



The importance of water transport on short-side chain perfluorosulfonic acid membrane fuel cells operating under low relative humidity



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H I G H L I G H T S

- Short-side chain PFSA ionomer membranes provided higher fuel cell performance than NRE-211 at 80 °C and 30% RH.
- A higher water flux through the membrane leads to a higher fuel cell performance.
- Rates of water permeation and effective proton mobility are related.
- Increasing a PFSA membrane's IEC does not always improve fuel cell performance.

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Polarization curves of fuel cells incorporating PFSA short-side chain (SSC) ionomer membranes having ion exchange capacity (IEC) 1.30, 1.37, 1.43 and 1.50 meq g⁻¹ and NRE-211 are compared. Under low humidity conditions, fuel cells incorporating SSC membranes show higher performance than NRE-211. SSC PFSA membranes possessing an IEC of 1.37 meq g⁻¹ exhibit the highest performance. Differences in fuel cell polarization curves are due to differences in the high frequency resistance, which in turn is found related to ex-situ measurements of both the effective proton mobility and the rate of water flux through the membrane, which also exhibit a maximum for membranes of IEC 1.37 meq g⁻¹. Water permeation and proton mobility are shown to be inherently linked, but it is found that simply increasing the membrane's IEC does not necessarily translate to increased water transport and effective proton mobility, despite the increased water content.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered an alternative energy conversion technology for vehicular applications to complement the internal combustion engine. The proton-conducting membrane is a key component in this technology as it serves as both the conductor of protons and separator of

electrodes and reactant gases. The archetypal membrane is based on a perfluorosulfonic acid (PFSA) ionomer, such as Nafion[®] [1], which consists of a hydrophobic polytetrafluoroethylene backbone and perfluorovinyl ether side chains terminated by a triflic acid group (–CF₂SO₃H). Although Nafion possesses many desirable attributes, it has the recognized limitation of insufficient proton conductivity under low humidity [2]. The short-side chain (SSC) version of PFSA, bearing a –OCF₂CF₂SO₃H pendant chain, has gained recent attention due to its higher degree of crystallinity and thermal resistance [3]. Tant et al. [4,5] and Moore and Martin [6] have previously highlighted a few of the differences between short- and long-side chain PFSA analogs. In the mid-1980s Ballard Power Systems demonstrated significant improvements in fuel cell

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performance using SSC membranes produced by Dow Chemical Co. [7].

Over the past decade simpler synthetic routes for producing SSC PFSA ionomer have emerged and several properties of these materials have been reported [8–14]. For example, Solvay Solexis [15] produces and markets Hyflon/Aquivion Ion membranes, reporting higher conductivity, similar mechanical properties, and higher ionic glass-transition temperatures with respect to Nafion. Ghielmi et al. [16] examined the water uptake of extruded, high IEC Hyflon 670 (IEC 1.49 meq g⁻¹) and 770 (IEC 1.30 meq g⁻¹) at 100 °C and reported much larger water uptakes compared to lower IEC analogs. Molecular modeling studies revealed that the hydronium ion diffusion coefficient in SSC PFSA membranes increases with water content [17]. Aricò et al. [13] found that Aquivion™-based MEAs in fuel cell stacks were able to sustain a higher temperature operation than Nafion-based cells. In previous publications, we described the results of fuel cell studies using high IEC, SSC PFSA ionomers as the proton-conducting medium dispersed in the catalyst layer [18,19]. Larger current densities were observed at elevated temperature and under lower relative humidity, compared to Nafion NR211.

Whereas a distinct advantage of SSC PFSA membranes has been demonstrated in fuel cells, a comprehensive understanding of the correlations between water permeation, proton conductivity, and fuel cell performance is not-so-well documented. A greater understanding of the role of transport properties in such materials is essential to optimize and improve fuel cell performance. This is because during fuel cell operation water is transported by electro-osmotic drag from anode to cathode and by back diffusion due to a water concentration gradient and diffusion-driven by pressure gradient [20,21]. Too little water in either the membrane or catalyst layer increases the ionic cell resistance, but too much causes flooding of the catalyst layer which suppresses the transport of gaseous reactants [22–24].

In the present work, fuel cell polarization performance data and water transport properties of short-side chain (SSC) PFSA membranes are studied under comparable conditions of temperature and relative humidity. SSC PFSA ionomers possessing IECs of 1.30, 1.37, 1.43 and 1.50 meq g⁻¹ were provided by Dongyue [25,26]. In contrast to our previous studies on SSC PFSA ionomer membranes in which membranes were cast from relatively high boiling point solvents (e.g., DMF) [26], we developed a solution casting process using alcoholic solutions in order to promote “greening” of the membrane fabrication process.

2. Experimental and materials

2.1. Membranes

Short-side chain PFSA ionomer was synthesized and provided by Dongyue as described previously [25,26]. PFSA ionomers possessed an IEC (equivalent weight, EW) of 1.30 (770), 1.37 (730), 1.43 (699) and 1.50 meq g⁻¹ (670 g eq⁻¹), as determined by titration 5–15 wt% PFSA ionomer solutions/dispersions were prepared using a mixture of ethanol, 1-propanol, ethylene glycol, and water (26:45:4:25 vol%). Membranes were cast onto a PTFE sheet using a doctor blade, dried at room temperature overnight, and annealed in a vacuum oven at 180 °C for 20 min. As pre-treatment, membranes were heated to 65 °C in 1.0 M sulfuric acid solution for 2 h, rinsed in de-ionized Milli-Q water (Millipore) several times and dried prior to use. For the purpose of this work, membranes are named SSC-1.30, SSC-1.37, SSC-1.43, SSC-1.50. Nafion® membrane (NRE-211, DuPont) was used as received. The fully hydrated thicknesses of SSC-1.30, SSC-1.37, SSC-1.43, SSC-1.50 and NRE-211 were 28 μm, 24 μm, 23 μm, 24 μm and 28 μm, respectively.

2.2. Fabrication of membrane–electrode-assemblies (MEAs)

Catalyst inks were prepared using a dispersion media mixture of 1:1 MeOH/water and 46 wt% Pt/C (Tanaka Kikinokogyo). The content of Nafion® ionomer in the catalyst layer was 30 wt%. The solids content of the inks was ~1 wt%. An automated spray coater (EFD Ultra TT series) was used to deposit the anode CL (0.2 mg Pt cm⁻²) and the cathode CL (0.4 mg Pt cm⁻²) directly onto the membrane. The catalyst-coated membranes (CCMs) possessed an electrode geometrical surface area of 5 × 5 cm². Detailed fabrication procedures have been previously described [19,27].

2.3. Single cell assembly and fuel cell testing protocol

Catalyst-coated membranes (CCMs) were sandwiched between sheets of two-layer gas diffusion layers (GDL, SIGRACET 24BC, SGL Carbon Group) and assembled into 25 cm² single cells possessing straight flow channels (Fuel Cell Technologies). Single cells were tested in a fuel cell test station (100 W, Scribner 850e, Scribner Associates Inc.), using hydrogen (2 L min⁻¹) and air (5 L min⁻¹) with no back pressure. The cells were conditioned for at least 6 h at 1 A cm⁻² under 100% RH at 80 °C.

The electrochemical surface area (ECSA) of cells was measured by cyclic voltammetry (CV) using a potentiostat (1287A, Solartron Analytical) operated at a sweep rate of 50 mV s⁻¹. Humidified hydrogen (0.5 SLPM) was fed to the anode, which operated as both counter and reference electrode, while humidified nitrogen (0.5 SLPM) was fed to the cathode (working electrode). After 15 min of purging, the N₂ flow was set to zero, and the cell was stabilized for 15 min. The ECSA was calculated from the integrated charge corresponding to the Pt–H desorption and adsorption peaks. The double-layer capacitance of the cathode catalyst layers (CCLs) was also obtained from the cyclic voltammograms. The errors reported are based on multiple (3) measurements.

2.4. Water content

Hydrated membrane volumes, V_{hyd} , were calculated by assuming that the volume change upon absorption is due to the volume of water incorporated, V_{water} . The latter was calculated from the difference between the weight of the hydrated membrane, W_{hyd} , and the dry weight, W_{dry} , and dividing by the density of water, ρ_{water} (1.0 g mL⁻¹).

$$V_{\text{water}} = \frac{W_{\text{hyd}} - W_{\text{dry}}}{\rho_{\text{water}}} \quad (1)$$

The water content, as a volume percentage, X_v , is expressed according to the following relationship:

$$\text{water content (vol\%)} = X_v = \frac{V_{\text{water}}}{V_{\text{hyd}}} 100\% \quad (2)$$

The acid concentration was determined according to:

$$[-\text{SO}_3\text{H}] = \frac{\text{moles of } -\text{SO}_3\text{H}}{V_{\text{hyd}}} \quad (3)$$

where $[-\text{SO}_3\text{H}]$ is the concentration of bound sulfonic acid; moles of $-\text{SO}_3\text{H}$, was calculated from the IEC and dry mass of the polymer; and V_{hyd} is the hydrated volume of the membrane.

2.5. Proton conductivity and proton mobility

In-plane conductivity measurements were performed using a 2-probe PTFE cell. Membranes were sandwiched between two Teflon

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