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Effect of free radical-induced degradation on water permeation through PFSA ionomer membranes

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ARTICLE INFO

Article history:

Received 29 April 2015

Accepted 23 July 2015

Available online 29 August 2015

Keywords:

Chemical degradation

Water transport

Water permeability

Nafion® membranes

ABSTRACT

The effects of chemical degradation, induced by Fenton's reagent reaction, upon water transport properties of Nafion® NR211 membranes are reported. Exposure to free radicals generated using Fenton's reagent causes morphological and structural changes to the membrane that exert a strong effect on transport properties. Liquid–liquid permeation (LLP), liquid–vapour permeation (LVP) and vapour–vapour permeation (VVP) measurements indicate that water permeability increases for degraded membranes as a result of enhanced water sorption (under both partially and fully hydrated conditions). Similarly, a higher water content is responsible for an increase in proton mobility; despite the observation that IEC and proton conductivity decrease.

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Introduction

Water transport through polymer membranes is crucial to the operation of proton exchange membrane fuel cells (PEMFCs) [1,2]. In addition to other critical functions, the membrane (typically a perfluorosulfonic acid ionomer such as Nafion®) acts as a water transport medium to maintain hydration levels across the cell [3,4]. If the hydration level across the membrane or ionomer in the catalyst layer is too low, poor proton conduction results [5]. If the hydration level is too high, excess water may flood pores in the catalyst layer and reduce the effectiveness of electrocatalytic sites [6]. Water transport data for membranes is thus critical to understanding fuel cell operation.

In-situ water transport measurements of an operating fuel cell membrane is tedious and technically challenging, complicated by the fact that in addition to the existence of electro-osmotic drag, there is a build up of water at the

cathode, back-transport of water from cathode to anode, and water ingresses and egresses the system through humidified gases [7]. In *ex-situ* water transport measurements, water permeation can be decoupled from other factors. *Ex-situ* measurements vary and have involved relatively simple measurements of rate of transport of water through a membrane, to more sophisticated techniques employing nuclear magnetic resonance spectroscopy (NMR) [8–14]. The dynamics of water transport in membranes can also be investigated using time-dependent gravimetric measurements such as dynamic vapour sorption analysis [15–17]. Steady-state water permeation in the membrane can be investigated using a permeation cell wherein a membrane is exposed to a chemical-potential gradient induced by a water-activity or pressure gradient [3,10,12,16–20]. Our previous study, using this technique, examined the impact of membrane thickness on water permeation through Nafion membranes and found that water permeation rates, do not increase linearly with decreasing thickness [20]. Other groups have also shown that

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<http://dx.doi.org/10.1016/j.ijhydene.2015.07.118>

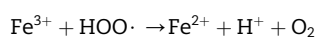
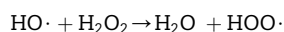
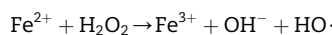
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hydraulic permeation increases with decreasing membrane thickness [22], decreasing equivalent weight (EW) [22] and increasing temperature [16,20,22].

To date, *ex-situ* water transport measurements have been exclusively reported for pristine membranes but it is well documented that membranes degrade during fuel cell operation [21,22]. It is reasonable to assume that water transport properties will change upon membrane degradation, and since the performance of a PEMFCs largely depends on the stability of this core component, performance will also be affected [23,24]. Despite the growing body of reported literature that addresses molecular processes of membrane degradation, reports on the effect of membrane degradation on water transport are lacking.

Regarding membrane degradation, it is generally accepted that chemical degradation proceeds mechanical degradation [25], and that chemical degradation is initiated by free radicals attack, even though the precise details are not fully agreed upon [23,26–28]. Radicals including hydroxyl (HO \cdot), hydroperoxyl (HOO \cdot) and hydrogen (H \cdot) have been detected by *in-situ* and *ex-situ* electron spin resonance (ESR) spectroscopy [27,29]. Fluoride ion emission [30] and loss of proton conductivity, leading to a decrease in cell performance, is commonly observed [31]. It is also suggested that transition metal ion contaminants, namely iron species, exacerbate free radical formation and accelerate membrane degradation [32].

The Fenton's reagent reaction is a commonly-used to generate free radicals for *ex-situ* degradation tests [22]. Free radicals are generated by the following reactions [27,28].



Healy et al. studied Nafion $^{\text{®}}$ membrane degradation by comparing *in-situ* vs. *ex-situ* (Fenton's reagent test) methods [33], and found that similar fluoroorganic fragments were generated by both methods. Others have monitored chemical and compositional changes of membranes using X-ray photoelectron spectroscopy (XPS) upon exposure to Fenton's reagent [24]. Others still have found that fluoride emission rates increase with concentration of –COOH polymer termini [34]. A recent NMR study by Ghassemzadeh et al. quantifiably identified structural changes of Nafion $^{\text{®}}$ NR211 membrane, finding fluorine loss, ion exchange capacity loss and polymer side chain cleavage upon increasing exposure to Fenton's reagent [23]. Qiao et al. and Hongssirikarn et al. observed a decrease in water content and proton conductivity of degraded PFSA ionomer membranes after treatment in H $_2$ O $_2$ [35,36]. *Ex-situ* methods to generate free radicals, besides Fenton's reagent, have also used to study membrane degradation, these include, gamma-ray [37], X-ray radiation [38], hydrothermal [39,40] and electron beam techniques [41]. Collette et al. studied water uptake of hydrothermally-aged Nafion $^{\text{®}}$ 112 and Nafion $^{\text{®}}$ 212 [39,40]. Water uptake was found to decrease with increasing aging time. A recent study from our group also found that water uptake Nafion $^{\text{®}}$ NR211 decreased upon exposure to free radicals generated by electron beam irradiation [41].

Water transport and membrane degradation are two important factors governing fuel cell performance. However, these two factors have generally been studied separately. In practice, these two factors are closely related. Moreover, to date, water permeation studies have largely been restricted to pristine membranes and relatively few studies have attempted to measure the water uptake of degraded Nafion $^{\text{®}}$ membranes. The majority of studies of water uptake of degraded membranes that have been reported are carried out at ambient temperature [35,42,43] but such conditions are not reflective of fuel cell operating conditions (40–100% RH and 60–80 $^{\circ}$ C). In this report, we examine the effect of membrane degradation on water transport performed using *ex-situ* measurements. In order to explain the data, we also study water sorption, IEC, proton conductivity, and examine the membrane morphology using SEM.

Experimental

Materials

Nafion $^{\text{®}}$ NR211 (Dupont, acid form) was provided by Ballard Power Systems Inc. 30 vol% H $_2$ O $_2$ (Caledon Laboratory Chemicals Ltd.) and 98% sulfuric acid (Anachemia) were diluted to 20 wt% and 1 M, respectively using Milli-pore water (18 M Ω). FeSO $_4$ ·7H $_2$ O, NaCl (99%, reagent grade) and 0.01 M NaOH were purchased from Sigma–Aldrich and used as-received.

Chemical degradation

Pieces of 10 \times 16 cm as-received NR211 membrane were immersed in Millipore water (18 M Ω) at 80 $^{\circ}$ C for at least 5 h in order to reach full hydration. 10 ppm Fe $^{2+}$ and 20 wt% H $_2$ O $_2$ were used for preparing Fenton's reagent solutions. This solution (1000 mL) was placed in a beaker, and NR211 immersed. A schematic diagram of the experimental setup is illustrated in Fig. 1. A glass frame was used for holding the membrane below the level of the solution. A watch-glass was used to minimize evaporation. Gas pressure was released from the top side of the beaker. Solutions were heated to 80 $^{\circ}$ C for different times (i.e., 0, 6, 12, 36, and 48 h) in the dark. The Fenton's reagent solution was renewed after specific time intervals. After a set reaction time, the sample was soaked in 1 M H $_2$ SO $_4$ (to convert the membrane to H $^+$ form prior to use) and rinsed with Millipore water thoroughly to remove residual free acid.

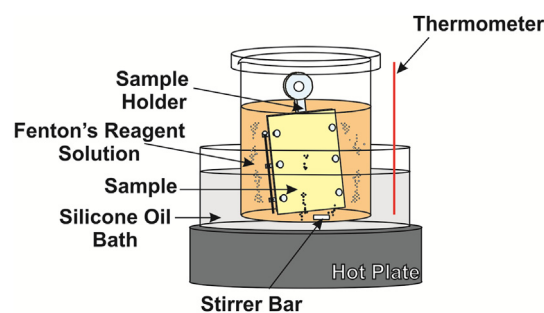


Fig. 1 – Schematic diagram of Fenton's reagent reaction setup.

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