

Investigation of PEMFC operation above 100 °C employing perfluorosulfonic acid silicon oxide composite membranes

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Abstract

Various perfluorosulfonic acid membranes (PFSAs) were studied as pure and silicon oxide composite membranes for operation in hydrogen/oxygen proton-exchange membrane fuel cells (PEMFCs) from 80 to 140 °C. The composite membranes were prepared either by impregnation of pre-formed PFSAs via sol–gel processing of a polymeric silicon oxide, recasting a film using solubilized PFSAs and a silicon oxide polymer/gel. All composite membranes had a silicon oxide content of less than or equal to 10% by weight. Decreasing the equivalent weight and thickness of the PFSAs, in addition to the incorporation of silicon oxide helped improve water management in a PEMFC at elevated temperatures. Fourier transform-infrared spectroscopy–attenuated total reflectance (FT-IR–ATR), and scanning electron microscopy (SEM) experiments indicated an evenly distributed siloxane polymer in all of the composite membranes. At a potential of 0.4 V the Aciplex 1004/silicon oxide composite membrane in a humidified H₂/O₂ PEMFC at 130 °C and a pressure of 3 atm delivered six times higher current density than unmodified Nafion 115 under the same conditions, and 1.73 times the current density when unmodified Nafion 115 was operated with humidified gases at 80 °C and 1 atm of pressure. Furthermore, the PEMFC performances with the PFSA/silicon oxide composite membranes were physically more robust than the control membranes (unmodified PFSAs), which degraded after high operation temperature and thermal cycling. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recent advances have made hydrogen/oxygen proton-exchange membrane fuel cells (PEMFCs) a potential alternative to internal combustion and diesel engines for transportation. [1] Cells of this type have also been suggested for stationary power generation. [1] These advances include the reduction of the platinum loading needed for electrocatalysis, and membranes with: (i) high specific conductivity (0.1 (Ω cm)⁻¹) (ii) good water retention and (iii) long lifetimes [2].

The advantages of PEMFCs over thermal engines are the ultra low or zero emissions of environmental pollutants (CO, NO, VOCs, and SO_x), fewer moving parts and higher theoretical efficiencies for energy conversion. [3] PEMFCs perform optimally with pure H₂ and O₂ as the reactant gases. Hydrogen is typically produced by fuel processing of liquid hydrocarbons or alcohols. The most developed systems are a steam reforming with water gas shift and a partial oxidation

method with methane, methanol or gasoline as the fuels, but in both of these cases, the CO level in the product gas stream is typically 50–100 ppm [4].

Carbon monoxide is a major problem because trace amounts of CO in the H₂ feed gas (more than 10 ppm) will poison the Pt anode electrocatalyst in the state-of-the-art PEMFCs operating at 80 °C. CO-tolerant electrocatalysts (such as Pt–Mo, Pt–Ru) have been investigated, but problems still exist with these electrocatalysts. They include (i) a 5–10 times higher Pt loading than required for pure platinum catalysts and (ii) maximum CO tolerance of ~50 ppm and (iii) an increased overpotential for the anodic reaction in the presence of low level CO [5–7]. An alternate approach to gain CO tolerance is to take advantage of the fact that the free energy of adsorption of carbon monoxide on Pt has a larger positive temperature dependence than that of H₂. Therefore, H₂ adsorption on Pt becomes competitive with CO adsorption, and at elevated temperature CO tolerance levels [8–10]. A quantitative analysis of the free energy for the H₂ and CO adsorption as a fraction of temperature [11] suggests that by elevating the operating temperature of the cell to 145 °C, CO tolerance at the anode should increase by

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a factor of ~ 20 (from 5–10 to 100–200 ppm). This effect has been shown experimentally in commercialized phosphoric acid fuel cell power plants. Cells of this type operating at 200 °C, demonstrate a CO tolerance of about 1% [12].

Other difficulties, encountered with PEMFCs, are the elaborate water and thermal management sub-systems needed to achieve optimal performance and maintain ideal operating temperatures. By elevating the temperature of the fuel cell stack, thermal management can be simplified due to more efficient waste heat rejection. However, current PEMFCs utilize sulfonated perfluoropolymer membranes and the ability of this type of proton-exchange membrane to conduct protons is proportional to its extent of hydration. Presently, reactant gases need to be humidified before entering the cell to avoid drying out the membrane. Membrane dehydration also causes the membrane to shrink, reducing the contact between the electrode and membrane, and may also introduce pinholes leading to the crossover of the reactant gases. Thus, the concept of operating a cell at higher temperatures to alleviate the CO poisoning problem introduces another dilemma; keeping the membrane hydrated in order to maintain proton conductivity and its mechanical properties.

This work analyzes parameters important to the performance of perfluorosulfonic acid membranes (PFSA) and the incorporation of silicon oxide for the operation of a PEMFC above 100 °C. Wakizoe et al. [2] and Chu et al. [13] investigated various forms of PFSA well below 100 °C in PEMFCs. They demonstrated that by lowering the equivalent weight (i.e. g of polymer per mol of sulfonate groups) and decreasing the thickness of the membrane, fuel cell performance improves due to decreased membrane resistivity. Watanabe et al. [14] and Antonucci et al. [15] have investigated reducing the water loss from Nafion to maintain proton conductivity by incorporating hydrophilic micron size metal oxide particles (e.g. SiO_2 , TiO_2) with some success. Mauritz et al. used a sol–gel technique to introduce a polymeric form of silicon oxide into Nafion. Using this method, it was shown that silicon oxide entered the fine hydrophilic channels ($\cong 50$ Å in diameter) of Nafion homogeneously. [16] Although improved membrane water retention at normal operating temperatures has been demonstrated, [17] no elevated H_2/O_2 PEMFC experiments above 100 °C have been reported by any of the aforementioned studies. We previously [11] showed using the Mauritz's synthetic procedure for the incorporation of silicon oxide in Nafion that water management within the PFSA improved at elevated temperatures in a H_2/O_2 PEMFC, demonstrating acceptable current densities up to at least 130 °C.

To solve both the CO poisoning, and the water–thermal management problems, present state-of-the-art PFSA, such as Nafion 115 need to be modified in order to remain hydrated at higher operating temperatures. In this study, it is proposed that the water management properties of the PFSA can be improved at temperatures above 100 °C by decreasing the equivalent weight and thickness of the

membrane and impregnating the membrane pores with a hydrophilic siloxane polymer. This was accomplished by either impregnating an extruded PFSA film via sol–gel processing of tetraethoxysilane, or by preparing a recast film, using solubilized PFSA and a silicon oxide polymer/gel. Tetraethoxysilane when reacted with water in an acidic medium undergoes polymerization to form a mixture of silicas (SiO_x) and siloxane polymer with terminal hydroxide and ethoxide groups. This material is referred to as $\text{SiO}_x/\text{OH}/\text{OEt}$. When PFSA is used as the acidic medium, the $\text{SiO}_x/\text{siloxane}$ polymer forms within the membrane.

2. Experimental

Pre-formed PFSA Aciplex 1004 (Asahi Chemical Inc.), Nafion 115, 112, 105 (DuPont Chemical) were pre-treated by re-fluxing it in a 50:50 mixture (v/v) of water and concentrated HNO_3 (70.8% HNO_3 , Fisher) for 6–8 h, followed by a 50:50 mixture (v/v) of water and concentrated H_2SO_4 (95–98% H_2SO_4 , Fisher) for 6–8 h to remove trace metal impurities. The membranes were then re-fluxed in dionized H_2O until the pH of the H_2O was equal to or greater than 6.5 indicating that all excess acid was removed from the membrane. After the membranes were dried for 24 h in a vacuum oven at 100 °C, they were immersed in a 2:1 mixture (v/v) of methanol/ H_2O for 5 min followed by immersion in a 3:2 mixture (v/v) of tetraethoxysilane (98% TEOS, Aldrich)/methanol for varied amounts of time. The duration of time varied according to the desired percentage of weight of silicon oxide and which membrane was used. After the treatment, the membrane was placed in a vacuum oven at 100 °C for 24 h [16]. The composite membranes were then re-fluxed in 3% by volume H_2O_2 for 1 h to remove organic impurities, two times in dionized H_2O for 1 h, in 0.5 M H_2SO_4 for 1 h and two times in dionized H_2O for 1 h.

Recast PFSA silicon oxide membranes were prepared by mixing 5% commercial PFSA solution Nafion (Dupont Chemical) or Aciplex (Asahi Chemical Inc.) with double its volume of isopropyl alcohol and varying amounts of a siloxane polymer solution. The siloxane polymer solution was prepared by mixing 2 ml of TEOS, 4.7 ml of dionized H_2O and 100 ml 0.1 M HCl for 3 h at room temperature [18]. The PFSA, isopropyl alcohol and siloxane polymer solution was then placed in an oven at 90 °C overnight. After the recast membranes were formed, they were post-treated in the same manner as the pre-formed PFSA/silicon oxide membranes.

Electron microprobe (CAMECA SX-50) analysis was used to obtain the distribution of Si and O over the cross-section of the composite membranes. Fourier transform-infrared spectroscopy–attenuated total reflectance (FT-IR–ATR) spectra were obtained using a Bio-Rad spectrometer (resolution = 2 cm^{-1}). A ZnSe crystal was used as the ATR plate with an angle of incidence of 45°.

The Pt/C fuel electrodes (E-TEK Inc.) with a Pt loading of 0.4 mg cm^{-2} , were impregnated with 0.6 mg cm^{-2} of PFSA (dry weight) by applying 12 mg cm^{-2} of 5% PFSA solution with a brush. The electrode area was 5 cm^2 . The membrane electrode assembly (MEA) was prepared by heating the electrode/membrane/electrode sandwich (active area of electrode was 5 cm^2) to $90 \text{ }^\circ\text{C}$ for 1 min in a Carver Hot-Press with no applied pressure, followed by increasing the temperature to $130 \text{ }^\circ\text{C}$ for 1 min with no applied pressure and finally hot-pressing the MEA at $130 \text{ }^\circ\text{C}$ and 2 MPa for 1 min. The MEA was positioned in a single cell test fixture, which was then installed in the fuel cell test station (Globetech Inc., GT-1000). The test station was equipped for the temperature-controlled humidification of the reactant gases (H_2 , O_2 and air) and for the temperature control of the single cell. Flow rates of the gases were controlled using mass flow controllers. The total pressure of the gases was controlled using back-pressure regulators.

For the performance evaluation of the PEMFC, the single cell was fed with humidified H_2 and O_2 at atmospheric pressure (reactant gas and water vapor pressure equal to 1 atm) and the temperature of the H_2 and O_2 humidifiers and of the single cell was raised slowly to 90, 88 and $80 \text{ }^\circ\text{C}$, respectively. During this period, the potential of the single cell was maintained at a constant value of 0.4 V, to reach an optimal hydration of the membrane using the water produced in the cell. After the single cell had reached steady-state conditions (i.e. current density remained constant over time at a fixed potential), cyclic voltammograms were recorded at a sweep range of 20 mV s^{-1} in the range of 0.1–1 V versus RHE for 1 h, in order to determine the electrochemically active surface area. Cell potential versus current density measurements were then made under the

desired conditions of temperature and pressure in the PEMFC. Identical procedures were followed for all PFSA. All PEMFC experiments were carried out at the cell temperatures of 80, 130 and $140 \text{ }^\circ\text{C}$ with the total pressure (reactant gas plus water vapor pressure) at 1 or 3 atm. The total cell pressure was varied so that the partial pressures of the reacting gases (O_2 and H_2) were maintained approximately constant independent of temperature. The flow rates of gases were two times stoichiometric.

3. Results and discussion

Electron microprobe data indicated a homogeneous and uniform distribution of Si and O across all Nafion and Nafion composite membranes as previously reported for a Nafion 115 silicon oxide membrane. [11] Homogeneity was observed down to 1μ resolution (the highest resolution investigated). FT-IR-ATR spectra of all composites illustrate absorption bands corresponding to the stretching frequencies of Si–O, Si–OH, Si–OEt, Si–O–Si in addition to the stretching frequencies associated with the Nafion membrane. [11] These two sets of data in conjunction show a uniformly distributed backbone of Si–O, Si–OH, Si–OEt and Si–O–Si within the PFSA of all membranes investigated.

Typical cyclic voltammograms for the cathode in the presence of 1 atm H_2 with the unmodified Nafion 115 and Nafion 115/silicon oxide membranes are shown in Fig. 1. Integration of the anodic peak at 0.1 V versus RHE ($\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$) and assuming a coulombic charge of $220 \mu\text{C cm}^{-2}$ for a smooth platinum surface, [2] an average roughness factor of $135 \text{ cm}^2 \text{ cm}^{-2}$ per geometric area for all

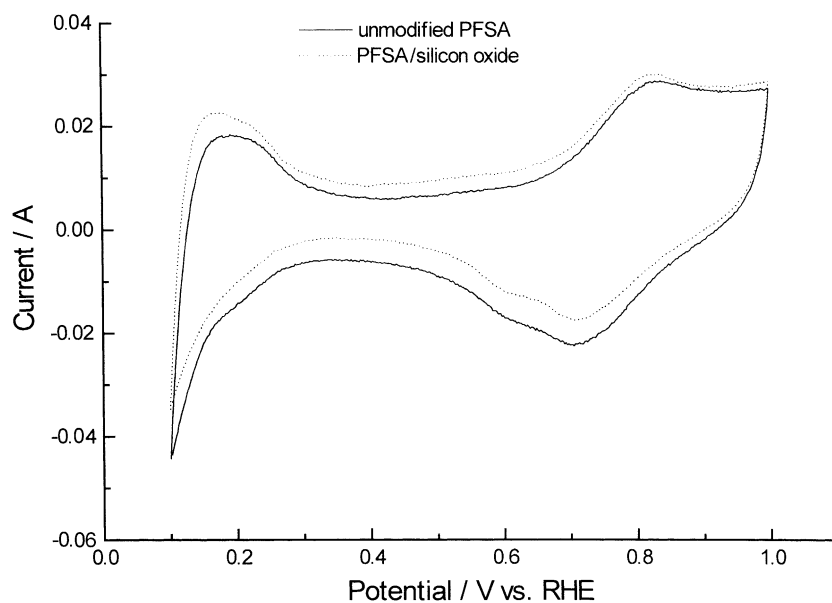


Fig. 1. Cyclic voltammograms (scan rate 20 mV s^{-1}) on cathodes (E-TEK electrodes 30% Pt/C, $0.4 \text{ mg Pt cm}^{-2}$) in PEMFCs (5 cm^2 cell) with unmodified PFSA (—) and PFSA/silicon oxide membranes (···); H_2 in the counter electrode and N_2 in the test electrode chambers, $80 \text{ }^\circ\text{C}$ and 1 atm.

Table 1
Electrode-kinetic parameters for PEMFCs with control and test membranes

Membrane	Temperature H ₂ /cell/O ₂ (°C)	Pressure (atm)	E _o (mV)	b (mV per decade)	i _o (mA cm ⁻²)	R (Ω cm ²)	Current density (mA cm ⁻²)	
							at 0.9 V	at 0.4 V
Hydrogen and oxygen used as fuels								
Control Nafion 115	90/80/88	1/1	991	43	4.0 E-6	0.28	6	1275
	130/130/130	3/3	1000	93	2.4 E-3	1.3	8	280
	130/140/130	3/3	937	87	4.3 E-4	2.1	8	200
Control Nafion recast	130/130/130	3/3	910	43	5.2 E-8	0.5	1	770
	130/140/130	3/3	900	42	3.1 E-8	2.4	–	207
Control Nafion 112	130/130/130	3/3	904	41	1.20 E-8	0.5	2	765
	130/140/130	3/3	898	41	8.45 E-9	0.83	–	465
Control Nafion 105	130/130/130	3/3	914	50	5.10 E-7	0.45	2	815
	130/140/130	3/3	904	38	2.8 E-9	1.4	2	300
Control Aciplex 1004	130/130/130	3/3	989	69	3.3 E-4	0.4	9	775
	130/140/130	3/3	961	62	4.76 E-5	1.0	7	380
Control Aciplex recast	130/130/130	3/3	934	61	1.46 E-5	0.4	5	885
	130/140/130	3/3	944	66	4.80 E-5	0.98	2.5	380
Nafion 115/silicon oxide (6%)	130/130/130	3/3	932	92	6.9 E-4	0.36	8.3	848
	130/140/130	3/3	930	96	8.7 E-4	0.81	8.1	389
Nafion recast/silicon oxide (10%)	130/130/130	3/3	932	72	9.1 E-5	0.33	4	969
	130/140/130	3/3	931	61	1.6 E-5	0.78	3	471
Nafion 112/silicon oxide (6%)	130/130/130	3/3	918	67	2.28 E-5	0.22	2	1395
	130/140/130	3/3	904	71	2.64 E-5	0.44	3	685
Nafion 105/silicon oxide (6%)	130/130/130	3/3	931	76	1.20 E-4	0.36	4	1145
	130/140/130	3/3	935	73	9.39 E-5	0.71	3	475
Aciplex 1004/silicon oxide (6%)	130/130/130	3/3	975	66	1.42 E-4	0.21	8	1725
	130/140/130	3/3	976	73	3.42 E-4	0.55	7	675
Aciplex recast/silicon oxide (10%)	130/130/130	3/3	918	70	3.61 E-5	0.28	6	1090
	130/140/130	3/3	906	70	2.43 E-5	0.63	–	505
Hydrogen and air used as fuels								
Control Nafion 115	130/130/130	3/3	888	61	2.57 E-6	1.59	–	217
	130/140/130	3/3	885	47	4.80 E-6	2.62	–	145
Control Nafion recast	130/130/130	3/3	861	58	4.52 E-7	1.27	–	335
	130/140/130	3/3	855	61	7.39 E-7	3.15	–	140
Control Nafion 112	130/130/130	3/3	882	33	3.05 E-11	0.96	–	410
	130/140/130	3/3	874	45	1.29 E-8	1.65	–	222
Control Nafion 105	130/130/130	3/3	906	42	2.04 E-9	0.98	1	407
	130/140/130	3/3	892	47	6.76 E-8	2.18	–	177
Control Aciplex 1004	130/130/130	3/3	887	33	4.33 E-11	0.99	–	430
	130/140/130	3/3	892	31	1.34 E-11	2.05	–	200
Nafion 115/silicon oxide (6%)	130/130/130	3/3	896	49	1.60 E-7	0.78	–	465
	130/140/130	3/3	892	38	1.35 E-9	1.91	–	210
Nafion recast/silicon oxide (10%)	130/130/130	3/3	918	37	3.93 E-9	0.73	3	570
	130/140/130	3/3	864	53	1.30 E-7	2.0	–	170
Nafion 112/silicon oxide (6%)	130/130/130	3/3	887	45	2.51 E-8	0.53	–	670
	130/140/130	3/3	884	57	8.86 E-7	0.73	–	445
Nafion 105/silicon oxide (6%)	130/130/130	3/3	900	58	2.13 E-6	0.61	–	565
	130/140/130	3/3	898	58	1.96 E-6	1.3	–	275
Aciplex 1004/silicon oxide (6%)	130/130/130	3/3	932	49	8.68 E-7	0.52	3	780
	130/140/130	3/3	906	43	3.07 E-8	1.4	–	317

of the unmodified and silicon oxide membranes was obtained.

The main objective of this study was to determine whether lowering the equivalent weight and reducing the thickness of the PFSA's with and without and silicon oxide would increase the current density obtained at a fixed potential at a temperature of 130 to 140 °C. By limiting the total pressure to 3 atm, the maximum operating temperature was limited to 140 °C with the humidification bottles set at 130 °C, since the equilibrium vapor pressure of water at 130 °C is 2.5 atm.

All cell potential (E) versus current density (i) data was analyzed by fitting experimental current–potential data points to Eq. (1)

$$E = E_o - b \log i - Ri \quad (1)$$

where E_o is the observed open cell potential, b the Tafel slope and R accounts for the linear variation of overpotential with current density primarily due to ohmic resistance. The exchange current density (i_o) of the oxygen reduction reaction can be calculated using Eq. (2)

$$i_o = 10^{(E_o - E_R)/b} \quad (2)$$

where E_R is the thermodynamic open cell potential; $E_R = 1.21$ V at 80 °C, $E_R = 1.20$ V at 130 °C, $E_R = 1.19$ V at 140 °C [19].

The electrode kinetic parameters derived from Eqs. (1) and (2) for all of the investigated PFSA's are presented in Table 1. These results are discussed later in this section.

We have chosen Nafion 115 operating at a single cell temperature of 80 °C with the hydrogen/oxygen gases pre-humidified at 90 and 88 °C, respectively and 1 atm of

pressure as the standard for fuel cell performance. Fig. 2 and Table 1 compares the various unmodified PFSA's when operated at a single cell temperature of 130 °C, with the hydrogen/oxygen gases pre-humidified at 130 °C and 3 atm of pressure. The partial pressure of the reactant gases (H_2/O_2) under both the 80 °C operating condition and the 130 °C operating condition is ~ 0.5 atm due to the increase of the equilibrium vapor pressure of water from ~ 0.5 atm at 80 °C to ~ 2.5 atm at 130 °C. Based on comparing the current densities and resistivities of the cell, the order of performance from best to worst is as follows:

Aciplex recast \sim Aciplex 1004 $>$ Nafion 105
 $>$ Nafion 112 $>$ Nafion recast $>$ Nafion 115

This trend can clearly be rationalized by considering the physical/chemical characteristics of the membranes presented in Table 2. The resistivity of the cell decreases as the equivalent weight and thickness of the PFSA's decreases. Nafion 112 and 115 have the same equivalent weight of 1100 g of polymer per mol of sulfonic acid, while Nafion 112 is 75 μ m thinner. The thinner Nafion membrane (112) exhibits a lower resistivity ($R = 0.5 \Omega \text{ cm}^2$ versus $1.3 \Omega \text{ cm}^2$). Nafion 105 and 115 have the same thickness of 125 μ m, while Nafion 105 has a higher sulfonate density (1000 equivalent weight versus 1100 equivalent weight). The lower equivalent weight Nafion membrane (105) provides a lower resistivity ($R = 0.45 \Omega \text{ cm}^2$ versus $1.3 \Omega \text{ cm}^2$). At a cell temperature of 130 °C, Nafion 105 exhibits the lowest resistivity versus the two other extruded Nafion membranes (115, 112) indicating that equivalent weight plays a larger role than membrane thickness in maintaining the proton conductivity at 130 °C. The two Aciplex membranes (recast

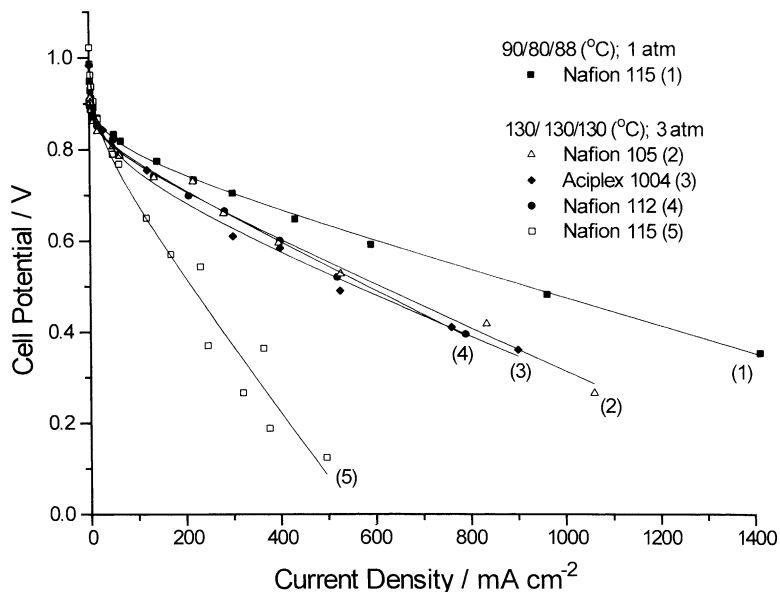


Fig. 2. Cell potential vs. current density of Nafion 115 control (■) H_2 humidifier temperature: 90 °C, O_2 humidifier temperature: 88 °C, cell temperature: 80 °C; pressure 1 atm. Nafion 105 control (Δ), Aciplex 1004 control (\blacklozenge), Nafion 112 control (\bullet), and Nafion 115 control (\square). H_2 and O_2 humidifier temperature: 130 °C, cell temperature: 130 °C; pressure of 3 atm.

Table 2
Physical and chemical makeup of electrolytes

Membrane	Thickness (μm)	Equivalent weight (g of polymer per mol of sulfonate)
Nafion 115	125	1100
Nafion recast	100–125	1050
Nafion 112	50	1100
Nafion 105	125	1000
Aciplex 1004	100	1000
Aciplex recast	100–125	1000
Nafion 115/silicon oxide	~ 137	1100
Nafion recast/silicon oxide	~ 125 –150	1050
Nafion 112/silicon oxide	~ 72	1100
Nafion 105/silicon oxide	~ 137	1000
Aciplex 1004/silicon oxide	~ 112	1000
Aciplex recast/silicon oxide	~ 125 –150	1000

and 1004) demonstrate the lowest resistivity ($R = 0.4 \Omega \text{ cm}^2$) of all of the PFSA's, with lower equivalent weights and thicknesses than Nafion 115 (1000 equivalent weight and $100 \mu\text{m}$ versus 1100 equivalent weight and $125 \mu\text{m}$ mils).

Although at 130°C Aciplex 1004 provides the best performance characteristics, at a single cell temperature of 140°C , and with pre-humidified reactant gases at 130°C and a total pressure of 3 atm (Fig. 3 and Table 1), Nafion 112 outperforms all of the other PFSA's with the overall trend remaining the same. This suggests that at a cell temperature of 140°C and reduced relative humidity (due to $T_{\text{humidifier}} < T_{\text{cell}}$), thickness plays a larger role than equivalent weight in maintaining adequate proton conductivity. Two reasons can be put forward for the improved water management characteristics of a thinner membrane

at elevated temperature and low relative humidity. First is a simple decrease in membrane resistance due to the decreased proton conductivity path. The second reason has to do with the dynamic water content within the membrane. At elevated temperatures and low humidity the anode in a PEMFC can be regarded as being relatively dry, while product water is formed at the cathode maintaining reasonable hydration in this region of the cell. This environment results in a water gradient across the membrane with the product water diffusing back toward the anode [14]. In thinner membranes the gradient is increased, enhancing the flow of water back toward the anode thereby maintaining improved hydration across the membrane.

Despite the variations of the PFSA's physical and chemical makeup, the resistivities of the PFSA's are still all higher than Nafion 115 when operated at 80°C and 1 atm of pressure. This is not the case when the PFSA's are doped with silicon oxide.

Fig. 4 (Table 1) shows the polarization curves of various doped PFSA's at a single cell temperature of 130°C , with pre-humidified reactant gases at 130°C and a pressure of 3 atm. As in the other polarization curves, the comparison standard is unmodified Nafion 115 shown at a single cell temperature of 80°C with the hydrogen/oxygen pre-humidified gases at 90 and 88°C , respectively and a pressure of 1 atm. In all cases, the PFSA/silicon oxide composite membrane shows resistivities 50% lower than their respective unmodified PFSA's under the same operating conditions. The observed resistivity trend from best to worst is as follows:

Aciplex 1004/silicon oxide > Nafion 112/silicon oxide
> Nafion 105/silicon oxide > Aciplex recast/silicon oxide
> Nafion recast/silicon oxide > Nafion 115/silicon oxide.

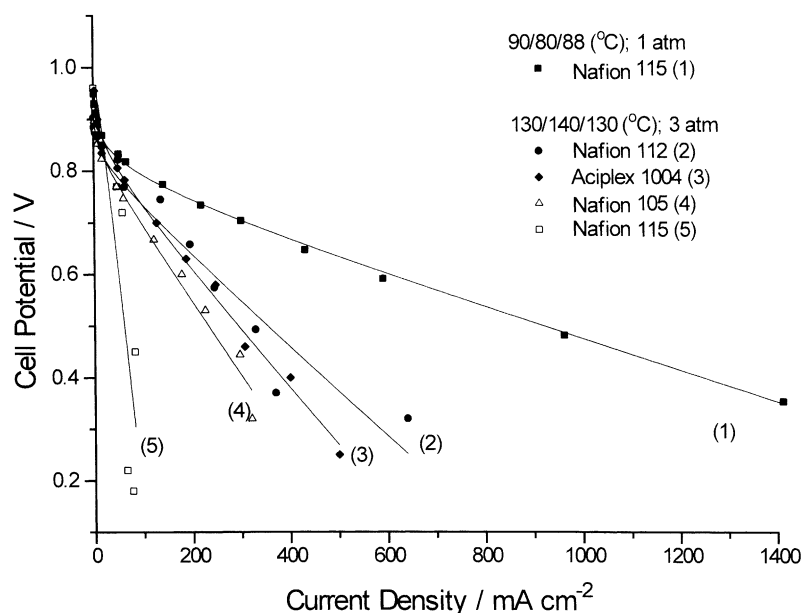


Fig. 3. Cell potential vs. current density of Nafion 115 control (■) H_2 humidifier temperature: 90°C , O_2 humidifier temperature: 88°C , cell temperature: 80°C ; pressure 1 atm. Nafion 112 control (●), Aciplex 1004 control (◆) Nafion 105 control (△), and Nafion 115 control (□). H_2 and O_2 humidifier temperature: 130°C , cell temperature: 140°C ; pressure of 3 atm.

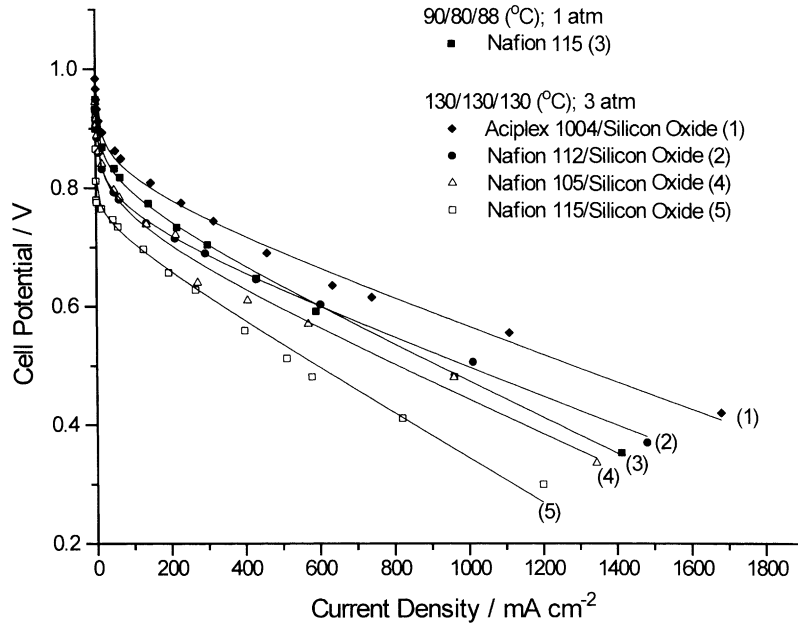


Fig. 4. Cell potential vs. current density of Nafion 115 control (■) H₂ humidifier temperature: 90 °C, O₂ humidifier temperature: 88 °C, cell temperature: 80 °C; pressure 1 atm. Aciplex 1004/silicon oxide (◆), Nafion 112/silicon oxide (●), Nafion 105/silicon oxide (△), and Nafion 115/silicon oxide (□). H₂ and O₂ humidifier temperature: 130 °C, cell temperature: 130 °C; pressure of 3 atm.

Two differences in the trend are seen in comparison to the unmodified PESAs at 130 °C unmodified PFSA's at 130 °C. The first is the Nafion 112 composite has a slightly lower resistivity than the Nafion 105 composite ($R = 0.22 \Omega \text{ cm}^2$ versus $0.26 \Omega \text{ cm}^2$) and the second is the Aciplex recast composite provides a relatively high resistivity. The first change can be explained by understanding that silicon oxide

helps water management in all of the PFSA's at 130 °C in a PEMFC, thereby placing more emphasis on membrane thickness than sulfonate density for superior proton conductivity. We previously showed [11] that 6% by weight was the optimal percentage of silicon oxide for the extruded PFSA's, while 10% by weight was found for the recast PFSA's. The incorporation of the silicon oxide increases

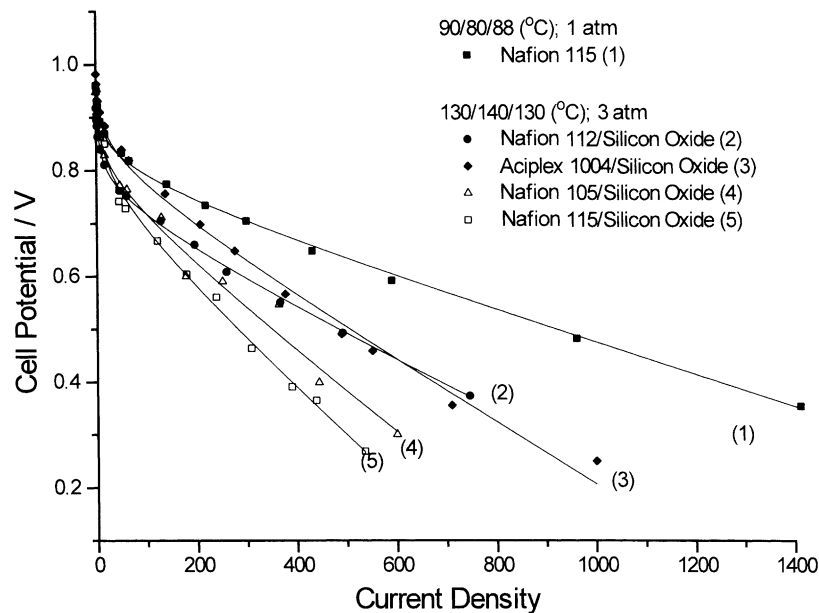


Fig. 5. Cell potential vs. current density of Nafion 115 control (■) H₂ humidifier temperature: 90 °C, O₂ humidifier temperature: 88 °C, cell temperature: 80 °C; pressure 1 atm. Nafion 112/silicon oxide (●), Aciplex 1004/silicon oxide (◆), Nafion 105/silicon oxide (△), and Nafion 115/silicon oxide (□). H₂ and O₂ humidifier temperature: 130 °C, cell temperature: 140 °C; pressure of 3 atm.

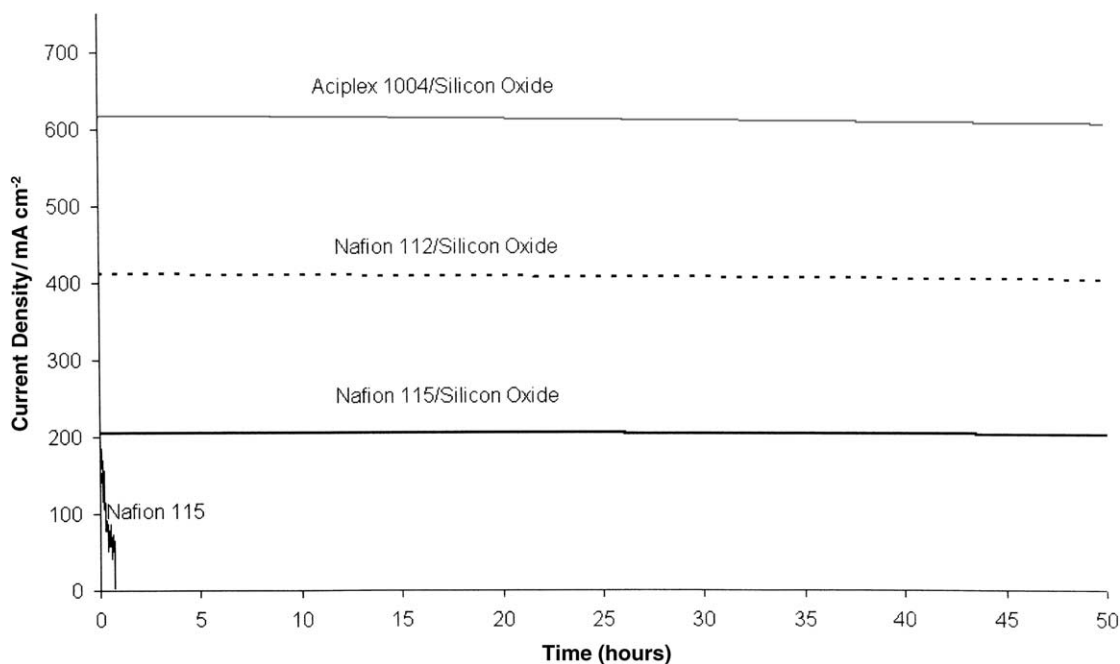


Fig. 6. Time performance test of Nafion 115, Aciplex 1004/silicon oxide, Nafion 112/silicon oxide and Nafion 115/silicon oxide at a pressure of 3 atm. H₂ and O₂ humidifier temperature: 130 °C, cell temperature: 130 °C. Potential 0.65 V.

the thickness of the PFSA—extruded PFSA increase by $\sim 12 \mu\text{m}$, recast PFSA increase by $\sim 25 \mu\text{m}$. The increased thickness of the Aciplex recast composite membrane contributed to its greater than expected resistivity when compared to the other extruded membranes. At 140 °C (Fig. 5, Table 1), Nafion 112/silicon oxide again shows the lowest resistivity consistent with the concept that thickness plays a larger role than equivalent weight for the composite membranes for effective membrane water management.

The Tafel region values for the unmodified PFSA range from 41 mV per decade for Nafion 112 membrane to 93 mV per decade for Nafion 115 at a cell temperature of 130 °C and 42 mV per decade for Nafion 112 to 87 mV per decade for Nafion 115 at a cell temperature of 140 °C (Table 1). A poor membrane/electrode interface due to membrane dehydration could be the cause for the large range of values. For the modified PFSA, consistent Tafel region values on the order of 70 mV per decade are seen at a cell temperature of 130 and 140 °C, indicating that the membrane/electrode interface was not compromised. The E_o values are also generally higher for the modified PFSA possibly due to decreased reactant gas crossover (Table 1).

When air is substituted for pure oxygen (Table 1) as the reactant gas at the cathode, current densities decrease by a factor of ~ 20 – 50% for both the modified and unmodified Nafion membranes under all test conditions. A theoretical decrease of $\sim 80\%$ is expected under stoichiometric conditions. However, the use of two times stoichiometric flow minimizes this effect.

A time performance test in which the cell current was monitored at a cell voltage of 0.65 V was performed on the

control Nafion 115 and the Nafion 115, 112 and Aciplex 1004 composite membranes (Fig. 6). The control Nafion 115 membrane's performance fell dramatically and within an hour no current was observed, while after 50 h of continuous operation at 0.65 V, the current output of the composite membrane remained unchanged indicating that the membrane's hydration was not transitional.

4. Conclusions

The method of sol-gel preparation of the polymeric silicon oxide and its impregnation into extruded PFSA or co-recasting with solubilized PFSA produces a uniform, homogeneous distribution of the silicon oxide in Nafion's nanoporous structure. Lower resistivities were attained at elevated temperatures in a PEMFC by decreasing the equivalent weight and thickness of the PFSA. All of the silicon oxide modified PFSA demonstrated improved water management at elevated temperatures with Aciplex 1004/silicon oxide providing the lowest resistivity at 130 °C. This made it possible for PEMFCs with the composite PFSA silicon oxide membranes to be operated at 130 °C exhibiting desirable current density levels for periods of time that suggest that practical high temperature PEMFCs can be constructed.

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