Performance Comparison of Proton Exchange Membrane Fuel Cells with Nafion and Aquivion Perfluorosulfonic Acids with Different Equivalent Weights as the Electrode Binders

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ABSTRACT: A perfluorosulfonic acid (PFSA) ionomer, used as the proton conductor in the catalyst layer, influences significantly the performance of proton exchange membrane fuel cell catalyst-coated membrane (CCM). In this paper, SSC-CCM is prepared by the SSC-PFSA (Aquivion, EW 720) ionomer, and the comparative sample (LSC-CCM) is based on the LSC-PFSA ionomer (Nafion, EW 1100). Compared with LSC-CCM, SSC-CCM shows higher porosity, larger electrochemical surface area (ECSA), and smaller high-frequency resistance. Polarization curves of SSC-CCM tested by the short stack show better performance than those of LSC-CCM, especially under the lower relative humidity operations. Moreover, the SSC-CCM outputs higher voltage and is more stable in the dynamic process with temperature continuously increasing under lower relative humidity operation. Such excellent performance of SSC-CCM is confirmed from the higher proton conductivity of SSC-PFSA under low relative humidity. These results indicate that the SSC-PFSA ionomer could be employed for the CCM catalyst layer under the operation conditions of low relative humidity and dynamic running for automotive applications.

1. INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are considered to be widely used in transportation, stationary, back-up power, submarine, and aerospace because of their high efficiency, long durability, zero emission, and low noise. The transportation is one of the most promising fields for PEMFC application on the large scale. For automotive applications, it is required to operate the fuel cell at higher temperatures (e.g., >100 °C) and under lower relative humidity (e.g., <60–70%) to improve reaction kinetics and simplify cooling and humidification subsystems.1 The membrane electrode assembly (MEA), composed of catalyst-coated membrane (CCM) and gas diffusion layer (GDL), is the core component of PEMFC. The CCM, where the electrochemical reaction occurs, and electricity is generated, significantly impacts the performance and durability of PEMFC.2,3 For automotive applications, CCM is also required for high power output, quick response, and long lifetime under the conditions of higher temperature and lower humidity.

The ionomers, used as proton conductors, are commonly employed in catalyst layers of CCM to form electrochemical reaction sites and improve proton conduction. Therefore, the ionomers contained in catalyst layers affect MEA’s performance significantly, especially for the dynamic characteristics. Although ionomer-free nanostructured thin film catalyst layers have been invented by the 3M company, their performances are still lower than those of ionomer-contained catalyst layers under dry conditions because of serious deteriorations of proton conductivity.4–6

Nowadays, the perfluorosulfonic acid (PFSA) polymers have been widely used as the ionomer owing to their high proton conductivity and chemical stability. Nafion, developed by the Dupont company, is the one of most commonly used PFSA ionomers for the catalyst layer of MEA. It is based on the long-side chain PFSA ionomer (LSC-PFSA) with five –CF2 groups in pendant side chains. The proton conductivity of Nafion, with a higher equivalent weight (EW 1100), would decrease quickly under working temperature higher than 90 °C or humidity at a relatively low level. The LSC-PFSA ionomers are suitable for the application under the conditions of temperature lower than 90 °C and relatively high humidity.7–9 In 1980s, a short-side chain PFSA ionomer (SSC-PFSA) with no fluorooether group in the pendant side chain, comprising only two –CF2 groups, was synthesized by the Dow Chemical Company.8 Although a significant improvement in the fuel cell performance was obtained,10–14 the complexity of the synthesis route to the SSC monomer greatly restricted the
industrial development. Subsequently, Solexis (now known as Solvay Specialty Polymers) was applied to the fluoro(vinylether) process for the production of the SSC monomer (Aquivion) on an industrial scale.\textsuperscript{11} The chemical structures of Na\textsubscript{ion} and Aquivion PFSA with different side chain lengths are presented in Figure 1.

![Diagram](https://example.com/diagram.png)

**Figure 1.** Na\textsubscript{ion} and Aquivion perfluorinated sulfonic acid ionomer structures.

At a given EW value, the SSC-PFSA of Aquivion type is characterized with a higher heat of fusion than that of LSC-PFSA (Na\textsubscript{ion}), which indicates that the SSC-PFSA exhibits higher crystallinity compared with LSC-PFSA.\textsuperscript{15} When the polymer EW is lower than 800, the SSC-PFSA still retains semi-crystallinity while the LSC-PFSA almost becomes amorphous and even gelatinous on exposure to water.\textsuperscript{16} In addition, the shorter side chain and absence of the pendant $\text{-CF}_{3}$ group lead to a higher glass transition temperature at a given polymer EW (\(T_{\text{g}}\) Na\textsubscript{ion} ca. 100°C, Aquivion ca. 140°C), which promotes a higher operating temperature of fuel cell.\textsuperscript{8,17,18}

The difference of proton exchange membranes based on LSC-PFSA and SSC-PFSA and their effect on CCM’s performance have been previously studied both ex situ and in fuel cell. It is showed that CCMs based on the Aquivion SSC-PFSA membrane exhibit higher polarization performance than the CCMs based on the Na\textsubscript{ion} LSC-PFSA membrane.\textsuperscript{19–21} Also, SSC-type CCMs sustain stable running even at 110°C while the maximum working temperature for LSC-type CCMs was 95°C.\textsuperscript{10,11} Moreover, the studies aiming to explain the PFSA morphology of SSC-PFSA as a function of EW are also carried out.\textsuperscript{22–25}

The development of SSC-PFSA resin to replace Na\textsubscript{ion} LSC-PFSA as the electrolyte membrane leads to the incorporation of novel ionomers in the catalyst layer.\textsuperscript{26–28} Jennifer Peron et al. reported an improvement in PEMFC polarization performance by using low EW PFSA in the cathode catalyst layer (CCL).\textsuperscript{26} The results of studies, carried out by Lei et al., showed that the CCM containing 10 wt % SSC-PFSA in CCL reaches the same performance as the LSC-PFSA-based CCM with 30 wt % ionomer.\textsuperscript{27} These results indicated that ionomers with lower EW led to a higher protonic conductivity in the catalyst layers and higher PEMFC performance under lower humidity operation. In addition to the performance, the SSC ionomer has higher stability and is more compatible with catalyst layers, which results in enhanced cell durability and higher Pt utilization in comparison to the LSC ionomer.\textsuperscript{29–35}

A distinct advantage of SSC-PFSA ionomer applied in the catalyst layer of CCMs has been demonstrated. As is well-known, it shows conspicuous ununiformity of flow filed in the high power stack. Further, the operation conditions for fuel cell engine usually have wide range and real-time dynamic changes. These two elements are the main reasons to influence the running stability and durability of PEMFC.\textsuperscript{34–36} Therefore, it is necessary to evaluate the running characteristics of SSC CCM in the kW-class stack and under dynamic operation simulating PEMFC for transportation.

In this work, LSC-PFSA (Na\textsubscript{ion} EW 1100) and the SSC-PFSA (Aquivion EW 720) ionomers are applied to manufacture CCMs to investigate the difference in running behaviors of SSC and LSC CCM operated under simulated PEMFC conditions for transportation. The proton conductivity of ionomers is experimented by water uptake and conductivity tests. The porous structure, high-frequency resistance, and electrochemical surface area of CCMs are characterized by mercury intrusion porosimetry and electrochemical tests. Furthermore, the two types of CCMs's static and dynamic fuel cell performances because of transportation conditions are carried out with detailed comparison.

2. RESULTS AND DISCUSSION

2.1. Water Uptake and Proton Conductivity. PFSA's proton conductivity is influenced significantly by the molecular chain and aggregation structure. The water uptake and proton conductivity of membranes cast with SSC-720 and LSC-1100 were measured in the same conditions.

As shown in Figure 2, the water uptake of both the SSC and LSC membranes increased as the immersion temperature increases. However, SSC-720's water uptake was higher than that of LSC-1100 during the temperature from 30 to 100°C. The water uptake of SSC-720 was about 15% higher than that of LSC-1100 during 60–80°C. Furthermore, the proton conductivity of the membranes was measured under temperature from 30 to 70°C and humidity from 20 to 100%, as displayed in Figure 3. Similar to the results of water uptake, the proton conductivity of both samples also increased as the test temperature and humidity increases. However, it was more sensitive for conductivity to humidity than temperature. The conductivity of SSC-720 was about an order of magnitude higher than that of LSC-1100 at 100 RH % while the two values were similar at 20 RH %.

![Graph](https://example.com/graph.png)

**Figure 2.** Water uptake of membranes cast with SSC-720 and LSC-1100 ionomers as the function of temperature.
transfer temperature, SSC-PFSA with a lower EW value could be synthesized. SSC-720 has more side chains ended with hydrophilic group per unit weight, compared with LSC-1100. Consequently, water uptake and proton conductivity of SSC-720 were higher than those of LSC-1100 under the same condition.

### 2.2. Catalyst Layer Porous Structure.

The continuous three-dimensional microporous structure in the catalyst layer of CCM supplied the reaction sites to ensure electrochemical reaction occurring quickly. Meanwhile, the porous structure in the catalyst layer also forms a pathway to ensure the gas permeation reaction from the flow channel to reactive site, and the generated water is expelled from the catalyst layer to flow channel. The microporous structure in the catalyst layer was influenced by the main material (catalyst, ionomer, and solvent) characterization, ink formula, and catalyst layer preparation technology. The porous structures of catalyst layer prepared by SSC-720 and LSC-1100 with the same ink formula and preparation process were characterized by the mercury intrusion method.

As the curves shown in Figure 4, both prepared catalyst layers' pore sizes are between 10 and 110 nm. However, the SSC-type catalyst layer presented wider pore diameter distribution compared with the LSC-type catalyst layer. It could be seen more clearly from data, as shown in Table 1, that porosity of the SSC-type catalyst layer with 57.07% was larger than that of the LSC type with 42.55%. Moreover, the average pore size of SSC-type catalyst layer was 91.7 nm while that of the LSC-type catalyst layer was only 51.4 nm, which indicated that there were larger pores in the former than in the latter. Difference of porous structure between the two samples demonstrated that the specific surface area and pore size of catalyst layer prepared by the SSC-PFSA ionomer were larger than those of the catalyst layer based on the LSC-PFSA ionomer, which might be beneficial for the electrochemical reaction and gas/water transmission.

### 2.3. Electrochemical and Polarization Performances.

The polarization curves of SSC-CCM and LSC-CCM were tested by single-cell stacks. The $I−V$ curves, as shown in Figure 5, indicated that the SSC-CCM exhibited better polarization performance compared with LSC-CCM. As the current density gradually increases, it was more remarkable that the voltage of SSC-CCM was higher than that of LSC-CCM. Furthermore, two CCMs’ high-frequency resistance (HFR) at each current density, also showed in Figure 4, displayed that the resistance of SSC-CCM was lower than LSC-CCM’s. The results of electrochemical active area (ECSA) measured by cyclic voltammetry (CV), as shown in Figure 6, showed that the H$_2$ absorption peak area of SSC-CCM was larger than LSC-CCM’s. As to the cathode Pt loading of 0.4 mg cm$^{-2}$, the calculated ECSA of SSC-CCM was 43.6 m$^2$ g$^{-1}$ while that of LSC-CCM was 37.3 m$^2$ g$^{-1}$, which was consistent with the results of the large pore area in the catalyst layer of SSC-CCM (Table 2).

Compared with the LSC-1100 ionomer, higher proton conductivity of SSC-720 contributed to lower HFR and larger ECSA of SSC-CCM, which ensured that the electrochemical reaction is carried out more effectively. In addition, larger porosity of SSC-type catalyst layer improved the gas or water transmission more easily. Consequently, SSC-CCM showed better performance than LSC-CCM.

| Table 1. Porous Structure Parameters of Catalyst Layers Prepared by SSC-720 and LSC-1100 Ionomers |
|---------------------------------------------|----------------|-----------------|
| sample          | porosity/% | average pore diameter (4V/A) /nm | total pore area/m$^2$ g$^{-1}$ |
| SSC-720          | 57.07      | 91.7            | 22.736          |
| LSC-1100         | 42.55      | 51.4            | 30.706          |

![Figure 3](image3.png)

**Figure 3.** Proton conductivity of membranes cast by SSC-720 and LSC-1100 as the function of temperature and humidity: (a) temperature; (b) humidity.

![Figure 4](image4.png)

**Figure 4.** Pore diameter distribution of catalyst layers prepared by SSC-720 and LSC-1100 ionomers.

![Figure 5](image5.png)

**Figure 5.** Polarization curves and HFR of the CCMs prepared by SSC-720 and LSC-1100 ionomers.
2.4. Static Performance Response to Operation Conditions. It is required that the fuel cell for transportation applications should have wide operation windows. It has been proved that the CCM prepared by the SSC-PFSA ionomer had better performance than that of the LSC-PFSA ionomer. A short stack was assembled with three samples of SSC-CCMs and three samples of LSC-CCMs to investigate the differences between their performance response to operation conditions (temperature and humidity).

2.4.1. Temperature. The relationship of polarization curves of CCMs for both samples with the increasing of operating temperature without external humidification, as shown in Figure 7. Without external humidification, it was seen clearly that the SSC-CCM exhibited better polarization performance than LSC-CCM at each working temperature. Also, with the temperature gradually increasing, it was more remarkable that the SSC-CCM’s performance was higher than LSC-CCM’s. Moreover, the voltages and HFRs of the two CCMs at 1.0 A cm\(^{-2}\) under the same operating temperature range of 30–60 °C are displayed in Figure 8. Compared with LSC-CCM, it could be seen that not only the voltage of SSC-CCM was higher but also the resistance of SSC-CCM was much lower. Furthermore, as the temperature increased, the voltage of both CCMs first gradually increased and their corresponding HFRs declined, and then they reached the maximum performance and the smallest resistance at 50 °C. When temperature went to 60 and 70 °C, the performance of the LSC-CCM dropped, and its HFR increased dramatically, while the performance of SSC-CCM declined slightly and its HFR almost remained in the same level at 50 °C.

Table 2. Electrochemical Active Area (ECSA) of Catalyst Layers Prepared by SSC-720 and LSC-1100 Ionomers

| sample  | SSC-CCM | LSC-CCM |
|---------|---------|---------|
| ECSA/m² | 43.6    | 37.3    |

Figure 6. Cyclic voltammogram curves of the CCMs prepared by SSC-720 and LSC-1100 ionomers.

Figure 7. Polarization curves of SSC-CCM and LSC-CCM at different operation temperatures without external humidification: (a) 30; (b) 40; (c) 50; and (d) 60 °C.

Figure 8. Voltage and HFR at a current density of 1.0 A cm\(^{-2}\) of SSC-CCM and LSC-CCM at different operation temperatures without external humidification.

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The relative humidity in the fuel cell would gradually decrease with the increase in working temperature during nonhumidification. The polarization performance and HFR of SSC-CCM and LSC-CCM with the variation of temperature indicated that SSC-CCM showed more significant advantage in performance under higher temperature and lower humidity, ascribed to its lower resistance under low humidity compared with LSC-CCM.

2.4.2. Humidity. In order to further study the different influences of operation humidity in the fuel cell on the performance of CCMs based on SSC- and LSC-PFSA ionomers, their polarization performance was tested under RH from 30 to 100%. Relative humidity in the stack was controlled by maintaining the stack temperature and adjusting humidifier’s dew point temperature. As the results shown in Figure 9, SSC-CCM had better polarization performance than LSC-CCM at each humidity from 30 to 100 RH %, and it had more obvious advantage in performance at lower humidity, which was similar with the results, as shown in Figure 7.

Voltages and HFRs of the two types of CCMs at a current density of 1.0 A cm$^{-2}$ under the humidity range from 30 to 100 RH % are displayed in Figure 10. As the humidity gradually increases, both CCMs’ voltages increased and their HFRs dropped. However, it could be seen more clearly that the RH was lower, and the differences of performance and HFR between SSC-CCM and LSC-CCM were more significant. The voltage of SSC-CCM was higher, about 21% at 30 RH % but only 3% at 100 RH %, than that of LSC-CCM. In addition, the performance and HFR at a current density of 1.0 A cm$^{-2}$ of SSC-CCM at 50 RH % achieved the same level as those of LSC-CCM at 80 RH %. It was further proved that the CCM-applied SSC-PFSA ionomer was more suitable to be used under lower humidity operation because of the higher proton conductivity of SSC-PFSA ionomer under low humidity.

2.5. Dynamic Performance Response to Operation Conditions. The fuel cell engine is commonly operated under dynamic running, including start-up, shut-down, cycle loading, and so forth. Hence, one of the most important requirements for fuel cells applied in transportation is fine flexibility to the frequent changes and wide range of operation conditions. In this part, it was studied that the voltage variation of SSC-CCM and LSC-CCM during the dynamic course of temperature continuously increased from room temperature to the common operation temperature for the fuel cell both under humidification and nonhumidification.

Figure 11 shows that the voltage curves of SSC-CCM and LSC-CCM during the dynamic courses of working temperature continuously varied under humidification and nonhumidification, respectively. As displayed in Figure 11a, with the operation temperature gradually rising at 100 RH %, the voltages of both SSC-CCM and LSC-CCM increased, and their growth rates were similar. This indicated that both SSC-CCM and LSC-CCM had stable output voltages during a wide range of operation conditions.
range of running temperature if humidity in the fuel cell was sufficient. When operation temperature continuously increased without external humidification, as shown in Figure 11b, the voltages of the two types of CCMs first increased gradually until 53 °C simultaneously. Also, both samples could continue running stably below 53 °C. As the temperature reached 57 °C, the voltage of SSC-CCM went on increasing and could remain stable. However, LSC-CCM's voltage started to decline gradually with the increasing running time. When temperature rising to 59 °C, SSC-CCM's voltage began to decrease lightly and could maintain about 0.65 V while LSC-CCM's performance dropped sharply to the initial value of 0.58 V after running for 30 min. When temperature going on climbing to 62 °C, SSC-CCM's voltage began to drop more quickly than before, but its descent rate was still obviously slower than that of LSC-CCM. After working at 62 °C for about 30 min, the voltage of SSC-CCM was still 0.62 V while that of LSC-CCM was only 0.54 V. Operation temperature of stack continuously increasing without external humidification leads to gradual decreasing of the local humidity in the fuel cell. Therefore, the phenomena, as shown in Figure 11b, revealed that SSC-CCM had higher output power and exhibited more stable running under low operation humidity and then also suggested that SSC-CCM could be applied to working at higher temperature when operation humidity could not be maintained at a high level, compared with LSC-CCM.

For practical automotive applications, the cell voltage should be higher than 0.6 V as high electrical efficiency is required, and operation humidity is required as low as possible to simplify the fuel cell system. It could be found, as shown in Figure 11b, that the voltage of LSC-CCM began to be lower than 0.6 V at 59 °C, and as comparison, SSC-CCM's voltage could always remain higher than 0.6 V during this process. It was further demonstrated that SSC-CCM could run in a wide humidity range while the LSC type was only used under high humidity conditions.

The different behaviors between SSC-CCM and LSC-CCM during the dynamic course could also be ascribed to the employed ionomers with different EW values in the catalyst layer. Because of the higher proton conductivity of SSC-720 under low relative humidity, SSC-CCM could output higher power and showed more running stability at high temperature under lower operation humidity and even dry condition with the comparison of LSC-CCM. The advantages exhibited by SSC-CCM illustrated that the SSC-PFSA ionomer could be employed as the ionomer to manufacture the catalyst layer for transportation applications.

3. CONCLUSIONS

The SSC-PFSA ionomer with EW 720 and the LSC-PFSA ionomer with EW 1100 are employed to prepare two types of CCMs to investigate the effects of PFSA ionomers with different side-chain structures in the catalyst layer on the porous structure and electrochemical performance under a wide operational range and dynamic conditions of CCMs. The manufactured SSC catalyst layer presents a looser porous structure with larger porosity and specific surface area, compared with LSC-CCM. It is showed by electrochemical measurements that SSC-CCM displays lower HFR and larger ECSA than LSC-CCM. Also, SSC-CCM performs better than LSC-CCM at various current densities by lower HFR and larger ECSA. Also, SSC-CCM presents a looser porous structure with larger porosity and specific surface area, compared with LSC-CCM. It is showed by electrochemical measurements that SSC-CCM displays lower HFR and larger ECSA than LSC-CCM. Also, SSC-CCM performs better than LSC-CCM at various current densities by lower HFR and larger ECSA.

4. EXPERIMENTAL SECTION

4.1. Preparation of CCM. The components of the inks for both CCM samples contained the ionomer, catalyst, and the solvent. The SSC-PFSA ionomer dispersion (Aquion D72-25BS, EW 720, Solvay Soolix) and LSC-PFSA ionomer dispersion (Nafion DS20, EW 1100, Dupont) were chosen. The dispersion solvent was a mixture of 1:1 isopropyl alcohol/water, and the catalyst was 40 wt % Pt/VC (Hispe 4000, Johnson Matthey). The solid contents for both inks were 5 wt %, and the ionomer contents in CCLs were 30 wt %.

The catalyst inks were mechanically stirred for 10 min and then ultrasonicated for 30 min to ensure that the ionomer and catalyst particles were well-mixed in the solvent. An automated spray coater (Prism 500, USI) was employed to spray the catalyst ink directly on the membrane (15 μm thick, M820.15, Gore). A vacuum plate with the temperature of 75 °C to hold the membrane, and the flow rate of ink is 0.002 SLPM during spraying. The Pt loading was total of 0.5 mg cm⁻² (anode 0.1 mg cm⁻² and cathode 0.4 mg cm⁻²), which was controlled by the ink volume sprayed on the membrane, and the volume was...
calculated by the solid content and mass density of ink. Then, the CCMs were dried at 130 °C for 0.5 h to remove the residual solvent. Two specifications with an active surface area of 25 cm² (50.0 mm × 50.0 mm) and 75 cm² (150.0 mm × 50.0 mm) for each kind of CCM were prepared for different testings.

The Aquilon ionomer and Nafion ionomer are noted as SSC-720 and LSC-1100, according to their EW values. The CCMs prepared by the SSC ionomer and LSC ionomer are noted as SSC-CCM and LSC-CCM, respectively.

4.2. Fuel Cell Assembly and Testing Protocol. The single-cell stack was assembled with the CCM of 25 cm² active area, GDL (29BC, SGL), and Teflon gasket (170 μm of both anode and cathode). The short stack including six cells was assembled with the CCM of 75 cm² active area, gas diffusion layer (29BC, SGL), and Teflon gasket (170 μm of both anode and cathode). Both CCMs were assembled together in one short stack, and each kind of CCM contained three samples. The compression of GDL was controlled at 25% when assembled the single cell and the short stack.

The stack was evaluated and conditioned by a fuel cell test station (200W, Home-made). Before the electrochemical and polarization curve measurements, all the CCM samples were activated at the current density of 1.0 A cm⁻², 100% relative humidity (RH), and 70 °C for at least 8 h, until the variation of the voltage was less than 3 mV in an hour. The stoichiometric ratios of the reactant gas were 1.6 for H₂ (purity 99.99%) in an anode and 2.2 for air in a cathode.

The electrochemical measurements (electrochemical impedance spectroscopy and cyclic voltammetry) and static polarization performance were carried out by the single-cell stack. The polarization curves under different operation conditions (temperature and relative humidity) and dynamic performance were tested by the short stack.

Polarization curves were measured with the current gradually increasing from open circuit voltage to higher 1.0 A cm⁻² and held for 10 min at each point. The cell potential at the steady state was obtained by averaging the data recorded every 5 s in the last 3 min. The stoichiometric ratios of the reactant gases were maintained at 1.6 for H₂ (purity 99.99%) in the anode and 2.2 for air in the cathode. The gas pressure was ambient. Each polarization curve was repeated three times, and the values were averaged.

4.3. Electrochemical Measurement. 4.3.1. High-Frequency Resistance. In order to measure the ionic resistance in the catalyst layer, high-frequency resistance (HFR) was in-situ measured by the electrochemical workstation (Reference 3000, Gamry) during the polarization curve test. The perturbation amplitude for the AC impedance was 5% of the direct current, and the frequency was 10 kHz, which would not disturb the electrochemical reaction of fuel cell.

4.3.2. Cyclic Voltammetry. Electrochemical surface area (ECSA) was measured with cyclic voltammetry (CV) by the electrochemical workstation (Reference 3000, Gamry). Humidified H₂ (0.01 SLPM, 70 °C, 100 RH %) and N₂ (0.02 SLPM, 70 °C, 100 RH %) were purged for 30 min at the anode and the cathode, respectively. Voltammograms were recorded using a 20 mV/s scan rate between 0 and 1.2 V. The final cycle of a set of five cycles was used for data analysis. The ECSA of MEAs was calculated from the integrated charge corresponding to the Pt—H adsorption peaks.

4.4. Water-Uptake Test. For ex situ analysis, the difference of SSC-PFSA and LSC-PFSA ionomers and the dispersion of SSC-720 ionomer and LSC-1100 ionomer mixed with dimethyl sulfoxide were cast into films by a doctor blade. The solvent was removed by drying at room temperature overnight, and the membranes were annealed at 160 °C under vacuum for 3 h. After this, two membranes were previously dried at 80 °C for 3 h and then were immersed in deionized water at 30, 50, 60, 80, and 100 °C for 1 h. The weight of the samples was weighted before and after this process. Excess liquid water was removed from the surface by the filter paper before reweighed. Three samples with the same size of each type of membrane were measured during the test, and the results were averaged.

The water uptake (W %) was obtained by eq 1.

\[
W \% = \frac{W_f - W_0}{W_0} \times 100\%
\]

where \(W_0\) and \(W_f\) are the masses of the membranes before and after water sorption, respectively.

4.5. Proton Conductivity Test. Resistance measurements were performed by the four-electrode method over the range of the temperature 30, 40, 50, 60, and 70 °C at a RH of 100% and the range of the RH 20, 40, 60, and 100% at a temperature of 60 °C. The membrane resistance was measured by the impedance Instrument (Keysight E4990A, TOYO Corporation China). Three samples with the same size of each type of membrane were measured during the test, and the results were measured.

The proton conductivity was calculated from eq 2.

\[
\sigma = \frac{L}{R \times S}
\]

where \(R\) is the measured resistance, \(L\) is the distance between the electrodes, and \(S\) is the sectional area of the membrane sample and can be calculated by thickness multiplied by the width of membrane.

4.6. Mercury Intrusion Porosimetry. The peak pore size and pore size distribution of the prepared catalyst layers containing SSC and LSC ionomers were examined by a Hg porosimeter (Micromeritics, Auto Pore IV 9500). The two CCMs were cut into pieces with about 2.0 g weight and dried at 80 °C for 3 h before measurement. Three samples of each type of CCM were measured during the test. The applied pressure ranged from 15 to 33,000 psia, corresponding to pore sizes of 10 μm to 10 nm in diameter. Detailed procedures are described in ref 7.

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Notes
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