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Effect of hydration on the mechanical properties and ion conduction in a polyethylene-b-poly(vinylbenzyl trimethylammonium) anion exchange membrane

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ABSTRACT

Anion exchange membranes (AEM) are promising solid polymer electrolytes utilized in alkali fuel cells and electrochemical energy conversion devices. AEMs must efficiently conduct ions while maintaining chemical and mechanical stability under a range of operating conditions. The ionic nature of AEMs leads to stiff and brittle membranes under dry conditions while at higher hydrations, water sorption causes significant softening and weakening of the membrane. In this work, a new polyethylene-b-poly(vinylbenzyl trimethylammonium) polymer (70 kg/mol) was cast into large (300 cm^2), thin (12 ± 3 μm) membranes. These membranes exhibited improved elasticity over previously tested AEMs, minimal dimensional swelling, and moderate ionic conductivity (5 ± 2 mS/cm at 50 °C, 95% RH in the bromide form). Extensional testing indicated a 95% reduction in Young's modulus between dry and hydrated states. Further investigation of the complex modulus as a function of hydration, by dynamic mechanical analysis, revealed a sharp decrease in modulus between dry and hydrated states. Mechanical softening was reversible, but the location of the transition displayed hysteresis between humidification and dehumidification. Conductivity increased after membrane softening; suggesting bulk mechanical properties can identify the hydration level required for improved ion transport. Understanding the relationship between ion conduction and mechanical properties will help guide AEM development and identify operating conditions for sustained performance.

1. Introduction

Anion exchange membranes (AEM) can be utilized as solid polymer electrolytes for alkali fuel cells and other electrochemical energy conversion devices such as elctrolyzers and redox flow batteries [1–3]. Compared to proton exchange membrane (PEM) fuel cells alkali AEM energy conversion devices benefit from facile kinetics and opportunities for non-precious metal catalysts [4–6]. As a relatively recent field of study, AEMs for energy conversion face a number of developmental challenges before commercial application can be realized. These challenges include chemical stability of the cationic group and polymer backbone, the possibility of lower ion transport compared to PEMs, and mechanical strength and durability of the membrane. The alkali environment of an AEM exposes the membrane to hydroxide ions that can attack the ionic group tethered to the polymer or the polymer backbone itself [3]. A significant amount of ongoing research is directed towards identifying alkali stable polymer chemistries and novel cation functionalities for chemically robust AEMs [7–10]. Transport of hydroxide, or other anions, in an AEM is inherently slower than protons in PEMs, and to compensate for this factor, ionic concentration is often increased in AEMs [1]. While increasing ion concentration in AEMs can improve ion conduction, a high ion concentration also increases water sorption in the membrane that can negatively impact mechanical integrity and durability [2]. Additionally, dimensional swelling resulting from water uptake can deform the membrane or cause delamination from catalyst layers. Repeated swelling cycles generate stresses inside the membrane that can create pinholes and cracks in the membrane [11]. A successful AEM must efficiently conduct anions and be chemically and mechanically stable over the lifetime of the device, however the complex interplay between these properties

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requires new AEM development to simultaneously consider ion conduction, stability, water sorption, and mechanical properties.

AEMs require a polymer chemistry of dual functionality, often achieved using copolymers, where one section of the polymer is ionic and hydrophilic to promote ion conduction while the other is hydrophobic to maintain the solid integrity of the membrane. Block copolymers are of particular interest due to their ability to phase separate into organized morphologies that generate well-defined ion conduction paths. Polystyrene based diblocks have been synthesized previously that organized into various morphologies including spheres, cylinders, and lamellae depending on the ratio of the polymer blocks [12]. While polystyrene based diblocks have showed good ionic conductivity and ordered morphologies [12,13], the high T_g polystyrene in an cationic membrane results in stiff, brittle films that do not have adequate mechanical durability for use in electrochemical devices. Replacing the hydrophobic block with a rubbery polymer, such as poly(methyl butylene), produced films with better elasticity and flexibility [14]. Similarly, polyethylene has been incorporated in AEMs. Ring-opening metathesis polymerization of ammonium functionalized cyclic olefins produced crosslinked and non-crosslinked polyethylene copolymer AEMs with good conductivity and mechanical durability [15,16]. Polyethylene based AEMs with flexible ammonium groups in a crosslinked matrix synthesized by metallocene-mediated copolymerization displayed adequate swelling and exceptional conductivity, 75–120 mS/cm [17]. Grafting vinylbenzyl chloride units on to polyethylene resin or free-standing films has generated AEMs with decent conductivity and chemical stability [18,19]. While copolymer and grafted polyethylene AEMs show promising performance, the cationic functionalities are of a random nature, and do not benefit from the well-defined morphologies produced in block copolymer systems. This work investigates a polyethylene-based diblock AEM that will combine organized polymer morphology and good mechanical properties.

Fuel cells operate in a dynamic environment in terms of temperature and humidity resulting in a range of hydration levels in AEMs. At high humidities, water is taken up by the polymer causing dimensional swelling of membranes [20,21]. Under dryer conditions, the membrane loses water causing film contraction and significant hygrothermal stresses in the polymer [21,22]. With repeated humidity cycling, these hygrothermal stresses can generate pinhole and cracks in the membrane that contribute to catastrophic failure [21,23,24]. AEMs must have adequate elasticity and elongation at dry conditions to accommodate for dimensional swelling without damaging the membrane or causing plastic deformation [20]. Limiting the dimensional swelling of an AEM will improve mechanical durability [20], but the ionic nature of the polymer and the fact that water is required to facilitate ion conduction makes swelling inevitable. Functionalization of a polymer with cations reduces elasticity and elongation [13], making it difficult to produce AEMs that maintain adequate mechanical durability. Additionally, water sorption in AEMs can severely soften and weaken AEMs when they are hydrated [25]. Producing AEMs that have sufficient elasticity and elongation at dry conditions and maintain adequate strength at hydrated conditions is a continued challenge. Characterization of mechanical properties over the complete range of operating temperatures and hydration levels is critical to the development of robust AEMs.

A polyethylene-b-poly(vinylbenzyl trimethylammonium) was synthesized by anionic polymerization and previously characterized in terms of basic morphology, conductivity, and mechanical properties as a function of block ratio [26]. This AEM polymer can be solution cast to produce large, thin films. In this study, a single block ratio was evaluated to determine mechanical properties as function of humidity and correlated to water content and ion conduction.

2. Experimental

The polyethylene-b-poly(vinylbenzyl bromide) (PE-b-PVBBr) polymer was synthesized as previously described [26]. Large area, ~300 cm^2, thin films, 10–15 µm were fabricated and characterized with respect to ionic conductivity, water uptake, swelling, and mechanical properties.

2.1. Membrane fabrication

For membrane casting the polymer was dissolved in xylene at a 10 wt% concentration, the solution was mixed at 90 °C for 2 h. An automatic film applicator (MTI Corporation's MSK-AFA-III, Richmond, CA) with a micrometer adjustable blade was used to draw the polymer solution at a consistent speed and thickness. A temperature-controlled hotplate was placed over the existing vacuum chuck of the film applicator. A glass plate was positioned on the hotplate and heated to 80 °C. The micrometer adjustable blade was kept in an oven at 80 °C until immediately prior to casting. The blade was removed from the oven, placed on the glass substrate, the hot polymer solution was poured in front of the blade, and the solution was drawn to a thin wet film. The blade was set to a gap height of 200 µm and drawn at a speed of 50 mm/s. After casting, the hotplate was kept at 80 °C for 30 min, after which the temperature control was turned off and the substrate allowed to cool. The film was allowed to dry overnight at room temperature in the fume hood. The next day, the polymer film was removed from the glass substrate. The film was further dried overnight in a vacuum oven at 80 °C to remove residual solvent. Vinylbenzyl trimethylammonium cation functionalities were generated by soaking the film in 25 wt% trimethylamine solution at room temperature for 2 days. After functionalization the film was washed repeatedly to remove excess trimethylamine and dried overnight in a vacuum oven at 40 °C. Films were characterized in the bromide counter ion form to avoid conversion of hydroxide ions to a mixture of carbonates and hydroxide ions.

2.2. Ion exchange capacity

Ion exchange capacity (IEC), number of cations per mass of polymer, of the membranes was measured by Mohr titration. Films were converted to the chloride form by soaking in 1 M NaCl for at least 48 h, followed by rigorous washing in distilled water to remove excess salt and drying in a vacuum oven. The chloride form films were soaked in 100 mL of 1 M $NaNO_3$ for 48 h. Aliquots of the $NaNO_3$ solution were titrated using a $AgNO_3$ solution with a K_2CrO_4 indicator. The end of the titration was defined by the presence of permanent rust colored precipitates in solution.

2.3. Ionic conductivity

In-plane ionic conductivity was measured by electrochemical impedance spectroscopy using a multichannel potentiostat (Bio-Logic VMP3) and a TestEquity environmental chamber. Impedance spectra were obtained over a frequency range of 1–10^6 Hz. Membrane resistance was determined by the low frequency intercept of Nyquist plot and membrane conductivity was calculated based on equation (1)

$$\sigma = \frac{l}{R \cdot t \cdot w} \quad (1)$$

Where R is the membrane resistance, l is the distance between electrodes, and t and w are the thickness and width of the membrane sample. Conductivity was measured as a function of temperature between 50 and 90 °C, at 95% relative humidity, to determine the activation energy for ion conduction. Conductivity