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Water permeation through anion exchange membranes

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HIGHLIGHTS

- Liquid and vapor water transport through anion exchange membranes.
- Interfacial and bulk water transport resistances were decoupled.
- The vapor/membrane interface is rate determining.
- HMT-PMBI is more permeable than Fumapem[®] FAA-3 and comparable to Nafion[®].

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ABSTRACT

An understanding of water permeation through solid polymer electrolyte (SPE) membranes is crucial to offset the unbalanced water activity within SPE fuel cells. We examine water permeation through an emerging class of anion exchange membranes, hexamethyl-*p*-terphenyl poly (dimethylbenzimidazolium) (HMT-PMBI), and compare it against series of membrane thickness for a commercial anion exchange membrane (AEM), Fumapem[®] FAA-3, and a series of proton exchange membranes, Nafion[®]. The HMT-PMBI membrane is found to possess higher water permeabilities than Fumapem[®] FAA-3 and comparable permeability than Nafion (H⁺).

By measuring water permeation through membranes of different thicknesses, we are able to decouple, for the first time, internal and interfacial water permeation resistances through *anion exchange membranes*. Permeation resistances on liquid/membrane interface is found to be negligible compared to that for vapor/membrane for both series of AEMs. Correspondingly, the resistance of liquid water permeation is found to be one order of magnitude smaller compared to that of vapor water permeation.

HMT-PMBI possesses larger effective internal water permeation coefficient than both Fumapem[®] FAA-3 and Nafion[®] membranes (60 and 18% larger, respectively). In contrast, the effective interfacial permeation coefficient of HMT-PMBI is found to be similar to Fumapem[®] ($\pm 5\%$) but smaller than Nafion[®](H⁺) (by 14%).

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1. Introduction

Anion exchange membranes (AEMs) are integral to several future energy storage and conversion devices [1]. For example, anion exchange membrane fuel cells (AEMFCs) offer the advantage over proton exchange membrane fuel cells in that they may be easier to utilize due to their relatively lower operating temperature [2]; they may utilize non-noble metal catalysts [3a, b]; and afford greater fuel flexibility [3b]. However, a significant challenge in AEMFC technology lies in the AEM, which must exhibit chemical stability to highly basic conditions, possess high ion conductivity in order to minimize Ohmic losses [2], and demonstrate adequate

water transport in order to offset critical issues of water management. Of these parameters, AEM stability and ion conductivity receive the most attention, with water transport receiving relatively little, even though it is widely accepted that the operation of fuel cells requires water management [5,6a,7]. In order to achieve optimal water management in the cell, a highly water-permeable membrane is required to facilitate the anode water removal towards the cathode in AEMFCs [4].

Ex-situ measurements of water permeation through membranes are typically employed to mimic the transport of water through membranes in an operating fuel cell [5], because the in-situ measurement of water permeation through membranes is complicated by the addition of electro-osmotic drag of water from cathode to anode [5]. These ex-situ measurements often use a permeation cell wherein a membrane is exposed to a differential

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activity of water or pressure gradient [5a-c,6]. The techniques are usually based on exposing a membrane to liquid water on both sides and using hydraulic pressure to drive water across the membrane (i.e., liquid-liquid water permeation -LLP), or exposing one side of the membrane to water vapour and the other to liquid water (i.e., liquid-vapour-LVP), or exposing both sides of the membrane to different activities of water vapour (vapour-vapour water permeation -VVP). Among these three permeation techniques, liquid-vapour water permeation (LVP) more accurately reflects the internal water transport conditions occurring in an operating fuel cell, whereas vapour-vapour water permeation (VVP) measurements reflect permeation conditions under zero or very low current operation. Liquid-liquid water permeation (LLP) measurements reflect permeation conditions for fuel cells operating with liquid fuels [6b].

Of particular interest to our group are the polybenzimidazolium anion exchange membranes (AEMs), which possess heterocyclic rings to delocalize positive charges [7]. A sterically, C2-protected poly(benzimidazolium) AEM, HMT-PMBI (Fig. 1), was chosen for this work due to its exceptional *in-situ* and *ex-situ* properties, its ease of synthetic scale-up, and its readily controllable ion-exchange capacity (IEC) [8]. HMT-PMBI is prepared by methylation of poly[2,2'-(2,2'',4,4'',6,6''-hexamethyl-*p*-terphenyl-3,3''-diyl)-5,5'-bibenzimidazole] (HMT-PBI). Through control of the degree of methylation (dm), between two and four methyl groups per repeat unit (50%–100% dm), the resulting IEC may be precisely controlled between zero and 2.33 mmol g⁻¹(I⁻ form) [9].

The goal of this work was to investigate *ex-situ* water permeation through HMT-PMBI membranes. This is the first study on water permeation through benzimidazolium-containing AEMs, and the first report of interfacial and internal water permeation resistances of AEMs in which these two permeation resistances are decoupled from the overall water permeation resistance. Liquid-liquid water permeation (LLP) experiments were performed on HMT-PMBI AEMs exchanged with various counter ions at 25 °C in order to obtain insight into water transport through fully-hydrated membranes. It should be noted that, although, the OH⁻ form of the AEMs are most pertinent to AEMFC operation, the CO₃²⁻ form of HMT-PMBI was chosen in-depth investigation of liquid-vapour water permeation (LVP) due to the rapid conversion of the OH⁻ form to mixed carbonates upon expose to CO₂ [10,11b]. LVP measurements were performed at 70 °C under low relative humidity (RH) on the vapour side, in order to mimic fuel cell operating conditions. Thickness dependences on rates of liquid-liquid permeation (LLP) and liquid-vapor permeation (LVP) through HMT-PMBI enabled the internal and interfacial water transport resistances to be deconvoluted from the total water transport resistance. Water transport through two series of commercial solid polymer electrolyte membranes: anion exchange membrane - Fumapem[®] FAA-3, and proton exchange membrane - Nafion[®], were also investigated for comparative purposes.

2. Experimental

2.1. Materials

K₂CO₃ and KCl were purchased from ACP chemicals. KI was

purchased from Caledon Laboratory Chemicals. K₂SO₄, KBr, and dimethylsulfoxide (DMSO) were purchased from BDH chemicals. KOH was purchased from Macron fine chemicals, KHCO₃ was purchased from Fisher Science Education. Decane was purchased from Fisher Scientific. All these chemicals were reagent grade and used as-received. Milli-pore water (18 MΩ) was used from Millipore Gradient Milli-Q.

Commercial Nafion[®] membranes, possessing an equivalent weight (EW) of 1100 g mol⁻¹ (IEC 0.91 mmol g⁻¹) and dry thicknesses of 25 (NR211), 54 (NRE212), 131 (NF115) and 181 μm (N117), were used as-received (Sigma-Aldrich). Fumapem[®] FAA3 membranes (abbreviated as Fumapem[®]) were supplied by Fumapem[®]-Tech and possessed dry thicknesses of 19, 24, 31, 40 and 50 μm. The synthesis of HMT-PMBI was reported previously [9]. HMT-PMBI membranes are reported with the respective degree of methylation rather than IEC as the IEC is dependent on the nature of the anion.

2.2. Membrane preparation

Membrane casting. HMT-PMBI membranes with 89.3% degree of methylation (dm) were prepared using the following method. HMT-PMBI (I⁻) was dissolved in DMSO by stirring and gently heating for 12 h to obtain solutions of 7 or 10 wt% polymer, respectively. After vacuum filtering through a glass fiber filter, the solution was cast on a levelled glass plate using a K202 Control Coater casting table and an adjustable doctor blade (RK Print Coat Instruments Ltd). The polymer film was dried in an oven at 85 °C for at least 12 h, peeled off the glass plate upon immersion in Milli-pore water, soaked in Milli-pore water for 24 h, and dried under vacuum at 80 °C for 24 h. The obtained HMT-PMBI membranes (I⁻, 89.3% degree of methylation) possessed dry thicknesses of 12, 23, 30, and 70 μm.

Ion exchange process. As-received Fumapem[®] FAA3 membranes (Br⁻ form) were submerged in 1 M K₂CO₃ and KCl solution to convert the membrane to the CO₃²⁻ and Cl⁻ form (exchanged twice). HMT-PMBI membranes were ion-exchanged according to our previously reported procedure [11a]. HMT-PMBI membranes (I⁻, 89.3% dm) were twice soaked in 1 M KOH, KHCO₃, K₂CO₃, K₂SO₄, KBr, or KCl aqueous solutions for at least 2 days each to obtain the OH⁻, HCO₃⁻, CO₃²⁻, SO₄²⁻, Br⁻, or Cl⁻ form of the membranes followed with washing with Milli-pore water (note: OH⁻ form were operated under Ar purged conditions, and this procedure may not remove all the CO₂) to remove residual ions. Membranes were stored in Milli-pore water prior to use.

2.3. Ion exchange capacity (IEC)

The IEC of Fumapem[®] FAA3 membranes was determined using the titration method on the membrane in its Cl⁻ form. The IECs of other anionic forms were calculated based on the IEC of the Cl⁻ form, noting the different atomic/molecular masses of the anions incorporated. Three pieces of as-received membranes (Br⁻ form, ~0.1 g) were soaked in 1 M KCl solution for 48 h to obtain the Cl⁻ form, soaked in Milli-pore water and washed with Milli-pore water to remove residual ions. The membranes (Cl⁻ form) were submerged in 0.5 M NaNO₃ for 48 h, fresh NaNO₃ solution was used

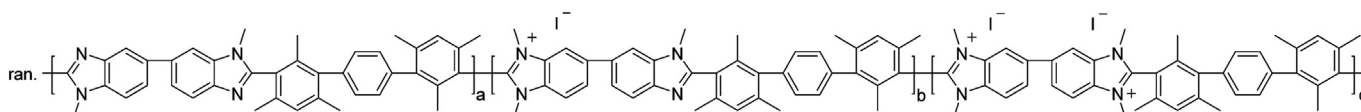


Fig. 1. Molecular structure of 50–100% dm HMT-PMBI (I⁻ form), where dm represents the degree of methylation.

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