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Solvent Processable Tetraalkylammonium-Functionalized Polyethylene for Use as an Alkaline Anion Exchange Membrane

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ABSTRACT: We report the synthesis of a solvent processable, tetraalkylammonium-functionalized polyethylene for use as an alkaline anion exchange membrane (AAEM). The membranes are insoluble in both pure water and aqueous methanol (50 vol % water) at 50 °C but exhibit excellent solubility in a variety of other aqueous alcohols (e.g., 5 wt % AAEM in aqueous *n*-propanol, 50 vol % water). These solubility characteristics extend the potential utility of this system for use as both an AAEM and ionomer electrode material from a single polymer composition. The AAEMs generated are mechanically strong and exhibit high hydroxide and carbonate conductivities.

Introduction

Fuel cells are devices that convert the chemical energy stored in a fuel directly into electricity and could potentially serve as a highly efficient and environmentally sustainable power generation technology.[1] Within a fuel cell, the polymer electrolyte membrane serves as the ion conducting medium between the anode and cathode and, as a result, is a central, and often performance-limiting, component of the fuel cell.[2] The most common polymer electrolyte membrane fuel cells operate under acidic conditions and are therefore proton conducting. Nafion, a proton exchange membrane (PEM), has dominated the field due its good processability, chemical and thermal stability, and proton conductivity (when properly hydrated).[3,4] Although PEM fuel cells offer excellent performance, they rely almost exclusively on platinum, a very expensive and scarce noble metal.[5] A major advantage of alkaline fuel cells, relative to acidic fuel cells, is their enhanced reaction kinetics for both oxygen reduction and fuel oxidation, permitting the use of less costly, non-noble-metal catalysts (e.g., Ni).[6] As a result, there is now considerable interest in hydroxide conducting polymer electrolyte membranes, also known as alkaline anion exchange membranes (AAEMs), for fuel cells operating under basic conditions.[7−16]

Recent developments reported by Varcoe and co-workers have shown that radiation grafting of poly(vinylbenzyl chloride) onto mixed fluorocarbon/hydrocarbon membranes, followed by amination, yields mechanically strong AAEMs with promising hydroxide conductivities.[7] Others have reported that polysulfones can act as scaffolds for successive post-polymerization modification reactions again yielding conductive AAEMs.[8−13] Moreover, Hibbs and co-workers have shown that AAEMs based on a poly(phenylene) backbone display impressive conductivities and alkaline stability.[14] We have recently reported the synthesis of a series of cross-linked AAEMs through the ring-opening metathesis polymerization (ROMP) of tetraalkylammonium-functionalized cyclic olefins.[15,16] Because of the exceptional functional group tolerance of Grubbs' second generation catalyst, this synthetic method has eliminated the need for post-polymerization modification, thereby allowing the facile synthesis of highly conductive and mechanically strong AAEMs. However, because of the cross-linked nature of the AAEMs, they are insoluble in all solvents, limiting their utility. As a result, we have also been interested in developing non-cross-linked copolymers that can offer benefits such as solvent processability and chemical tunability. Herein we report on the synthesis of highly conductive and solvent processable tetraalkylammonium-functionalized polyethylene for use as an AAEM.

Results and Discussion

Compound **1** (Scheme 1) was readily synthesized from inexpensive starting materials. The lack of β-hydrogen atoms in **1** prevents Hofmann elimination degradation from occurring in the hydroxide form, increasing the ammonium ion stability.[17] Additionally, trimethylammonium groups have been shown to be reasonably stable, exhibiting negligible degradation under alkaline conditions at elevated temperatures when properly hydrated.[18]

We used ROMP to synthesize copolymers of varying composition by introducing Grubbs' second generation catalyst ([Ru]) to a chloroform/methanol solution of cyclooctene (COE) and **1** at 20 °C in air (Scheme 1). After 1 h, the solvents and trace unreacted COE were removed under vacuum, and the subsequent polymer washed with chloroform to remove unreacted **1** with yields exceeding 90%. The relative ratio of the two monomers (determined by ^{1}H NMR spectroscopy) remains nearly constant throughout the reaction, indicative of a random copolymerization. These copolymers were cast into thin films and the iodide counterion was exchanged for a hydroxide to generate AAEMs, but unfortunately they displayed poor mechanical properties due to considerable swelling in water. Moreover, it has been previously noted that unsaturated polymers synthesized via ROMP may not be stable under ambient conditions for prolonged periods due to oxidative degradation, and this is critical as fuel cell membranes are exposed to harsh oxidizing and reducing conditions during operation.[19,20] Therefore, all the unsaturated copolymer samples were hydrogenated to produce a saturated backbone with the expectation that these concerns over stability

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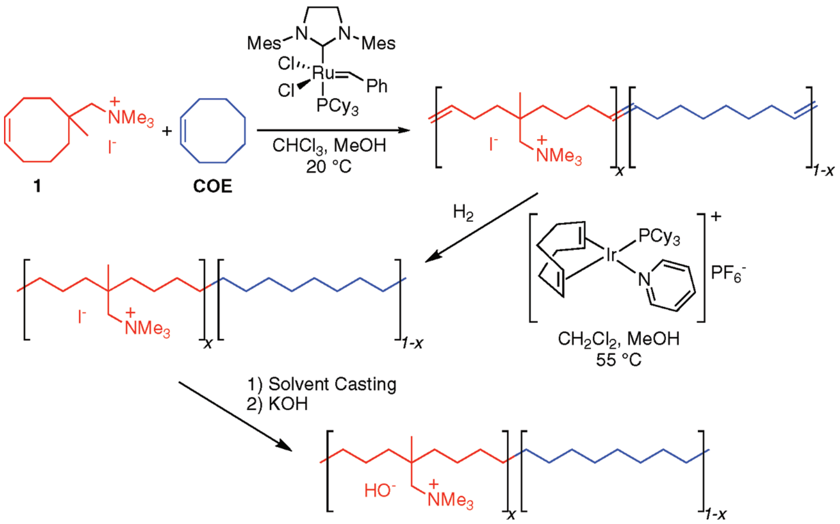
Scheme 1. Procedure for Alkaline Anion Exchange Membrane (AAEM) Synthesis

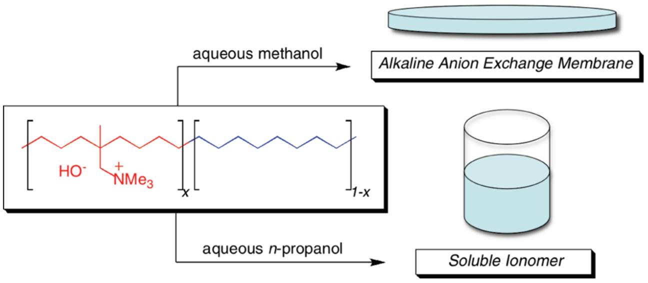


would be eliminated. It should be noted that even though oxidative radical degradation is a concern with hydrocarbon-based PEMs, it has been shown that this degradation pathway may be hindered under the highly alkaline conditions intrinsic to AAEM operation.[6,21] Preparation of the saturated copolymers was accomplished by hydrogenating the polyolefins using Crabtree's catalyst ([COD]Ir(Py)(PCy$_3$)]PF$_6$, Scheme 1) and hydrogen gas. Quantitative conversion was typically complete within 17 h as confirmed by the complete disappearance of olefinic resonances in the ^{1}H NMR spectrum, effectively yielding tetraalkylammonium-functionalized polyethylene. Furthermore, it was expected that this polyethylene backbone would provide the hydrophobic support necessary for the high ion incorporation required to maximize conductivity without the detrimental loss of mechanical stability due to swelling. Supporting this are reports in which PEMs are blended with polyethylene to provide additional mechanical support, decreased membrane swelling, and increased methanol crossover tolerance.[22,23]

The hydrogenated copolymers in the iodide form were dissolved in a chloroform/methanol cosolvent mixture and cast onto a fluoropolymer-lined metal dish preheated to 40 °C from which the volatiles were slowly evaporated. The films were removed from the dish and dried under vacuum to exhaustively remove residual solvent. Analysis of the thin films by transmission electron microscopy (TEM) revealed no microphase separation, possibly suggesting a random distribution of tetraalkylammonium ions (see Figures S1 and S2 in the Supporting Information). Ion exchange was accomplished by soaking the films in 1 M potassium hydroxide, furnishing transparent and nearly colorless AAEMs. Overall, the AAEMs are easily handled, exhibiting excellent flexibility and strength. Typical film thicknesses ranged from 20 to 50 μm; however, membranes as thin as 10 μm were synthesized without any loss of mechanical integrity. Thinner AAEMs are desirable due to their decreased ionic resistance, resulting in increased fuel cell performance.

A significant challenge in alkaline fuel cell research is the development of an alkaline analogue of commercially available solutions of Nafion.[6] It should be noted that although Nafion technically forms dispersions, they are commonly called solutions and will be referred to as such. Nafion is insoluble in water and aqueous methanol but soluble in mixtures of other low boiling point solvents including ethanol and *n*-propanol. This solvent processability allows Nafion to be impregnated into the electrocatalyst layers, producing an ionomer electrode material found in high performing PEM fuel cells.[24] A critical consequence of this solvent processability is that the same polymer can be used as both the polymer electrolyte membrane and ionomer electrode material. Surprisingly, the AAEMs are completely insoluble in both pure water and aqueous methanol at 50 °C (50 vol % water), allowing the use of methanol as a fuel, but exhibit excellent solubility in a variety of other aqueous alcohols (e.g., 5 wt % AAEM in aqueous *n*-propanol, 50 vol % water; see Tables S1 and S2 in the Supporting Information). This solvent processability (Scheme 2) potentially extends the utility of this system for use as both a fuel cell membrane *and* ionomer electrode material from a single polymer, much like Nafion.

Scheme 2. AAEM and Soluble Ionomer from One Polymer



The optimized AAEMs, with respect to mechanical properties and hydroxide ion conductivity, had 29 mol % (AAEM-29) or 33 mol % (AAEM-33) **1**. Attempts to synthesize AAEMs with a higher mol % **1** led to materials with excessive swelling, while increasing the mol % COE led to decreased hydroxide conductivity. Detailed characterization data for both optimized AAEM compositions are provided in Table 1. The ion exchange capacities (IECs) for AAEM-29 and AAEM-33 are 1.29 and 1.50 mmol OH$^-$/g, respectively. These IECs are within the range of previously reported AAEMs and both commercial and noncommercial ionomer electrode materials.

It has been shown that sufficient water uptake of AAEMs is needed to form interconnected hydrated domains, thereby maximizing ion conductivity; however, excessive water uptake may also result in a detrimental loss of mechanical integrity and decreased ion conductivity.[8,10] The gravimetric water uptake (WU) values of the optimized AAEMs were measured and, as expected, increasing the ionic content of the AAEMs led to an increase in WU with AAEM-29 and AAEM-33 exhibiting WUs of 97% and 132%, respectively. While the WU of these materials were higher than most other examples of AAEMs, the hydroxide conductivity was maintained at a reasonable level.

Table 1. AAEM Characterization Data

measurement	AAEM-29	AAEM-33
mol % **1**[a]	29	33
IEC (mmol OH^-/g I^-)[b]	1.29 ± 0.08	1.50 ± 0.07
% water uptake[c]	97 ± 10	132 ± 10
tensile strength at break (MPa)[d]	9 ± 2	6 ± 1
% strain at break[d]	170 ± 40	130 ± 40
OH^- σ_{20} (mS/cm)[e]	40 ± 2	48 ± 3
OH^- σ_{50} (mS/cm)[e]	59 ± 2	65 ± 3
CO_3^{2-} σ_{20} (mS/cm)[f]	12 ± 1	13 ± 1
CO_3^{2-} σ_{50} (mS/cm)[f]	29 ± 3	30 ± 2

[a] Determined by ^1H NMR spectroscopy. [b] Ion exchange capacity determined by back-titration, average of three trials. [c] Gravimetric water uptakes of the fully hydrated membranes, average of five trials. [d] Mechanical testing of the films in the iodide form, average of six trials. [e] Hydroxide conductivities of the AAEMs fully immersed in degassed water at 20 and 50 °C, average of four trials. [f] Carbonate conductivities of the AAEMs fully immersed in degassed water at 20 and 50 °C, average of three trials.

Tensile stress−strain measurements were performed in order to evaluate the mechanical properties of both samples. AAEM-29 had a tensile strength at break of 9 MPa at a strain of 170%, while the AAEM-33 sample showed a tensile strength at break of 6 MPa at a strain of 130%. Although Varcoe and co-workers report materials that display greater tensile strength at break (13−18 MPa), they also exhibit considerably less strain at break (45−70%).[7] Similarly, we have reported two classes of cross-linked materials that demonstrate greater tensile strength at break but also show less strain at break.[15,16] Nonetheless, the present system certainly exhibits the mechanical strength required to function as a fuel cell membrane and underscores the ability of polyethylene to act as a robust polymer backbone for ion-conducting membranes.

The in-plane hydroxide conductivity for each film composition was measured at 20 and 50 °C. AAEM-29 exhibits conductivities of 40 mS/cm at 20 °C and 59 mS/cm at 50 °C. More notably, AAEM-33 conducts at 48 mS/cm at 20 °C and 65 mS/cm at 50 °C. By comparison, Varcoe and co-workers reported conductivities of 27 mS/cm at 20 °C and 34 mS/cm at 50 °C for their fluorinated system.[7] Cornelius and co-workers observe conductivities of 35 mS/cm at 30 °C for their polysulfone-based AAEMs[8] while Hibbs and co-workers report 50 mS/cm for their poly(phenylene)-based AAEMs.[14] Moreover, we have reported a polycyclooctene-based cross-linked AAEM that has outstanding conductivities of 69 mS/cm at 20 °C and 111 mS/cm at 50 °C.[16] However, all of the above referenced AAEMs are insoluble, potentially limiting their utility strictly for use as membranes.

In order to investigate the effect of carbonation on membrane conductivity, AAEM-29 and AAEM-33 in their iodide form were converted to the carbonate form by immersing them in 1 M potassium carbonate. The in-plane carbonate conductivity for each film composition was measured at 20 and 50 °C. AAEM-29 exhibits carbonate conductivities of 12 mS/cm at 20 °C and 29 mS/cm at 50 °C while AAEM-33 conducts at 13 mS/cm at 20 °C and 30 mS/cm at 50 °C. By comparison, Varcoe and co-workers reported carbonate conductivities of 11 mS/cm at 20 °C and 22 mS/cm at 50 °C.[7] Although these results indicate decreased ionic conductivity of the AAEMs after carbonation, other studies suggest this may not severely impact fuel cell performance as hydroxide anions are continuously regenerated by oxygen reduction at the cathode.[25]

As previously mentioned, a significant challenge in alkaline fuel cell research has been the development of an AAEM that is insoluble in water and aqueous methanol but soluble in mixtures of other low boiling point solvents such as *n*-propanol (removal of a high boiling point solvent is considered difficult and unsafe in the presence of finely dispersed catalysts).[6] Zhang and co-workers have recently reported a highly conductive partially fluorinated polysulfone (84 mS/cm at 20 °C) that is soluble in *n*-propanol; however, there is no mention of its solubility in methanol.[11] Furthermore, the membrane became gel-like when placed in water at 60 °C. Yan and co-workers synthesized a soluble quaternary phosphonium-functionalized polysulfone for use as an alkaline ionomer electrode material that is considerably more conductive (27 mS/cm at 20 °C) than commercially available analogues (e.g., Tokuyama Co. product code: AS-4, exhibits a conductivity of 13 mS/cm),[26] but unfortunately, these materials are soluble in pure and aqueous methanol (50 vol % water) likely precluding the use of methanol as a fuel.[27] By comparison, the current system displays excellent conductivities, is soluble in aqueous *n*-propanol (50 vol % water), and is insoluble in aqueous methanol (50 vol % water).

Conclusion

In summary, we have developed a tetraalkylammonium-functionalized polyethylene that exhibits excellent mechanical strength and high hydroxide conductivity, in addition to being solvent processable. This solvent processability extends the potential utility of this system for use as both an AAEM and ionomer electrode material from a single polymer composition. Future work will focus on studying the chemical stability and performance of these materials under fuel cell operating conditions as well as synthesizing and investigating the use of novel cations.

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Supporting Information Available: Experimental procedures and characterization of synthetic intermediates of **1** and subsequent polymers; photograph of film synthesis assembly and TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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