



Short communication

Fuel cell catalyst layers containing short-side-chain perfluorosulfonic acid ionomers

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ARTICLE INFO

Article history:

Received 26 April 2010

Received in revised form 15 June 2010

Accepted 16 June 2010

Available online 23 June 2010

Keywords:

Short-side-chain PFSA ionomer

PEMFC

Catalyst layers

Low equivalent weight

Fuel cells

PEM

ABSTRACT

Porous catalyst layers (CLs) containing short-side-chain (SSC) perfluorosulfonic acid (PFSA) ionomers of different ion exchange capacity (IEC: 1.3, 1.4 and 1.5 meq g⁻¹) were deposited onto Nafion 211 to form catalyst-coated membranes. The porosity of SSC-PFSA-based CLs is larger than Nafion-CL analogues. CLs incorporating SSC ionomer extend the current density of fuel cell polarization curves at elevated temperature and lower relative humidity compared to those based on long-side chain PFSA (e.g., Nafion)-based CLs. Fuel cell polarization performance was greatly improved at 110 °C and 30% relative humidity (RH) when SSC PFSI was incorporated into the catalyst layer.

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1. Introduction

Perfluorosulfonic acid (PFSA) ionomers are commonly employed in PEMFCs catalyst layers (CLs) to ensure proton transport between the PEM and reaction sites in the CL [1,2]. Current PEMFCs utilize long-side-chain (LSC) PFSA ionomer, e.g. Nafion, and much has been reported on the structure–properties relationships of LSC-PFSA-based CLs [3]. During CL fabrication, carbon-supported Pt and ionomer segregates on various length scales into bicontinuous percolating phases, the optimal Nafion content being ~30–35 wt% [4–8]. For automotive applications it is preferable that PEMFCs operate at temperatures >100 °C and low RH but LSC-PFSA ionomer loses proton conductivity above 90 °C and under lower RH [9]. Attention is thus being paid to short-side-chain (SSC) PFSA ionomers, as they possess longer sequence lengths between side chains (for a given IEC) that translate to a higher degree of crystallinity and higher thermal transition temperatures than LSC analogues [10,11]. Moreover, the enhanced

crystallinity enables the preparation of higher IEC PFSA ionomers that do not dissolve or become too gelatinous upon exposure to water. SSC-PFSA ionomer was developed by Dow Chemicals in the mid-1980s, however, due to the complexity and cost of synthesis of the functional monomer further development was abandoned [12]. A simpler route for the synthesis of SSC ionomer was developed and marketed under the trade name Aquivion[®] (previously Hyflon[®]) by Solvay Solexis [12]. SSC-PFSA ionomer membranes (PEMs) have been previously characterised ex situ and in fuel cells [10,13–15], as have theoretical studies aiming to explain the morphology of SSC-PFSA as a function of IEC [16,17]. The development of new ionomers to replace Nafion as a membrane has led to the incorporation of new ionomers in the catalyst layer. The influence of parameters such as ion exchange capacity and ionomer content of the catalyst layer has been previously reported for LSC-PFSA [8,18,19] and for several non-perfluorinated polymers, examples of which include sulfonated polyetherketones [20–24], polyimides [25], polybenzimidazoles [26], sulfonated polysulfones and polyethersulfones [27–29].

However, despite the importance of the ionomer in the CL [1,2], reports on the incorporation of SSC-PFSA, and the effect of incorporating high IEC ionomer, are absent. In this work the influence of SSC-PFSA, and IEC, on fuel cell CL performance is reported and compared to Nafion ionomer. The IECs of SSC-PFSA studied were 1.3, 1.4, and 1.5 meq g⁻¹, i.e. much higher than that of Nafion

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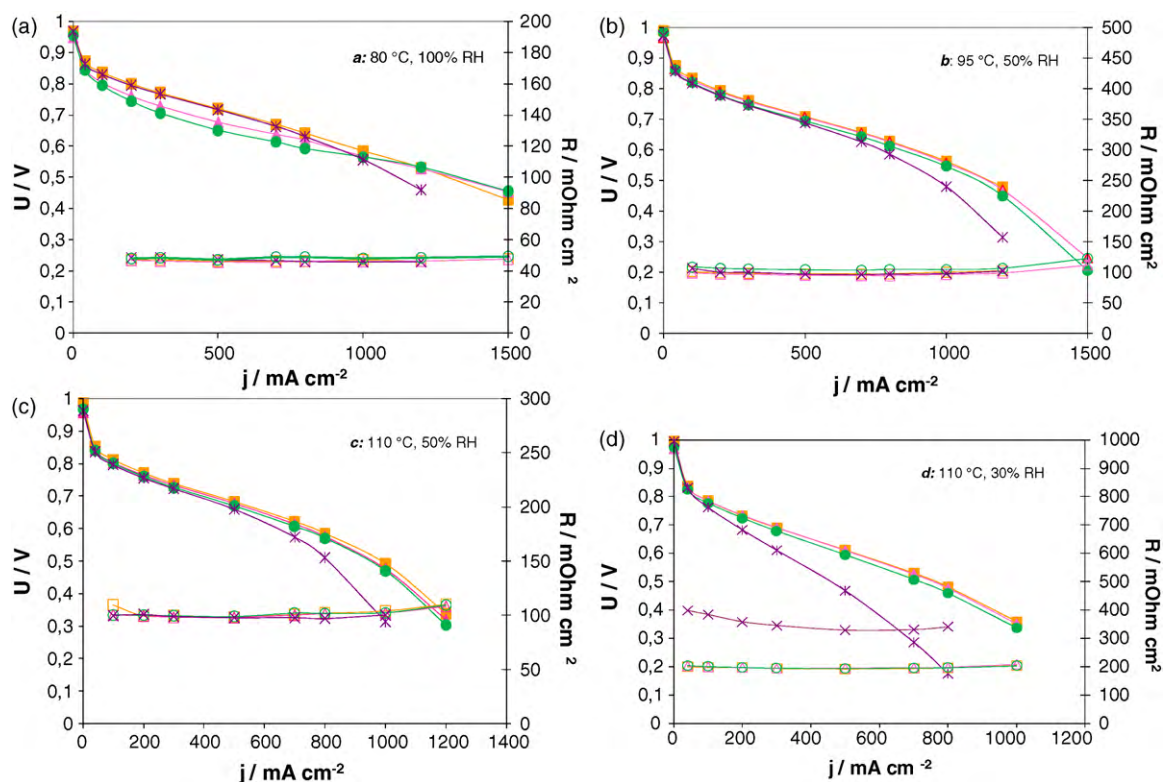


Fig. 1. H₂/air polarization curves (filled) and HFR (open) for MEAs composed of Nafion 211 PEM, and CLs containing SSC-1.3 (■); SSC-1.4 (▲); SSC-1.5 (●); and Nafion (×). (a) 80 °C/100% RH; (b) 95 °C/50% RH; (c) 110 °C/50% RH; (d) 110 °C/30% RH.

(0.95–1.00 meq g⁻¹). Electrochemical properties and fuel cell performance of SSC-PFSA-based CLs were studied as a function of temperature and RH.

2. Experimental

Nafion membranes (NR211) and dispersions (D-520) were purchased from Aldrich. Short-side-chain ionomers were provided by Shanghai Jia Tong University and synthesized as described previously [12] from CF₂CF(OCF₂CF₂SO₂F) monomer. Short-side-chain (SSC) PFSA ionomers having IEC (equivalent weight, EW) 1.3 (770), 1.4 (715) and 1.5 meq g⁻¹ (670 g_{polymer}/n_{SO₃H}) were used. In the text these are distinguished using SSC-1.3, SSC-1.4, SSC-1.5 terminology.

Catalyst inks were prepared as described in Ref. [30]. Catalyst-coated membranes (CCMs) were prepared by spraying catalyst ink onto as-received NR211 membranes. For each electrode, the Pt loading was 0.4 mg cm⁻², and the ionomer content was 30 wt% of the total mass of the CL. 24BC type gas diffusion layers (SGL) were used for fuel cell testing. Membrane-electrode-assemblies (MEAs) were tested in a 25 cm² single-cell possessing straight-flow channels using a Scribner 870C fuel cell test station, hydrogen (2 L min⁻¹) and air (5 L min⁻¹) with no back-pressure. Cells were conditioned for at least 4 h at 1 A cm⁻². The ionic conductivity of

the CLs was determined using in situ electrochemical impedance spectroscopy (EIS) under H₂/N₂ 0.5/0.5 L min⁻¹ using the technique reported elsewhere [30].

For ex situ analyses of SSC-PFSA ionomers, a 5 wt% dispersion in water/alcohol was cast into films using a doctor blade. Solvent was removed by drying at r.t. overnight, and the membrane annealed at 160 °C under vacuum for 3 h. Water uptake was measured using the mass difference between dry membranes (80 °C, under vacuum overnight) and membranes that were conditioned in water at r.t. In-plane conductivity measurements were performed using a Solartron 1260. Temperature and RH were controlled with an ESPEC SH-240 chamber. Uncertainties were calculated from measurements performed under the same conditions on multiple samples.

3. Results and discussion

Polarization curves obtained at 80 °C 100% RH for SSC-PFSA and Nafion-based CLs, all employing a Nafion NR211 PEM, are shown in Fig. 1a. At current densities <1 A cm⁻² MEAs containing SSC-1.3 based CLs show similar performance compared to the Nafion analogue, but under higher current densities the voltage generated exceeds that for Nafion-CLs. SSC-1.4 and SSC 1.5 CLs show lower performance under lower current densities but the curves are comparable to SSC-1.3 for current densities >1 A cm⁻². The

Table 1
Ex situ properties of CLs containing SSC-PFSA ionomer.

Ionomer	IEC (meq g ⁻¹)	Water uptake ^a (wt%)	$\sigma_{\text{membrane}}^a$ (S cm ⁻¹)	σ_{CL}^b (S cm ⁻¹) ^b
SSC-1.3	1.3 ± 0.03	45 ± 6	0.087 ± 0.003	0.018 ± 0.004
SSC-1.4	1.4 ± 0.02	150 ± 11	0.097 ± 0.003	0.023 ± 0.005
SSC-1.5	1.5 ± 0.04	250 ± 18	0.11 ± 0.008	0.047 ± 0.007
Nafion 211	1.0 ± 0.03	23 ± 3	0.075 ± 0.003	0.025 ± 0.004

^a Obtained after equilibration in liquid water at r.t.

^b Measured in situ at 80 °C/100% RH under H₂/N₂.

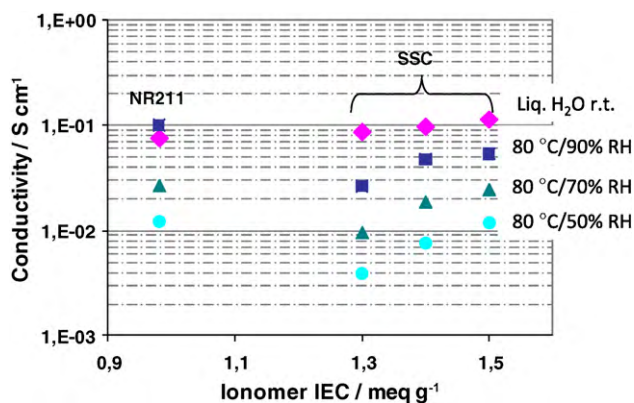


Fig. 2. Influence of IEC on conductivity properties SSC-PFSA at r.t./fully hydrated (◆); at 80 °C/90% RH (■); 80 °C/70% RH (▲) and 80 °C/50% RH (●).

ionic resistances of the CLs, measured at 80 °C and 100% RH, are displayed in Table 1. Within the SSC-PFSA ionomer series, the resistance decreases as IEC of the ionomer increases. The conductivity of CLs prepared from commercial LSC-PFSA (Nafion) lies in the same range as the SSC-PFSA ionomers: higher than SSC-1.3-based CLs but lower than SSC-1.5.

Polarization curves were also obtained under increasing temperature and diminishing RH, i.e., conditions favoured for automotive applications. Polarization curves obtained at 95 °C/50% RH, 110 °C/50% RH, and 110 °C/30% RH are shown in Fig. 1b–d, respectively. At 95 °C/50% RH the performance of SSC-PFSA CLs, with respect to Nafion-based CLs, increases. At even higher temperatures (110 °C/50% RH and 110 °C/30% RH), the relative performance of SSC-PFSA CLs is significantly higher. Furthermore, over the whole range of current density, the fuel cell performances for SSC-PFSA ionomer with increasing IEC are similar. Under the same conditions, and at current densities >50 mA cm⁻², the resistance of SSC-PFSA-CL MEAs (determined by current-interrupt and HFR methods) is much lower than the Nafion analogue. These resistance measurements characteristically report the resistance of the membrane during fuel cell operation. Since NR211 is the PEM used in all of the MEAs studied, the data indicate that incorporating SSC-PFSA ionomer into the CL reduces the membrane resistance during operation under conditions of elevated temperature (110 °C) and reduced RH (30%), and most likely facilitates this by reducing the extent of membrane dehydration. This corroborates findings from Xu et al. [18] who showed enhanced performance at 120 °C/35% RH using high IEC LSC-PFSA. According to Xu et al. [18] and Liu et al. [19] the optimum performance for high IEC PFSA is obtained for lower ionomer loading compared to Nafion-CL. It is reasonable to assume that the performance of the systems discussed above could be further improved by finding the optimum ionomer content for each IEC in the catalyst layer.

Ex situ measurements of proton conductivity and water uptake of SSC-PFSA ionomers were undertaken in order to provide insight into the reason for the enhanced performance of the SSC-PFSA CLs. These parameters were measured on SSC-PFSA in the form of membranes and compared with commercial NR211 membrane. Proton conductivity, measured in liquid water at r.t., and at 80 °C, as a function of RH, is shown in Fig. 2. Under the conditions studied, the ionomer conductivity increases with IEC. Despite the higher IEC of the SSC-PFSA membranes the protonic conductivity is generally lower than the commercial LSC membrane, except under fully hydrated conditions. From this we infer that arguments based on the conductivity of the ionomer alone cannot explain the enhanced fuel cell performance of SSC-PFSA CLs at elevated temperature. However, it is noted that SSC-PFSA, in the form of

membranes absorb more water than NR211. For example, fully hydrated SSC-PFSA membranes having IECs 1.3, 1.4, and 1.5 absorb 45, 150 and 250 wt% water, respectively. For NR211, it is 23 wt%. Although water sorption measurements at elevated temperature and reduced RH would provide a more meaningful comparison, it is reasonable to assume that SSC-PFSA would absorb more water than Nafion 211 at elevated temperature.

4. Conclusion

A series of SSC ionomers with IECs ranging from 1.3 to 1.5 meq g⁻¹ have been characterised in catalyst layers, and compared with a commercial LSC-PFSA ionomer. The conductivity of the SSC-PFSA ionomer both as a membrane and in the catalyst layer increases with IEC. At elevated temperatures and lower relative humidity, the incorporation of high IEC SSC-PFSA ionomer in CLs leads to a significant improvement in the high current density regime of fuel cell performance curves compared to Nafion. It is postulated that SSC-PFSA, with its much higher IEC, mitigates the effects of dehydration at elevated temperature and lower relative humidity.

Acknowledgement

We gratefully acknowledge Shandong Dongyue Chemical Co. Ltd. for synthesis of the SSC-PFSA ionomers.

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