The impact of short side chain ionomer on polymer electrolyte membrane fuel cell performance and durability

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HIGHLIGHTS

- Investigated the impact of short-side chain (SSC) ionomer in catalyst layers.
- Achieved higher Pt utilization and active surface area by using SSC ionomer.
- Obtained higher durability of PEM fuel cells via accelerated stress test.
- Observed significant impact of SSC ionomer for higher Pt loading cells.
- Measured higher degradation of the cell performance for low Pt loading cells.

ARTICLE INFO

ABSTRACT

For polymer electrolyte membrane fuel cells (PEMFCs), the importance of durability is widely recognized, but less attention has been paid to the role of ionomers. In this study, the importance of ionomer structure in achieving high PEMFC performance and durability are investigated experimentally for different catalyst-ionomer ratios and catalyst loadings in scaled up cell (45 cm^2). The results are compared with a conventional long side chain ionomer (LSC) under the same preparation and testing conditions. Catalyst layers (CLs) fabricated with 25 wt% of short side chain (SSC) ionomer display higher performance than 17 wt% and 30 wt%. A similar trend is also demonstrated when using the LSC ionomer. However, it is found that SSC ionomer is more compatible with CLs than LSC. This compatibility is ascribed to the higher stability of the SSC ionomer. In addition, higher performance, Pt utilization, and active surface area are measured for membrane electrode assemblies (MEAs) prepared with SSC in comparison to LSC under the same ratio. Based on the accelerated stress tests, SSC ionomer has a positive role in improving durability, as the maximum power density after 30,000 cycles decreases by 21% and 48% for MEAs prepared by SSC and LSC, respectively. Moreover, the losses in performance are more than two times greater than when the Pt loading is decreased from 0.5 mg/cm^2 to 0.125 mg/cm^2. These results highlight the importance of ionomer structure in cell performance and durability at high and low Pt loadings.

1. Introduction

Durability and cost are the two main challenges in the commercialization of polymer electrolyte membrane fuel cells (PEMFC) [1–3]. They are closely related, and strongly influenced by many factors as well as their interactions, including the types of catalyst, solvent and ionomer, catalyst ink composition and preparation, and processes for membrane electrode assembly (MEA) manufacturing [4–7]. Cost reduction has been significantly focused through substantial reduction in the Pt catalyst loading, from 28 mg/cm^2 to < 0.5 mg/cm^2 during the last 50 years, through the development of the catalyst and MEA manufacturing processes [8–10]. The United States Department of Energy (US-DOE) has set a target of 0.125 mg/cm^2 for the total Pt loading in PEMFCs by 2020 [11].

However, further substantial reduction in the Pt loading would often be accompanied with reduction in the durability. Decreasing Pt loading without sacrificing either cell performance or durability may be achieved by developing highly efficient catalyst layers (CLs), optimizing Pt utilization, with optimum ratios between the solid active Pt nanoparticles, ionomers, and void regions for reactant supply [12–15]. The effect of different MEA manufacturing processes on cell performance has been investigated [16], and the importance of catalyst types and deposition methods has been studied, but less attention has been paid to the role of ionomer [17–20].

The ionomer used in CLs affects the ionic conductivity, catalyst utilization, mass transport, and binding materials [21], and the amount of ionomer applied can be critical to cell performance. Excessive ionomer in CLs blocks the gas transport paths in the pores of the electrode (decreasing porosity), hinders the mass transport of reactants and by-products, and also reduces electronic conductivity. In contrast, insufficient ionomer decreases proton transport, leading to significantly reduced catalyst utilization. Therefore, the amount of ionomer that covers the Pt nanoparticles has noticeable impact on cell performance and durability. In addition to the amount of ionomer in CLs, the structure of ionomer also plays an important role in performance and durability. In PEMFC operation, catalyst and support oxidation can alter the surface roughness as well as morphology, which directly affect the interaction of Pt nanoparticles with ionomer [22–25]. The most commonly used ionomer is perfluorosulfonic acid, made of a hydrophobic perfluorinated backbone with perfluoropolyether as side chains. These side chains terminate in a sulfonic functional group. The equivalent weight (EW g mol^{-1}) and proton conductivity depend on the ratio of both monomers. This ionomer is available under the trade name Nafion, and can be classified as a long side chain (LSC) ionomer. Although this ionomer has been demonstrated to have promising properties for PEMFC applications, it also has some limitations, for instance, a narrow range of operation temperature ($< 90\,°C$) as well as poor proton conductivity under low humidity condition [26,27].

Operating PEMFCs at higher temperature and lower humidity condition is possible via employing short side chain ionomer (SSC) membranes [28], and it is desirable due to faster reaction kinetics, simpler humidification system needed, and better carbon monoxide tolerance [29–31]. Generally, SSC ionomer has a structure almost identical to Nafion's (LSC), with shorter pendant side chains, and was first synthesized by Dow Chemical [32]. This ionomer demonstrates higher crystallinity, higher thermal transition temperature, and higher ion exchange capacity (IEC) when compared to LSC ionomer; hence, improved fuel cell performance was reported back in the 1980s [33]. In spite of SSC ionomer's many advantages, the complexity of the manufacturing processes halted its development [32]. Later, in 2010, a simpler method, developed by Solvay-Solexis, allowed it to be produced at a price comparable to Nafion's. In brief, LSC ionomer is prepared via copolymerization of sulfonyl fluoride vinyl ether (SFVE) with tetrafluoroethylene (TFE). This route of synthesis produces a polytetrafluoroethylene backbone with perfluoroether side chain which is ended by sulfonic acid group [13,34]. SSC ionomer is developed by Solvey with no fluoroether chain in the structure. This ionomer also is used the copolymerization of TFE with SFVE [35]. Although a number of simulations and experimental studies have been reported, mainly on SSC ionomer membranes, reports on using SSC ionomer in CLs are limited [36]. Jeon et al. [30] demonstrated a positive impact on the cell performance by applying the SSC ionomer in a catalyst layer and membrane. The same study attributed the improved performance to better protonic conductivity, and the lower charge transfer resistance of the SSC membrane. In another study [37], the impact of SSC ionomer on CLs is compared to that of Nafion (LSC) under high temperature and low humidity condition. The obtained polarization curves reveal that applying LSC ionomer leads to better performance than SSC ionomer under a 30% ratio. However, applying lower ratios of SSC can lead to results comparable to those for LSC ionomer. Higher cell performance using SSC under partially humidified conditions was also reported [38].

Despite its important roles, few studies have considered the impact of SSC ionomer on the performance and durability of PEMFCs. Therefore, the objective of the present work is to investigate how the SSC ionomer in the CLs affects Pt utilization, cell performance, and cell durability (life time). A systematic investigation is carried out to examine the effect of different SSC ratios on fuel cell performance using high Pt loading of 0.5 mg/cm^2. Comparisons are made with the conventional LSC (Nafion) ionomer under identical preparation and testing conditions. Further, the MEAs that perform best are characterized based on active surface area, Pt utilization, and durability. Finally, the impact of SSC on cell performance and durability is also investigated under low total Pt loading of 0.125 mg/cm^2.

2. Experimental

2.1. Materials

Nafion 211 is employed as the membrane. Johnson Matthey HiSPEC™ Fuel Cell Catalyst (9100) is used as the catalyst. Two different ionomers are applied to make the catalyst ink, Nafion (5 wt%-D521-DuPont) alcohol based with the equivalent weight (EW) of 1100, and ionomer (25 wt%-Solvay-Solexis (Aquivion) water based with the equivalent weight (EW) of 790. The former is denoted as LSC, and the latter as SSC, and both LSC and SSC ionomers have comparable prices. Iso-propanol (99.9% purity) is utilized as a solvent. Carbon paper (AvCarb with the thickness of 212.6 ± 1.4 μm) is used as the gas diffusion layers (GDLs).

2.2. Catalyst characterizations

The surface morphology of the 60% Pt/C is characterized by using transmission electron microscopy (HRTEM) (200MC TEM). In addition, the structures of the samples are analyzed through X-ray diffraction (XRD) with a Brucker D8 Focus using a Cu Ka- X-ray source operated at room temperature. The structure of the catalyst is determined by Eva-Software. The crystal structure is refined by applying the Rietveld technique along with the GSAS 2000 software package [39].

2.3. Ink preparation

The catalyst ink is prepared by dispersing the proper amount of the Pt/C catalyst, with iso-propanol, and either SSC or LSC ionomers. Different ionomer ratios of 17%, 25%, and 30% are applied. The prepared ink is placed in an ultrasonic bath for 1 h to reach a uniform suspension.

2.4. Membrane electrode assembly (MEA) preparation

The CLs are directly sprayed on the membrane, which is first located on a vacuum table, at a temperature of 60 °C. Two different Pt loadings, 0.5 mg/cm^2 and 0.125 mg/cm^2, are used in this study, denoted as high and low loadings, respectively. MEA is fabricated by sandwiching the prepared catalyzed-membrane between two GDLs. MEAs are labeled based on the type of applied ionomer and its ratio. For example, an MEA containing 25% SSC ionomer is labeled as SSC-25.

2.5. Analysis and performance of membrane-electrode assemblies (MEA)

The polarization performances and the power densities of the various MEAs fabricated with different ionomers and catalyst loadings are obtained by using a commercial fully automated fuel cell test station (Greenlight- G20). The active area of the tested MEAs is 45 cm^2. The MEA is located between two graphite flow plates and pressurized to a desirable level by using a controllable air bladder. Performance tests are conducted at the fixed operating conditions of cell temperature and pressure of 75 °C and 35 kPag. Fully humidified hydrogen and air streams with the flow rate of 4.45 and 9 slpm are supplied to the cathode and anode side, respectively. Each polarization test is repeated three times on three different days to ensure the repeatability of all the results obtained. The electrochemically active surface areas (EAS) of the selected MEAs are analyzed by in-situ cyclic voltammograms, taken by two-electrode assemblies while nitrogen and hydrogen are passing through the cathode and anode. During the test, the cathode acts as a working electrode, while the anode works as both counter and reference electrodes. The voltammogram is recorded at a scan rate of