



## Full Length Article

## Impact of ionomer in the catalyst layers on proton exchange membrane fuel cell performance under different reactant flows and pressures

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## ABSTRACT

To achieve a good performance, proton exchange membrane fuel cells (PEMFCs) require a delicate water balance through the design of cells and selection of operating conditions. In this study, the impact of ionomers with different side-chain lengths, having different water retention capability, serving as binder in the catalyst layers is investigated experimentally for both catalyst layer structure and the resulting cell performance under a wide range of reactant flows and cell operating pressures. The results show that cells with the short side-chain (SSC) ionomers, having a higher water retention capability, achieve a higher cell performance, active surface area, platinum utilization, and porosity than the cells made by the conventional long side-chain (LSC) even under fully humidified condition, in contrast with studies reported in literature. This is achieved for the high reactant flow, which has a higher water removal capability. The SSC ionomer with the low equivalent weight of 720 results in a significantly higher cell performance with the maximum power density of  $1.3 \text{ W/cm}^2$  at the high reactant flow. SSC with the equivalent weight of 790 has a good balance between water retention and water removal in the catalyst layer at a lower airflow. The performance of the cells with the SSCs is better, and it is far less sensitive than, the cells with the LSC when the operating pressure is increased.

## 1. Introduction

Perfluorosulfonic acid (PFSA) ionomers are employed as polymeric electrolytes and binder agents in the catalyst layers (CLs) to provide the required proton conductivity and binding inside proton exchange membrane fuel cells (PEMFCs) [1–4]. Introducing PFSA directly onto the CLs has greatly improved fuel cell performance, a development detailed in the literature [5–8]. It is widely recognized that the amount of ionomer in the CLs significantly affects the ionic transport, catalyst utilization and reactant transport properties, in addition to the binding of the particular nature of the materials in the CLs [9–14]. These PFSA ionomers are commercially available in two forms: long and short side chain (or LSCs and SSCs, respectively) [15]. PEMFCs based on an LSC ionomer (Nafion) have been extensively investigated in terms of in- and ex-situ experimental diagnoses and numerical simulations. Also, well reported in the literature are their effects on fuel cell performance under various key operating conditions [16–19].

PFSA ionomers with shorter side chain lengths were first commercialized by Dow Chemical [20]. The higher glass transition temperatures, proton conductivities, and water retention ability, and the reduced mechanical deformation of these SSC ionomers were proved by

different characterization techniques [21,22]. The characterization results and cell performance demonstrated a better performance of PEMFCs made with SSC ionomers (as an electrolyte) than with LSC ionomers (Nafion 211, 212 and the like) at high temperature and low humidity condition [23,24]. Despite these advantages, the complexity of the synthesis processes halted their production. In 2010, Solvay-Solexis developed an uncomplicated method for producing these ionomers at prices comparable to those for LSC ionomers. Although a number of studies have investigated SSC ionomers as electrolytes in PEMFCs, few have applied SSC ionomers in the CLs and investigated the associated impact on the cell performance [25].

In 2011 [26], SSC ionomers with different ion exchange capacities (IECs) were used in the CLs, and the cell performance was compared with that of CLs containing LSC ionomers. The results indicated ionomers with a higher IEC led to a higher protonic conductivity in the CLs. In addition, under low humidity operation (30% relative humidity), SSC-based MEAs resulted in a higher cell performance in all three regions of the polarization: the activation, ohmic, and concentration regions. However, LSC-based MEAs showed higher performance at low current densities under fully humidified (100%) condition. Further, higher porosity in the CLs made with SSC ionomers was claimed, but

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with only limited evidence. Chao et al. [27] later assessed the performance of CLs made with different ratios of SSC ionomer, and compared the resulting cell performance to that of cells whose CLs were made with LSC ionomer. They showed that cells with lower SSC ionomer levels (10%) in the CLs perform similarly to cells with LSC ionomer levels of 30% under high humidity condition, and better cell performance was achieved by using 20% SSC ionomer under low humidity condition [28,29]. Recently, Cho et al. [30] reported an improvement in cell performance when the SSC ionomer ratio was increased in the cathode side to 40%, again at low humidity operation. In addition to the cell performance, SSC ionomer results in enhanced cell durability, and SSC ionomer has higher stability, which prevents less ionomer thinning, and Pt detachment in comparison to the LSC ionomer [31].

It is clear that employing SSC ionomers in the CLs is beneficial for PEMFC performance. However, beside protonic conductivity for the CLs, the morphology, porosity, active surface area and catalyst utilization, that is, the kinetic and mass transport properties of the CLs, play important roles in the cell performance [32], and the impact of SSC on the CL structure should be investigated. Further, SSC ionomers can increase water retention in the CLs, hence can be expected to perform better in reduced humidity condition, but not necessarily in the fully humidified operation, as noticed in the literature. However, water retention or removal/transport in the CLs can be significantly influenced by the operating conditions, such as cell pressure and reactant flow rates. As a result, the performance of the cells that have been prepared using different SSC ionomers in the CLs should be evaluated under different operating conditions such as cell pressure and reactant flow rates.

Therefore, the objective of the present study is to investigate the influence of ionomers with different equivalent weights, that include the conventional LSC and various SSC ionomers, on the CLs in PEMFCs; and to study the performance of the cells made of these different ionomers in the CLs under different cell operating pressures and reactant flow rates. Therefore, a high Pt loading of 0.5 mg/cm<sup>2</sup> is selected to avoid the sensitivity arising from the Pt loading and to have a high transport resistance arising from a thick CL so that the impact of ionomer structures on the cell performance can be highlighted. In the present study, a scaled-up cell (with an electrode geometric area of 45 cm<sup>2</sup>) is implemented. The morphology, porosity, active surface area and catalyst utilization of the CLs made with the different ionomers are measured, and the performance of the cells with these CLs is obtained under various cell operating pressures and reactant flow rates. Comparison is made with the CLs and cells made of the conventional LSC (Nafion) ionomer under the identical CL/cell preparation and testing conditions.

## 2. Experimental

The catalyst ink is prepared by dispersing an appropriate amount of a commercial 50% Pt/C (TEC10E50E) catalyst, with iso-propanol, and different types of ionomers. Short and long side chain ionomers with equivalent weights (EW) of 720, 790, and 1100 are applied in the catalyst ink with the same ratios, manufactured by Solvay-Solexis and DuPont, respectively, with similar commercial prices. The prepared ink is placed in an ultrasonic bath for 1 h to reach a uniform suspension. Afterward, CLs are made by depositing the catalyst ink on the membrane (Nafion 211) using a vacuum table at 60 °C. The active areas of the membrane-electrode assemblies (MEAs) are 45 cm<sup>2</sup>, and total Pt loading is 0.5 mg/cm<sup>2</sup>. The MEA is placed between two bipolar plates and pressurized to a desirable level by using a controllable air bladder. For brevity and consistency, the MEAs containing SSC ionomers with EWs of 720 and 790 are designated as SSC-7 and SSC-8, respectively, and the MEAs containing Nafion (EW of 1100) is referred to as LSC. The morphologies of the CLs with the different ionomers are studied via a scanning electron microscope (Zeiss GeminiSEM 300). Images are taken after deposition of 5 nm gold coating on the top surface of the catalyst

layers. CL porosity is measured via the Method of Standard Porosimetry (MSP), which was developed based on the capillary equilibrium [33,34]. In-situ electrochemical cyclic voltammetry is applied to calculate the electrochemically active surface areas (EAS) of the selected MEAs, and Pt utilization, while nitrogen and hydrogen are purged through the cathode and anode, respectively. The scan rate is set at 0.05 V/s. The cathode and anode sides act as in a working electrode and counter electrode, respectively. The performance of the MEAs based on the different ionomers is compared by polarization and power density curves. Performance tests are conducted at different flow rates of reactants, referred to as **high flow rate** (Hydrogen gas at 4.450 slpm and air at 9 slpm), **moderate** (stoichiometry ratio of 1.5 for the anode and 4 for the cathode), and **low flow rate** (stoichiometry ratio of 1.5 for the anode and 2 for the cathode). Performance tests are conducted at different pressures of 0 kPag, 35 kPag, 75 kPag and 150 kPag with the operating temperature set at 75 °C.

## 3. Results and discussion

### 3.1. Morphology and porosity of the catalyst layers (CLs)

Fig. 1 shows the SEM images of the top surface of the CLs made with the different ionomers. All the samples show a similar dense surface. However, the CLs with SSC-7 and SSC-8 have a homogeneous surface with higher porosity than the LSC surface. This homogeneity in the CL structure of higher porosity is beneficial to enhance the mass transport and proton conductivity of the CLs [35,36]. Unlike the CLs with SSC-7 and SSC-8, the CL with the LSC has thin and thick regions with agglomeration, which may affect the continuity of proton conduction region, adhesion to the membrane and oxygen diffusion. Higher porosity of the CLs using SSC ionomer is also proved by the measurement of the porosity using the Method of Standard Porosimetry, and the results are compared with the baseline (CL with the LSC ionomer). Porosity of the electrodes with the CL made with the SSC having the EW of 720 and 790 are measured as  $73.1 \pm 1.0\%$  and  $70.4 \pm 1.0\%$ , while it is  $68.8 \pm 1.0\%$  for the electrodes with the CL made with the LSC [37]. It might be mentioned that Fig. 1(c) appears that LSC ionomer is more agglomerated on the surface of the CLs, which makes harder to be focused for a sharp image, indicating that the LSC in the CLs results in the Nafion agglomeration on the CLs.

### 3.2. Active surface area and Pt utilization

In-situ cyclic voltammograms of the different MEAs at the temperature of 80 °C and relative humidity of 100% are shown in Fig. 2. The cycling conditions are set based on the US Department of Energy (DOE) operational conditions [38]. Based on the CL morphology, it is expected that the lack of uniformity in the CLs with LSC will affect the triple phase boundary and decrease the active surface area. The SSC-based MEAs, like the LSC-based MEA, demonstrate common characteristic features of hydrogen adsorption and desorption on the Pt surface. However, hydrogen adsorption and desorption charges, which are quantitatively present in the electrochemical active surface area (ECSA), are better evolved on the SSC-based MEAs. The ECSA is calculated based on the following formula,

$$ECSA = \frac{Q_{ads}}{Q_{ref} \cdot m_{Pt}}$$

where  $Q_{ads}$ ,  $Q_{ref}$ , and  $m_{Pt}$  are the charge of hydrogen adsorption, adequate charge for monolayer adsorption, and Pt loading, respectively.

The calculated ECSA are 60 m<sup>2</sup>/g, 59 m<sup>2</sup>/g, and 52 m<sup>2</sup>/g for the MEAs with SSC-7, SSC-8 and LSC, respectively. The higher ECSA for SSC-7 can be associated with the better coverage of Pt nanoparticles due to the shorter side chain of this ionomer, and with better contact with the membrane due to the uniformity of the CL, as shown in Fig. 1. Pt utilization ( $U_{Pt}$ ) is calculated using the ECSA data and the size of the

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