SEBS30. The DF was estimated to be 0.16 mols of chloromethyl groups / mol of polymer repeat unit. Appendix V, Figure A5.3. shows the $^1$H NMR of the chloromethylated SEBS polymer with a 35:65 molar ratio of styrene to rubber (CMSEBS35). The DF for this polymer was calculated to be 0.22 mol/mol. CMSEBS30 and CMSEBS35 were reacted with TMA to obtain the following AEMs: SEBS30-TMA, SEBS35-TMA (reaction schemes in Figure 5.1.). Since the AEMs could not be dissolved in the common deuterated solvents, it was not possible to confirm the reaction outcome by using NMR spectroscopy. Instead, FTIR was employed to confirm the formation of the desired AEMs. Appendix V, Figure A5.4. shows the FTIR spectra of SEBS30-TMA and CMSEBS30. A new FTIR peak at ca.893 cm$^{-1}$ was assigned to the C-N bond stretching, which confirmed the formation of the SEBS30-TMA AEM. Similar findings were obtained for SEBS35-TMA.[60] Moreover, IEC determination confirmed the quaternization of CMSEBS and the completion of the reaction. Additional characterization for SEBS30-TMA, SEBS35-TMA, along with benchmark AEMs (Tokuyama A201) were performed (Table 5.1.). The experimental IEC was determined by using Volhard titration. The theoretical IECs calculated (from the relative areas of $^1$H NMR peaks “e”, “b” and “d”) for SEBS30-TMA and SEBS35-TMA were 1.52 mmol/g, and 1.99 mmol/g respectively. Quaternization reaction yields for SEBS30-TMA and SEBS35-TMA were 89% and 97%, respectively.
When the molar ratio of polystyrene in SEBS increases, the polymer backbone (and the AEM membranes resulting from it) becomes more rigid. When the molar ratio of rubber to styrene increases, the polymer backbone becomes more elastic. It is possible to tune the mechanical properties to make them adequate for the application by changing the molar ratio between polystyrene and rubber in the AEM. We concluded from tensile tests that SEBS-based AEMs (SEBS30-TMA and SEBS35-TMA) were very elastic (with elongations at break around 500% of initial length). Due to their rubber-like nature the ultimate tensile strength were relatively low (3-4 MPa) when compared with other AEM materials. However, based on our experience working with these AEMs, we deem them sufficient strong to be assembled and operated for long periods.
of time in electrochemical cells. The elasticity of SEBS-based AEMs facilitates their assembly in electrochemical devices such as flow batteries or fuel cells, where they are compressed and subjected to stresses during long-term operation. The ultimate tensile stress for SEBS35-TMA was higher than that of SEBS30-TMA due to SEBS35-TMA having a larger molar ratio of styrene in the polymer backbone.

**Table 5.1.** Properties of the SEBS-based AEMs synthesized in this work.

<table>
<thead>
<tr>
<th></th>
<th>SEBS30-TMA</th>
<th>SEBS35-TMA</th>
<th>Tokuyama A201</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental IEC (mmol/g)</strong></td>
<td>1.35±0.02</td>
<td>1.93±0.02</td>
<td>1.60±0.09</td>
</tr>
<tr>
<td><strong>Chloride conductivity (@ 70°C, mS/cm)</strong></td>
<td>18±3</td>
<td>34±2</td>
<td>26±3</td>
</tr>
<tr>
<td><strong>Ultimate tensile stress (MPa)</strong></td>
<td>3.1±0.6</td>
<td>3.8±0.2</td>
<td>78±3</td>
</tr>
<tr>
<td><strong>Elongation at break (%)</strong></td>
<td>536±7</td>
<td>499±1</td>
<td>371±14</td>
</tr>
<tr>
<td><strong>Water uptake (%)</strong></td>
<td>52.0</td>
<td>121.5</td>
<td>41</td>
</tr>
<tr>
<td><strong>Swelling ratio (%)</strong></td>
<td>56.9</td>
<td>254.0</td>
<td>47.3</td>
</tr>
<tr>
<td><strong>Perm-selectivity (%)</strong></td>
<td>73</td>
<td>51</td>
<td>80</td>
</tr>
<tr>
<td><strong>Transport numbers (tCl−; tK+)</strong></td>
<td>(0.87:0.13)</td>
<td>(0.76:0.24)</td>
<td>(0.90:0.10)</td>
</tr>
</tbody>
</table>

Notes. Data for Tokuyama A201 (benchmark AEM) were included for comparison purposes. The tensile tests were done at 25 °C and 100% relative humidity. Water uptake and swelling ratio measurement were performed at 30 °C.

Membrane permselectivity and transport numbers were determined by measuring the voltage difference across the membrane in a diffusion cell, where the membrane was placed between two KCl solutions of different concentrations (0.5 M and 0.1 M) [61]. The transport number for Cl− in SEBS30-TMA was 0.87, which was very close to the benchmark AEM used in our study (0.9). In general, we observed that the anion transport numbers (and permselectivity) decreased when the AEM IEC increased (SEBS35-TMA). This was attributed to the presence of more ionic channels that allowed cationic species to permeate through membrane.
A four-probe (in-plane) conductivity cell was used to determine the AEM ionic (chloride form) conductivity (Figure 5.2.). The chloride conductivity of SEBS35-TMA was higher than that of the benchmark AEM at all temperatures. At 70 °C, the chloride ionic conductivity of SEBS35-TMA was 34 mS/cm whereas it was 26 mS/cm for the benchmark AEM. Block copolymers can provide a better pathway to access higher conductivities when compared with aromatic-backbone-based polymers such as poly(phenylene oxide) (PPO) and polysulfone (PSF). This is consequence of the block copolymer’s ability to yield a phase-separated morphology with wide and interconnected ionic channels that favor ion transport [30].

Figure 5.2. Chloride ion conductivity of SEBS-based AEMs and Tokuyama A210.
SEBS-based AEM oxidative stability was evaluated *ex situ* by immersion of the membranes in 1.5 M VO$_2^+$ + 3 M H$_2$SO$_4$ for up to 500 hours (Figure 5.3.). It was found that the IEC decreased from 1.35 mmol/g to 1.2 mmol/g (after 500 hours in the highly oxidizing vanadium (V) solution). The membrane permselectivity also decreased slightly from 0.73 to 0.66 (chloride transport number decreased from 0.87 to 0.83). No significant changes in the ionic conductivity were observed during the 500 hours of the test.

SEBS-based AEMs also showed excellent stability and performance the vanadium/cerium RFB. A RFB operated with 0.5 M V$^{2+}$/V$^{3+}$ anolyte and 0.5 M Ce$^{4+}$/Ce$^{3+}$ catholyte (in 1 M H$_2$SO$_4$) was run continuously with the SEBS30-based AEM separator for 60 charge-discharge cycles. After 60 charge-discharge cycles (350 hours), we disassembled the RFB and characterized the membrane to identify signs of degradation. The IEC and the ionic conductivity of SEBS30-TMA dropped 18% and 20%, respectively. Tensile tests were also performed to assess any mechanical
degradation of the AEM during operation inside the cell. No decrease in the ultimate stress and elongation at break were observed. Thus, we can conclude these SEBS-based AEMs showed good stability in acidic electrochemical devices.

Figure 5.4. shows the changes in the RFB capacity (normalized by the initial capacity) of V-Ce RFBs run with SEBS30-TMA, SEBS35-TMA and Nafion® 212 separators. The RFBs were run continuously for up to 20 cycles by charge/discharge at a current density of 50 mA cm⁻². The RFBs operated with SEBS-based AEMs showed much lower capacity loss during operation –10% capacity fade for SEBS30-TMA was observed after 20 cycles. In contrast, RFBs operated with Nafion® 212 separators yielded a capacity fade of 40% after 20 cycles. AEMs are selective for the passage of anions and largely reject the cations (active species) due to Donnan exclusion. This renders them more suitable for electrode-decoupled RFBs wherein cation transport from one electrode to the other is largely irreversible.

Figure 5.4. Change in capacity during V-Ce RFB charge/discharge cycling. Comparison of RFBs assembled with the SEBS-based AEMs and with Nafion®212.
The initial energy efficiency (Figure 5.5.) for the batteries employing SEBS30-TMA, SEBS35-TMA, and Nafion® 212 were 86%, 80% and 80%, respectively. After 20 charge/discharge cycles, the energy efficiency for SEBS30-TMA, SEBS35-TMA, and Nafion® 212 dropped 12%, 30% and 10%, respectively. Appendix V, Figures A5.6.-A5.8. show the charge/discharge curves for cycles 1 and 20 for the three membrane separators. The decrease in RFB capacity and nominal voltage was more pronounced in Nafion® 212 and SEBS35-TMA than in SEBS30-TMA. Postmortem analysis exposed mechanical failure in SEBS35-TMA after 20 cycles. The efficiency drop arose not only from the membrane degradation, but also from the increase in kinetic losses (loss in activity of the carbon-felt electrodes) as has been reported previously [62]. The coulombic efficiency for SEBS30-TMA and Nafion® 212 (see Appendix V, Figure A5.5.) remained constant (ca. 98%) throughout the test.

Figure 5.5. Energy efficiency for V-Ce RFBs assembled with the SEBS-based AEMs and Nafion®212 as separators. The RFB was charged and discharged at a current density of 50 mA cm$^{-2}$. 
5.4 Conclusion

A series of polystyrene-\textit{block}-poly(ethylene-\textit{ran}-butylene)-\textit{block}-polystyrene (SEBS)-based AEMs were synthesized via chloromethylation of SEBS followed by quaternization with trimethylamine (TMA). Reaction conditions allowed the synthesis of AEMs with large ionic conductivities (chloride ion conductivity of 34 mS/cm at 70ºC) and IECs (\textit{ca.} 2 mmol/g). In comparison, the Tokuyama A201 benchmark had a chloride ion conductivity of 26 mS/cm and an IEC of 1.6 mmol/g.

An electrode-decoupled V-Ce RFB operated with SEBS30-TMA AEM as the separator showed lower capacity fade (10% after 20 cycles) than a similar RFB operated with Nafion® 212 as the separator (40% after 20 cycles). This confirmed that an AEM separator, by virtue of Donnan exclusion, exhibited enhanced selectivity towards anion vs. cation transport, thereby enabling the use of decoupled chemistries at the electrodes.

The oxidative stability of the SEBS-based AEM was evaluated \textit{ex situ} for 500 hours by immersion in V (V) in concentrated acid. There was no change in the ionic conductivity over this timeframe. The membrane permselectivity (0.73 to 0.66) and IEC (1.35 mmol/g to 1.2 mmol/g) exhibited modest declines in this timeframe. \textit{In situ} RFB experiments showed that after 60 charge-discharge cycles, the IEC and the ionic conductivity of SEBS30-TMA dropped by 18% and 20%, respectively. There was no measurable change in mechanical properties. The good chemical and mechanical stability, high ionic conductivities, and high perm-selectivity observed suggest that SEBS-based AEMs are excellent separator candidates for electrode-decoupled RFBs.
5.5 References


Chapter 6: Conclusion and Future work
Directions
This chapter summarizes the major findings of the works presented in this dissertation and provides suggestions on the future research directions.

6.1 Alkaline stability of AEMs (Chapter 2 and 3)

Most commonly used benzyl-trimethylammonium groups fixed onto backbones are prone to nucleophilic attack from OH⁻ ions due to the electro-withdrawing nature of the aromatic backbone. Additionally, the delocalized π-electrons of the aromatic ring could stabilize free radicals formed during fuel cell operation resulting in the degradation of the AEM.

The present dissertation examines the alkaline stability of novel cation group such as imidazolium-based cation and phosphonium-based cation. 1-D NMR spectroscopy was used to probe the AEM structure to unearth any signs of AEM degradation after exposure to alkali. The predominant degradation process was posited the opening of the imidazole ring. It is suggested that substituting all the hydrogen atoms on the imidazolium ring will improve the alkaline stability of imidazolium-based AEMs, provided that an appropriate backbone and cation-grafting strategy (use of spacers) is employed. Ex situ alkaline stability tests showed that PPO-TTMPP (phosphonium-based AEM) had the best stability thanks to steric hindrance effect to protect cation group from nucleophilic attack from OH⁻, losing only 10% of its initial IEC after 30 days in 1 M KOH (60 °C). In contrast, SEBS30-TMA (benzyl-trimethylammonium) lost 28% of the initial IEC after 30 days under same experimental conditions.

The future direction to improve alkaline stability of cation groups in AEMs would be two-fold. First, synthesize AEMs that contains cycloaliphatic functional groups would improve alkaline stability of AEMs. The structure of a piperidinium-based AEM is shown in Figure 6.1. The resistance of the cycloaliphatic quaternary ammonium functional groups against β-elimination and
ring-opening substitution reactions are due to geometric constraints of the ring structure on the transition states. The unfavorable bond length and bond angle will inhibit the degradation reactions especially $\beta$-elimination.

![Chemical structure of piperidinium-based AEM](image)

Figure 6.1. Chemical structure of piperidinium-based AEM

Second, the presence of unsaturated or aromatic groups that withdraw electrons from the cationic functional groups and hence cause it to be prone to nucleophilic attack, rendering the ionomer/membrane unstable. A fundamental change in the type of backbone employed is needed to satisfy the alkaline stability requirements for its use in electrochemical devices. A potential feasible approach is shown in Figure 6.2.
Figure 6.2. Illustration of synthesis scheme of a, crosslinker (N,N’-tetraallylpiperazinium chloride), b, monomer 2 (diallylpyrrolidinium chloride), c, the pathway to make crosslinked pure cycloaliphatic-based AEM (CP1), and d, the pathway to make the crosslinked pure cycloaliphatic-based AEM (CP2).
6.2 pH-gradient-enabled microscale bipolar interface for electrochemical conversion

Electrochemical energy conversion devices usually operate at uniform pH or over a narrow pH range. The uniform pH environment of these devices frequently hampers the facility of one of the half-cell reactions.

The present dissertation shows a pH-gradient-enabled microscale bipolar interface (PMBI) in a direct sodium borohydride fuel cell (DBFC). This PMBI enables decoupled pH at the two electrodes and enhances half-cell reaction kinetics, expands the selection of electrocatalysts (especially non-noble-metal electrocatalysts) that can be used, and broadens the selection of (combinations of) fuels and oxidants that can be employed. The PMBI-based DBFC yielded a current density of 330 mA/cm² at 1.5 V and a peak power density of 630 mW/cm² at 1 V. The high OCV (1.95 V) and high performance at high voltage were attributed to the effective separation of anolyte and catholyte locally at the electrocatalytically active sites.

A future direction can be employing PMBI configuration for other liquid fuel cell system such as direct methanol fuel cell (Figure 6.3.), where the crossover of fuels and oxidants impede the performance of the system. By using PMBI configuration, we can potentially obtain a direct methanol fuel cell with a high current density at >1.2 V.
Figure 6.3. Illustration of a direct methanol fuel cell with a PMBI configuration
Appendix I. Supporting Tables for Chapter 1
Table A1.1. Selected high performance AEMFC configurations and their improvement over time.

<table>
<thead>
<tr>
<th>Year (reference)</th>
<th>$P_{\text{max}}$ (mW cm$^{-2}$)</th>
<th>$E$ at $P_{\text{max}}$ (V)</th>
<th>$T_{\text{Operating}}$ (°C)</th>
<th>Anode composition</th>
<th>Cathode composition</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006 (Varco et al.)[1]</td>
<td>110</td>
<td>0.4</td>
<td>50</td>
<td>0.5 mg cm$^{-2}$ Pt/C on carbon cloth with proprietary PTFE loading + N,N',N'-tetramethylhexane-1,6-diamine) functionalized Poly(vinyl benzyl chloride) hydroxide layer</td>
<td>Same as anode</td>
<td></td>
</tr>
<tr>
<td>2007 (Tamai n et. al.)[2]</td>
<td>125</td>
<td>0.45</td>
<td>50</td>
<td>0.5 mg cm$^{-2}$ Pt/C on carbon cloth with proprietary PTFE loading + 0.75 mg cm$^{-2}$ N,N',N'-tetramethylhexane-1,6-diamine) functionalized Poly(vinyl benzyl chloride) hydroxide layer</td>
<td>0.5 mg cm$^{-2}$ Pt/C on carbon cloth with 0.75 mg cm$^{-2}$ N,N',N'-tetramethylhexane-1,6-diamine) functionalized Poly(vinyl benzyl chloride) binder</td>
<td>Water transport to cathode reactive sites was improved by – (i) making the AEM thinner and (ii) removing PTFE binder from the cathode.</td>
</tr>
<tr>
<td>2010 (Poynton et. al.)[3]</td>
<td>230</td>
<td>0.4</td>
<td>50</td>
<td>0.5 mg cm$^{-2}$ Pt/C on gas diffusion electrode with N,N',N'-tetramethylhexane-1,6-diamine) functionalized Poly(vinyl benzyl chloride) binder</td>
<td>Same as anode</td>
<td></td>
</tr>
<tr>
<td>2013 (Zhao et. al.)[4]</td>
<td>340 (265 @ 50°C)</td>
<td>0.46</td>
<td>60</td>
<td>0.4 mg cm$^{-2}$ Pt/C with 20 wt% Tokuyama AS-4 binder</td>
<td>Same as anode</td>
<td>Lack of a conductive ionomer coat on the electrodes and low swelling contributed comparatively lower performance.</td>
</tr>
<tr>
<td>2015 (Li et. al.)[5]</td>
<td>600</td>
<td>0.4</td>
<td>60</td>
<td>0.4 mg cm$^{-2}$ Pt/C 20 wt% quaternary muonium polysulfone binder</td>
<td>Same as anode</td>
<td>Demonstrated improved carbonation resistance</td>
</tr>
<tr>
<td>2016 (Ponce - Gonzal</td>
<td>650</td>
<td>0.42</td>
<td>60</td>
<td>0.4 mg cm$^{-2}$ PtRu/C with 20 wt% quaternary muonium polysulfone binder</td>
<td>0.4 mg cm$^{-2}$ Pt/C with 20 wt% quaternary</td>
<td>Improved alkali resistance demonstrated</td>
</tr>
<tr>
<td>Year</td>
<td>Authors</td>
<td>Membrane Formulation</td>
<td>Pt/C Catalyst</td>
<td>PtRu/C Catalyst</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>---------</td>
<td>----------------------</td>
<td>---------------</td>
<td>-----------------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>2017</td>
<td>Wang et al. [7]</td>
<td>0.4 mg cm⁻² PtRu/C on gas diffusion electrode with fine ground trimethylamine functionalized Poly(vinyl benzyl chloride) grafted poly(ethylene-co-tetrafluoroethylene) binder</td>
<td>0.4 mg cm⁻² Pt/C on carbon cloth with fine ground trimethylamine functionalized Poly(vinyl benzyl chloride) grafted poly(ethylene-co-tetrafluoroethylene) binder</td>
<td>Improvements largely attributed to optimization of the separator preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2018</td>
<td>Wang et al. [8]</td>
<td>0.4 mg cm⁻² PtRu/C on gas diffusion electrode with fine ground trimethylamine functionalized Poly(vinyl benzyl chloride) grafted poly(ethylene-co-tetrafluoroethylene) binder</td>
<td>0.4 mg cm⁻² Pt/C on carbon cloth with fine ground trimethylamine functionalized Poly(vinyl benzyl chloride) grafted poly(ethylene-co-tetrafluoroethylene) binder</td>
<td>&lt;30μm Membranes developed. LDPE gives improved thermal stability.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2018</td>
<td>Omasta et al. [9]</td>
<td>0.6 mg cm⁻² PtRu/C on gas diffusion electrode with fine ground trimethylamine functionalized Poly(vinyl benzyl chloride) grafted poly(ethylene-co-tetrafluoroethylene) binder</td>
<td>0.4 mg cm⁻² Pt/C on carbon cloth with fine ground trimethylamine functionalized Poly(vinyl benzyl chloride) grafted poly(ethylene-co-tetrafluoroethylene) binder + 5wt% PTFE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2018</td>
<td>Maurya et al. [10]</td>
<td>0.5 mg cm⁻² PtRu/C on gas diffusion electrodes with trimethylamine functionalized Quaternized poly(fluorene)s binder</td>
<td>0.6 mg cm⁻² Pt/C on gas diffusion electrodes with trimethylamine functionalized Quaternized poly(fluorene)s binder</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table A1.2. Summary of representative literature for DBFC performance improvements over time.

<table>
<thead>
<tr>
<th>Anode catalyst</th>
<th>Cathode catalyst</th>
<th>Oxidant</th>
<th>Operating temperature (°C)</th>
<th>Peak power density (mW cm(^{-2}))</th>
<th>OCP (V)</th>
<th>Current density at 1.5V (mA cm(^{-2}))</th>
<th>Year published-Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C (0.5)</td>
<td>Au/C (0.5)</td>
<td>H(_2)O(_2)</td>
<td>60</td>
<td>680</td>
<td>1.95</td>
<td>240</td>
<td>2007 [11]</td>
</tr>
<tr>
<td>Ni:Pt(2 5:1)/C (1)</td>
<td>Pd/C (1)</td>
<td>H(_2)O(_2)</td>
<td>60</td>
<td>665</td>
<td>1.80</td>
<td>350</td>
<td>2010 [12]</td>
</tr>
<tr>
<td>Pt/C (1) + Ni</td>
<td>Pt/C (1)</td>
<td>H(_2)O(_2)</td>
<td>70</td>
<td>110</td>
<td>1.50</td>
<td>NA(^*)</td>
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<tr>
<td>Pd/C (1) +Ni</td>
<td>Pt/C (1)</td>
<td>H(_2)O(_2)</td>
<td>70</td>
<td>290</td>
<td>1.70</td>
<td>50</td>
<td>2018 [14]</td>
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<tr>
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<td>Pt/C (1)</td>
<td>H(_2)O(_2)</td>
<td>70</td>
<td>300</td>
<td>1.80</td>
<td>100</td>
<td>2018 [14]</td>
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<tr>
<td>Pd/C (3) +Ni</td>
<td>Pt/C (3)</td>
<td>H(_2)O(_2)</td>
<td>70</td>
<td>630</td>
<td>1.95</td>
<td>330</td>
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References


Appendix II. Supporting Materials for Chapter 2
NMR characterization

NMR measurements were carried out on a Bruker Avance 360 MHz NMR spectrometer. For the characterization of the AEMs and identification of any degradation products, the following NMR experiments were done: 1) $^1$H NMR (spectra collected at 360 MHz, 48 scans) 2) correlation spectroscopy (COSY). The resolution employed during the acquisition of COSY spectra was 2048x128 and the number of scans ranged from 8 to 16 depending of the quality of the spectrum required. The samples were prepared by dissolving approximately 30-50 mg of polymer in 1 mL of deuterated solvent (dimethylsulfoxide-d6 and dimethylformamide-d7 for anion exchange membranes (AEM), and chloroform-d for brominated polymers and modified imidazolium AEMs). 35 μL of tetramethylsilane (TMS) was added as the internal standard for calibrating the chemical shift (δ=0 ppm for $^1$H). Further details of the methods employed can be found in our previous works [1, 2].
Figure A2.1. $^1$H NMR spectrum of 1-heptyl-2methyl-imidazole (2MI-C7).

The assignment of peaks “1” to “6(6’)” was done with the help of the COSY spectrum (see Fig. A2.2.). The peaks from 1 to 4 correspond to the protons on long alkyl chain. Peaks from 5 to 6(6’) correspond to the protons on the imidazolium ring. The 1H NMR was done in chloroform-d with TMS, which was used as internal standard for calibrating the chemical shift for 1H.
Figure A2.2. COSY spectrum of 1-heptyl-2methyl-imidazole (2MI-C7).

Diagonal peaks correspond to the peaks in the $^1$H-NMR spectrum, while the cross peaks indicate couplings between pairs of protons separated by a C-C bond. The NMR experiment was done in chloroform-d with TMS used as the internal standard for calibrating the chemical shift for $^1$H.
Figure A2.3. $^1$H NMR spectrum of 1-dodecyl-2methyl-imidazole (2MI-C12).

The assignment of peaks “1” to “6(6’)” was done with the help of the COSY spectrum (see Fig. A2.4.). Peaks from 1 to 4 correspond to the protons on long alkyl chain. Peaks from 5 to 6(6’) correspond to the protons on the imidazole ring. The $^1$H NMR was done in chloroform-d with TMS as internal standard for calibrating the chemical shift for $^1$H.
Figure A2.4. COSY spectrum of 1-dodecyl-2methyl-imidazole (2MI-C12). Diagonal peaks correspond to the peaks in the $^1$H-NMR spectrum, while the cross peaks indicate couplings between pairs of protons separated by a C-C bond. The NMR experiment was done in chloroform-d with TMS used as the internal standard for calibrating the chemical shift for $^1$H.
Figure A2.5. $^1$H NMR spectrum of brominated PPO (BrPPO).

The peaks from 1 to 5 correspond to the protons on PPO. The degree of functionalization (DF) is approximately 0.36 mol bromomethyl groups per polymer repeating units. The $^1$H NMR was done in chloroform-d with TMS, which was used as internal standard for calibrating the chemical shift for $^1$H.
Figure A2.6. $^1$H NMR spectrum of 1-methylimidazole-based AEM (P1).

Peaks from 1 to 5 correspond to the protons on the BrPPO polymer backbone. Peaks from 6(6’) to 7 correspond to the protons on the imidazolium ring. Peak 8 corresponds to the proton belonging to the methyl group that connects with the imidazolium ring. The $^1$H NMR was done in dimethyl sulfoxide-d6 with TMS, which was used as internal standard for calibrating the chemical shift for $^1$H.
Figure A2.7. $^1$H NMR spectrum of 1,2-dimethylimidazole-based AEM (P12).

The peaks from 1 to 5 correspond to the protons on the BrPPO polymer backbone. Peaks from 6(6’) to 7 correspond to the protons on the imidazolium ring. Peak 8 corresponds to the proton belonging to the methyl group that connects with the imidazolium ring. The $^1$H NMR was done in dimethylformamide-d7 with TMS which was used as internal standard for calibrating the chemical shift for $^1$H.
The peaks from 1 to 5 correspond to the protons on the BrPPO polymer backbone. The peaks from 6 to 6’ to 7 correspond to the protons on the imidazolium ring. The peaks from 8 to 11 correspond to the protons on the alkyl long chain which connect to the imidazolium ring. The $^1$H NMR was done in dimethylformamide-d7 with TMS, which was used as internal standard for calibrating the chemical shift for $^1$H.
Figure A2.9. $^1$H NMR spectrum of an AEM based on 1-dodecyl-2methyl-imidazole (PC12).

The peaks from 1 to 5 correspond to the protons on the BrPPO polymer backbone. Peaks from 6(6’) to 7 correspond to the protons on the imidazolium ring. Peaks from 8 to 11 correspond to the protons on the alkyl long chain, which connect to the imidazolium ring. The $^1$H NMR was done in dimethylformamide-d7 with TMS added as an internal standard for calibrating the chemical shift for $^1$H.
Figure A2.10. $^1$H NMR spectrum of BrPPO with a six-carbon pendant chain (PPO-KC6Br).

The alkyl chain contained a ketone group in the benzyl position. Peaks from 1 to 4 correspond to the protons on the PPO. Peak 9 corresponds to the proton on the bromomethyl group. Peaks from 5 to 8 correspond to the protons on the carbon spacer chain. The brominated polymer had 0.31 mol of bromine per polymer repeat unit. The NMR experiment was done in chloroform-d with TMS used as the internal standard for calibrating the chemical shift for $^1$H.
Figure A2.11. $^1$H NMR spectrum of brominated polyphenylene oxide with a six-carbon pendant chain after the reduction of the ketone group (PPO-C6Br).

The peaks from 1 to 4 correspond to the protons on PPO backbone. Peaks from 5 to 10 correspond to the protons on the alkyl carbon spacer chain. Peak 10 corresponds to the proton on the bromomethyl group. The polymer shown in the spectrum had 0.31 mol of bromohexyl groups per polymer repeat unit. The NMR experiment was done in chloroform-d with TMS used as the internal standard for calibrating the chemical shift for $^1$H.
Peaks 1 to 4 correspond to the protons on the PPO backbone. Peaks 5 to 10 correspond to the protons on the six-carbon spacer chain. Peaks 6 to 9 and 3 to 4 overlap and could not be resolved. Peaks 11 and 12 correspond to the protons on the imidazolium ring. Peak 13 corresponds to the protons on the methyl group at position N-3 (nitrogen not connected with the polymer backbone). The NMR experiment was done in dimethyl sulfoxide-d6 with TMS used as the internal standard for calibrating the chemical shift for $^1$H.
Peaks 1 to 4 correspond to the protons on the PPO backbone. Peaks 5 to 10 correspond to the protons on the six-carbon spacer chain. Peaks 6 to 9 and 3 to 4 overlap and could not be resolved. Peaks 11 and 12 correspond to the protons on the imidazolium ring. Peak 13 corresponds to the protons on the methyl group at position N-3 (nitrogen not connected with the polymer backbone).

The NMR experiment was done in dimethylformamide-d7 with TMS used as the internal standard for calibrating the chemical shift for $^1$H.
Figure A2.14. $^1$H NMR spectrum of an AEM based on 1-heptyl-2methyl-imidazole, and with a six carbon alkyl chain to separate the cation from the backbone (PXC7).

Peaks 1 to 4 correspond to the protons on the PPO backbone. Peaks 5 to 10 correspond to the protons on the six-carbon spacer chain. Peaks 11 and 12 correspond to the protons on the imidazolium ring. Peaks 13 to 15 correspond to the protons on the alkyl chain attached to the N-3 position. The NMR experiment was done in dimethylformamide-d7 with TMS used as the internal standard for calibrating the chemical shift for $^1$H.
Figure A2.15. $^1$H NMR spectrum of an AEM based on 1-dodecyl-2methyl-imidazole, and with a six carbon alkyl chain to separate the cation from the backbone (PXC12).

Peaks from 1 to 4 correspond to the protons on the PPO backbone. Peaks from 5 to 10 correspond to the protons on the six-carbon spacer. Peaks from 11 to 12 correspond to the protons on the imidazolium ring. Peaks from 13 to 15 correspond to the protons on the alkyl long chain, which connect to the N-3 position. The NMR experiment was done in dimethylformamide-d7 with TMS used as the internal standard for calibrating the chemical shift for $^1$H.
Table A2.1. Ion exchange capacity of imidazolium-based AEMs evaluated in this work.

<table>
<thead>
<tr>
<th>AEMs</th>
<th>Theoretical IEC (From $^1$H NMR) (mmol Cl/g)</th>
<th>Ion exchange capacity (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>1.69</td>
<td>1.66±0.02</td>
</tr>
<tr>
<td>P12</td>
<td>2.15</td>
<td>2.04±0.02</td>
</tr>
<tr>
<td>PC7</td>
<td>1.45</td>
<td>0.78±0.05</td>
</tr>
<tr>
<td>PC12</td>
<td>1.31</td>
<td>0.92±0.01</td>
</tr>
<tr>
<td>PX1</td>
<td>1.58</td>
<td>1.47±0.02</td>
</tr>
<tr>
<td>PX12</td>
<td>2.07</td>
<td>2.00±0.02</td>
</tr>
<tr>
<td>PXC7</td>
<td>1.37</td>
<td>0.78±0.02</td>
</tr>
<tr>
<td>PXC12</td>
<td>1.25</td>
<td>0.90±0.01</td>
</tr>
</tbody>
</table>

References

Appendix III. Supporting Materials for Chapter 3
Peaks a and c correspond to the protons on aliphatic backbone. Peaks b and d correspond to the protons the aromatic ring. The $^1$H NMR experiment was performed in chloroform-d with TMS, which was used as an internal standard for calibrating the chemical shift of $^1$H.
Peaks a and c correspond to the protons on aliphatic backbone. Peaks b and d correspond to the protons the aromatic ring. The new peak e demonstrated that the chloromethylation reaction occurred in the SEBS. The DF value for CMSEBS30 was calculated by using equation:

\[
\frac{\text{Area}(e)}{\text{Area}(b)} \times 0.3
\]

The $^1$H NMR experiment was performed in chloroform-d with TMS, which was used as an internal standard for calibrating the chemical shift of $^1$H.
Peaks a and c correspond to the protons on aliphatic backbone. Peaks b and d correspond to the protons the aromatic ring. The new peak e demonstrated that the chloromethylation reaction occurred in the SEBS. The DF value for CMSEBS35 was calculated by using equation:

$$\frac{\text{Area}(e)}{2} \times 0.35$$

[2]

The $^1$H NMR experiment was performed in chloroform-$d$ with TMS, which was used as an internal standard for calibrating the chemical shift of $^1$H.
Figure A3.4. FT-IR spectra for CMSEBS30 and SEBS30-TMA.
Figure A3.5. $^1$H NMR spectrum of brominated PPO (BrPPO).

The peaks from 1 to 5 correspond to the protons on PPO. The degree of functionalization (DF) is approximately 0.36 mol bromomethyl groups per polymer repeating units. The $^1$H NMR was done in chloroform-d with TMS, which was used as internal standard for calibrating the chemical shift for $^1$H.
Figure A3.6. $^1$H NMR spectrum of PPO-based AEM (PPO-TMA).

Peaks a, b, c, e and f correspond to the protons on the BrPPO polymer backbone. Peak g corresponds to the protons on quaternary ammonium cation. Peak d corresponds to the proton belonging to the methyl group that connects with quaternary ammonium cation. The $^1$H NMR was done in dimethyl sulfoxide-d6 with TMS, which was used as internal standard for calibrating the chemical shift for $^1$H.
The AEM had a DF of approx. 1 mol of quaternary ammonium per polymer repeat unit. The NMR experiment was done in dimethylsulfoxide-d6 with tetramethylsilane (TMS) used as the internal standard for calibrating the chemical shift for $^1$H.
Figure A3.8. $^1$H NMR spectrum of BrPPO with a six-carbon pendant chain (PPO-KC6Br).

The alkyl chain contained a ketone group in the benzyl position. Peaks from 1 to 4 correspond to the protons on the PPO. Peak 9 corresponds to the proton on the bromomethyl group. Peaks from 5 to 8 correspond to the protons on the carbon spacer chain. The brominated polymer had 0.31 mol of bromine per polymer repeat unit. The NMR experiment was done in chloroform-d with TMS used as the internal standard for calibrating the chemical shift for $^1$H.
Figure A3.9. $^1$H NMR spectrum of brominated polyphenylene oxide with a six-carbon pendant chain after the reduction of the ketone group (PPO-C6Br).

The peaks from 1 to 4 correspond to the protons on PPO backbone. Peaks from 5 to 10 correspond to the protons on the alkyl carbon spacer chain. Peak 10 corresponds to the proton on the bromomethyl group. The polymer shown in the spectrum had 0.31 mol of bromohexyl groups per polymer repeat unit. The NMR experiment was done in chloroform-d with TMS used as the internal standard for calibrating the chemical shift for $^1$H.
Figure A3.10. \(^1\)H NMR spectrum of PPO-C6-TMA AEM.

The AEM polymer had a DF of 0.31 mol of quaternary ammonium per polymer repeat unit. The NMR experiment was done in dimethylsulfoxide-d6 with tetramethylsilane (TMS) as the internal standard for calibrating the chemical shift for \(^1\)H.
Figure A3.11. Impedance spectroscopy at 0.8 V for an MEA with SEBS35-TMA as binder and SEBS30-TMA as AEM separator.
Figure A3.12. Impedance spectroscopy at 0.8 V for a MEA with SEBS30-TMA as AEM separator. AEMFC operated with H₂/O₂ at 70 °C and 98% relative humidity.
Figure A3.13. Change of area specific resistance during constant voltage hold test (0.55V for 12 hours) for a MEA prepared with SEBS30-TMA as separator and PPO-TMA as binder.
Figure A3.14. Change of area specific resistance during constant voltage hold test (0.55V for 12 hours) for a MEA prepared with SEBS30-TMA as separator and PPO-C6-TMA as binder.
Appendix IV. Supporting Materials for Chapter 4
Discussion on selection of borohydride oxidation and peroxide reduction electrocatalysts

Electrocatalysts such as Ni, Pt, and Pd have good catalytic activity towards both the electrochemical oxidation and the chemical hydrolysis of NaBH$_4$ [1, 2]. DBFCs with Ni, Pt or Pd at the anode yield high power densities, but have low faradic efficiencies, e.g., 50% for Ni and Pt [3]. Celikkan et al. observed that among all the metal catalysts, Au is the most effective and Ni is the least effective electrocatalyst for the borohydride oxidation reaction (in terms of the number of electrons being transferred, not in terms of power density) [4]. Chatenet et al. found that the electrooxidation of borohydride yields 7-8 electrons on gold and silver disk electrodes, and only 4 electrons on platinum disk electrodes [5]. The relatively higher utilization efficiency of gold and silver electrodes towards the electrooxidation of borohydride is primarily due to their low activity for the hydrolysis of borohydride. However, gold and silver exhibit sluggish kinetics towards the borohydride oxidation reaction (BOR) [6, 7]. A comprehensive understanding of BOR kinetics and catalysis also requires an understanding of passivation mechanisms. Finkelstein et al. [8] showed that BH$_3$OH$^-$ oxidation creates surface poison species on Au and Pt (with Pt being more BOR active than Au) and suggest an in situ cleaning protocol to address the same. Oliveira et al. [9, 10] showed in successive papers that the addition of a Pd monolayer to Pt(111), which is typically the most electroactive Pt crystal plane, enhances its BOR activity. This enhancement was shown to be the likely result of changes in intermediate binding energy resulting in altered reaction mechanisms and the slower hydrogen evolution reaction on Pd. Surface passivation by BH$_{x,ad}$ intermediates and BO$_x$ products was observed, but forced convection as typical in a fuel cell was found to mitigate BO$_x$ passivation while the oxophilicity of Pd permitted the facile removal of BH$_{x,ad}$. Overall, Pd was seen to exhibit sluggish passivation and HER kinetics while offering higher BOR activity compared to even the most active Pt crystal plane, which makes it a near ideal BOR
catalyst. Both Finkelstein et al. [8] and Braesch et al. [11] showed that the different conclusions drawn from typical electroanalytical measurements (cyclic voltammograms, rotating disk electrode studies etc.) compared to fuel cell studies was the result of the temporal dynamics of the poisoning process and the concentration of the borohydride in the electrolyte. Typical electroanalytical techniques operate at time scales that do not allow for significant poisoning to occur and the lower concentrations used in these studies also obscures the contribution of side-reactions. Olu et al. [12] recently proposed a comprehensive microkinetic model for the BOR that accounts for both passivating reactions and BH$_4^-$ concentration effects. The model considers both a “fully-dissociative” pathway involving direct formation of the BH$_{ads}$ intermediate and a “partially-dissociative” pathway where a BH$_3,ads$ intermediate may form either BH$_3$OH$^-$ or BH$_{ads}$. The HER side reaction was considered to occur by the slow Heyrovsky-Volmer mechanism on Au and the fast Tafel mechanism on Pt. Au electrodes were found to exclusively exhibit the “partially-dissociative” pathway, which in combination with facile H$_2$ evolution with even the smallest BOR currents renders Au a poor BOR catalyst. Pt predominantly exhibited the “fully-dissociative” behavior at low BH$_4^-$ concentrations and predominantly exhibited the “partially-dissociative” behavior at high BH$_4^-$ concentrations. Additionally, at high concentrations of BH$_4^-$, Pd was found to retain promising BOR activity in a DBFC anode, while gold is usually the worst BOR electrocatalyst [11]. Thus, the above mechanistic understanding and practical activity measurements in a DBFC convinced us to choose Pd as the catalyst for our system. For practical applications, it is more desirable to have large current and power densities for the BOR. Pd catalyst loaded on nickel foam has been employed at the anode to achieve high DBFC performance (a peak power density of 250 mW/cm$^2$) [13]. It has been pointed out that nickel foam has a positive contribution to achieve high open circuit voltage (OCV) in a DBFC [1]. In our work, based on the
above considerations, Pd/C deposited on Ni foam was selected as the anode catalyst for the BOR. For the reduction of hydrogen peroxide, the use of Pt as the cathode catalyst has yielded good performance (a peak power density of 325 mW/cm²) in a DBFC [14] and hence was chosen as our cathode catalyst.

**Half-cell and overall reactions in a DBFC**

Anode:  $\text{BH}_4^- + 8\text{OH}^- \rightarrow \text{BO}_2^- + 6\text{H}_2\text{O} + 8\text{e}^-$ \quad E_{0,a}^0 = -1.24\text{V vs. SHE} \quad (1)$

Cathode: $\text{4H}_2\text{O}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow 8\text{H}_2\text{O}$ \quad E_{0,c}^0 = 1.77\text{V vs. SHE} \quad (2)$

Overall reaction: $\text{BH}_4^- + 4\text{H}_2\text{O}_2 + 8\text{H}^+ + 8\text{OH}^- \rightarrow \text{BO}_2^- + 14\text{H}_2\text{O}$ \quad E^0 = 3.01\text{V} \quad (3)$

The junction potential correction has been evaluated to be:

$$3\text{M KOH} \mid \mid 1.5\text{M H}_2\text{SO}_4$$ \quad E_j = 0.83\text{V} \quad (4)$

This value was estimated based on the detailed derivation provided by Unlu et. al.[15] and together with equation (3) yields the net cell voltage.

Net cell voltage: \quad $E^0 - E_j = 2.18\ \text{V}$ \quad (5)$

**Derivation of the pH dependent standard electrode potential for the Borohydride electrooxidation reaction (BOR)**

Consider the following reaction occurring at the anode of a DBFC

$\text{BH}_4^- + 8\text{OH}^- \rightarrow \text{BO}_2^- + 6\text{H}_2\text{O} + 8\text{e}^- \quad E^0 = -1.24\ \text{V vs. SHE}$

The reduction potential at any condition can be described by the Nernst equation as follows –

$$E = E^0 - \frac{RT}{nF} \ln \left( \frac{[\text{BH}_4^-][\text{OH}^-]^8}{[\text{BO}_2^-][\text{H}_2\text{O}]^6} \right) \quad (6)$$
At 25°C, assuming an 8e⁻ transfer reaction, the equation may be simplified as –

\[ E = -1.24 - \frac{0.0592}{8} \log[OH^-] \] V vs. SHE (7)

Given that pOH is defined as -\log_{10}[OH⁻] and that pH + pOH = 14, we may simplify the above equation as –

\[ E = -1.24 + 0.0592 \cdot (14 - pH) \] V vs. SHE (8)

Upon converting to the saturated calomel electrode scale, the above equation may be expressed as –

\[ E = (-1.24 + 0.059 \times (14 - pH) - 0.241) \] V vs. SCE (9)

Similarly, the pH dependent standard electrode potential for the hydrogen electrooxidation reaction (HOR) may be expressed as –

\[ E^0 = (-0.059 \times pH - 0.241) \] V vs. SCE (10)

**Calculation of BOR limiting currents**

The BOR limiting current was calculated using the Levich equation, which is:

\[ i_{Levich} = 0.62nFAD_{BH_4^-}^2 \omega^{\frac{1}{2}} \nu^{-\frac{1}{6}}C_{BH_4^-} \] (10)

Where \( F = 96485 \) C mol\(^{-1} \), \( A = 0.19625 \) cm\(^2 \) and \( C_{BH_4^-} = 1.5\)M. The diffusion coefficient \( (D_{BH_4^-}) \) and viscosity \( (\nu) \) values were obtained from the work of Chatenet et al. [16]. The limiting current was calculated for a variety of catalysts and/or poisoning scenarios by varying the number of electrons \( n \) as depicted in Figure A4.11(a). The instability of the electrolyte precludes the experimental determination of the diffusion coefficient and viscosities for a variety of electrolyte compositions. Thus, the variations in these parameters and their impact on the limiting current was examined by performing a sensitivity analysis where the diffusion coefficient and viscosity was
increased and decreased by an order of magnitude. Figures A4.11(b). and (c). depict the impact of this analysis where we find that diffusion coefficient has a much higher impact than the viscosity. Unfortunately, deconvoluting the impact of the flow rate, concentrations, catalytic activity etc. during device operation is non-trivial, as slowing down the flow rate to measure a limiting current will lead to changes in the pH while increasing the overpotential while maintaining the flow rate will lead to other electrochemical side reactions becoming dominant. Thus, while these limiting current values serve as a bound on the values expected in a DBFC, direct comparison between these values and currents measured in a cell are not straightforward.

![Graph](image)

Figure A4.1. *Ex situ* stability test of a DBFC (5 cm² active-area) with an all-CEM configuration.
Figure A4.2. *Ex situ* stability test of a DBFC (5 cm² active-area) with an all-AEM configuration.
Figure A4.3. *Ex situ* stability test of a DBFC (5 cm$^2$ active-area) with a pH-gradient-enabled microscale bipolar interface (PMBI) configuration.

Figure A4.4. Performance of DBFCs (5 cm$^2$ active-area) with a PMBI configuration.
Figure A4.5. Performance of a DBFC with a PMBI configuration in a 25 cm² active-area cell.
Peaks a and c correspond to the protons on aliphatic backbone. Peak b corresponds to the protons on the aromatic ring. The new peak e demonstrated that the chloromethylation reaction occurred in the SEBS. The DF value for CMSEBS55 was calculated by using the following equation:

$$\frac{\text{Area}(e)}{\text{Area}(b) + \frac{\text{Area}(e)}{2}} \times 0.55.$$ 

The $^1$H NMR experiment was performed in chloroform-d with TMS, which was used as an internal standard for calibrating the chemical shift of $^1$H.
The FTIR peak appearing at *ca.* 1344 cm\(^{-1}\) was assigned to the C-N bond stretching, confirming the formation of SEBS55-TMA. Similar results were observed for other SEBS-based AEMs [17, 18].
A very large hydroxide ion conductivity (210 mS/cm) was obtained by SEBS55-TMA at 70 °C. Also, a very large chloride ion conductivity (110 mS/cm) was achieved by SEBS55-TMA at the same temperature. Our previous synthesized AEM material (SEBS30-TMA) [19] had an IEC of 1.35 mmol/g and a hydroxide ion conductivity of 110 mS/cm at 70 °C. SEBS55-TMA had almost twice hydroxide ion conductivity than SEBS30-TMA. The high ion conductivity of SEBS55-TMA was attributed to microphase separation at the molecular level. The phase separated morphology of the tri-block copolymer (SEBS55-TMA) was confirmed by AFM (Figure A4.8A.). The size of ionic domains (dark domain of Figure A4.8A.) was approximately 32~36 nm.

Figure A4.8. A) AFM images (DMT modulus) of SEBS55-TMA; B) Ionic conductivity of SEBS55-TMA.
For the anode (Figure A4.9 (i)), Pd was deposited uniformly onto the surface of nickel foam. The thickness of catalyst layer was 5-6 μm. There are two competing reaction (electro-oxidation and hydrolysis of borohydride ions) that occur when borohydride ions diffuse on the catalyst layer. The hydrolysis of borohydride results in the formation of H₂. The porous structure of nickel foam is helpful to exclude the H₂ bubbles and make the catalyst site selective towards borohydride oxidation. Moreover, the porous structure of nickel foam can facilitate the mass transfer of the solubilized sodium borohydride fuel [20]. The cathode is shown in Figure A4.9 (ii). Pt was deposited onto a hydrophilic microporous carbon layer, which favored enhanced water flux to the cathode.
Figure A4.10. The diffusion cell to calculate the permselectivity and transport number of Nafion®117.

This picture describes the permselectivity test of cations through Nafion®117. The transport number for cation ($t_+$) was calculated to be 98% and the transport number for anion ($t_-$) was calculated to be 2%. The permselectivity was calculated to be 0.96.
Figure A4.11. Levich plots for the BOR (a) at different n values; (b) varying the diffusion coefficient; (c) varying the viscosity.
Table A4.1. Ion exchange capacity and ionic conductivity of SEBS55-TMA.

<table>
<thead>
<tr>
<th>AEI</th>
<th>Theoretical IEC (From $^1$H NMR)</th>
<th>Ion exchange capacity</th>
<th>Hydroxide ion conductivity (@70 °C, mS/cm)</th>
<th>Chloride ion conductivity (@70 °C, mS/cm)</th>
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<tbody>
<tr>
<td>SEBS55-TMA</td>
<td>2.6</td>
<td>2.11±0.05</td>
<td>210±15</td>
<td>110±1.40</td>
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</table>

Note: The error bars represent the standard error with n=3.

Table A4.2. Peak power densities of DBFCs with all-CEM, all-AEM, and PMBI configurations.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Peak power density with flow rate of 0.4 mL min$^{-1}$ cm$^{-2}$ (mW cm$^{-2}$)</th>
<th>Peak power density with flow rate of 4.8 mL min$^{-1}$ cm$^{-2}$ (mW cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All-CEM</td>
<td>55±8</td>
<td>NA</td>
</tr>
<tr>
<td>All-AEM</td>
<td>282±10</td>
<td>NA</td>
</tr>
<tr>
<td>PMBI</td>
<td>300±13</td>
<td>628±20</td>
</tr>
</tbody>
</table>

Note: The error bars represent the standard error with n=3.

References


Appendix V. Supporting Materials for Chapter 5
Figure A5.1. \(^1\)H NMR spectrum of SEBS.

Peaks a and c correspond to the protons on aliphatic backbone. Peaks b and d correspond to the protons the aromatic ring. The \(^1\)H NMR experiment was performed in chloroform-d with TMS, which was used as an internal standard for calibrating the chemical shift of \(^1\)H.
Peaks a and c correspond to the protons on aliphatic backbone. Peaks b and d correspond to the protons the aromatic ring. The new peak e demonstrated that the chloromethylation reaction occurred in the SEBS. The DF value for CMSEBS30 was calculated by using equation:

$$\frac{\text{Area}(e)}{2} \times \frac{\text{Area}(b)+\text{Area}(e)}{5} \times 0.3$$

[1]

The $^1H$ NMR experiment was performed in chloroform-d with TMS, which was used as an internal standard for calibrating the chemical shift of $^1H$. 
Peaks a and c correspond to the protons on aliphatic backbone. Peaks b and d correspond to the protons the aromatic ring. The new peak e demonstrated that the chloromethylation reaction occurred in the SEBS. The DF value for CMSEBS35 was calculated by using equation:

\[
\frac{\text{Area}(e)}{2} \times 0.35 \times \frac{\text{Area}(b)+\text{Area}(e)}{5}
\]

[2]

The $^1$H NMR experiment was performed in chloroform-d with TMS, which was used as an internal standard for calibrating the chemical shift of $^1$H.
Figure A5.4. FT-IR transmittance data for CMSEBS30 and SEBS30-TMA.

Figure A5.5. The RFB efficiency obtained using SEBS30-TMA as separator to run a V-Ce RFB.
Figure A5.6. A V-Ce RFB charge/discharge curves using SEBS30-TMA AEM as the separator.

Figure A5.7. A V-Ce RFB charge/discharge curves using SEBS35-TMA AEM as the separator.
Figure A5.8. A V-Ce RFB charge/discharge curves using Nafion®212 as the separator
Appendix VI. Curriculum Vitae

EDUCATION

Washington University in Saint Louis, Saint Louis, MO, 2016-2019
Ph.D candidate, Energy, Environmental and Chemical Engineering, GPA: 3.85/4.0

Illinois Institute of Technology, Chicago, IL, 2012-2014
Master, Chemical Engineering, GPA: 3.80/4.0

Yantai University (China), Yantai, China, 2008-2012
Bachelor, Polymer Materials and Engineering, GPA: 3.42/4.0

RESEARCH EXPERIENCE

Washington University in Saint Louis/ Advisor: Professor Vijay Ramani, Saint Louis, MO, 08/2014-09/2019
Topic: synthesis and characterization of novel alkaline stable anion exchange polymer membranes for energy storage and conversion devices

- Design reinforced triblock copolymers as separators for redox-decoupled flow batteries
- Develop highly conductive, thin, and stable anion exchange polymer membranes as separators for H₂/O₂ fuel cells
• Optimize highly selective microscale bipolar interface (anion exchange membrane/proton exchange membrane) applicable for direct sodium borohydride/hydrogen peroxide fuel cells

**Illinois Institute of Technology**/Advisor: Assistant Professor Nancy W. Karuri, Chicago, IL, 08/2013-05/2014

Topic: artificial scaffold for wound healing

**Yantai University**/Advisor: Professor Zhirong Xin, Yantai, China, 08/2011-05/2012

Topic: synthesis of Gemini-surfactants

**PUBLICATIONS**

6 first author peer-review articles, 5 co-author peer-review articles and 1 first author book chapter

12. Z. Wang, M. Mandal, G. Huang, P. Kohl, V. Ramani, Tailoring Anion Exchange Ionomers in pH-gradient-enabled Microscale Bipolar Interfaces in Direct Borohydride Fuel Cells, *submitted*

11. Y. Zhao, X. Li, W. Li, Z. Wang, S. Wang, X. Xie, V. Ramani, A High-Performance Membrane Electrode Assembly for PEM Fuel Cell with Poly(arylene ether sulfone) Nanofibers as Effective Membrane Reinforcements, *in revision*


with quaternary ammonium groups via a hexyl spacer, *Journal of The Electrochemical Society*, 2015, 162 (10), F1236-F1242


**PRESENTATION**


2. *Z. Wang*, Bipolar Polymer Electrolyte Interfaces as Separators for High Performance Direct Borohydride Fuel Cells, 233rd *ECS meeting*, 2018


**PATENTS**

1. Triblock Copolymer Based Anion Exchange Membranes (AEMs) As Separators in Electrochemical Devices. US Patent App. 16/052,973, 2019

2. Microscale-Bipolar-Interface-Enabled pH Gradients in Electrochemical Devices. (pending)
GRANTS


SUPERVISED STUDENTS

Graduate student

1. Miao Li – M.S. Degree, *Dec 2016- May 2018*

Undergraduate student

1. Kent Kuchnir *Jan, Jan 2017- Jun 2017*

HONOR

05/2018 Student travel grant for the 233rd Electrochemical Society (ECS) meeting

08/2017 Student committee for new faculty search

09/2011 Scholarship for Merit Students

04/2011 Excellent Student Leader

10/2010 First Award, English Drama Competition
TEACHING EXPERIENCE

Teaching assistant for Washington University in Saint Louis: EECE 403 (Chemical Reaction Engineering); EECE 531 (Environmental Organic Chemistry); EECE 203 (Thermodynamics I).

Teaching assistant for Illinois Institute of Technology: CHE 525 (Chemical Reaction Engineering).

SERVICE

Peer review

Referee for the journals: Journal of Power Sources (n=1);