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Silicon Oxide Nafion Composite Membranes for Proton-Exchange Membrane Fuel Cell Operation at 80-140°C

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Silicon oxide/Nafion composite membranes were studied for operation in hydrogen/oxygen proton-exchange membrane fuel cells (PEMFCs) from 80 to 140°C. The composite membranes were prepared either by an impregnation of Nafion 115 via sol-gel processing of tetraethoxysilane or by preparing a recast film, using solubilized Nafion 115 and a silicon oxide polymer/gel. Tetraethoxysilane, when reacted with water in an acidic medium, undergoes polymerization to form a mixture of SiO_2 and siloxane polymer with product hydroxide and ethoxide groups. This material is referred to as SiO_s/-OH/-OEt. When Nafion is used as the acidic medium, the SiO_2/siloxane polymer forms within the membrane. All composite membranes had a silicon oxide content of less than or equal to 10 wt % . The silicon oxide improved the water retention of the composite membranes, increasing proton conductivity at elevated temperatures. Attenuated total reflectance-Fourier transform infrared spectroscopy and scanning electron microscopy experiments indicated an evenly distributed siloxane polymer of SiO_2/-OH/-OEt in the composite membranes. At a potential of 0.4 V, silicon oxide/Nafion 115 composite membranes delivered four times the current density obtained with unmodified Nafion 115 in a H_2/O_2 PEMFC at 130°C and a pressure of 3 atm. Furthermore, silicon oxide-modified membranes were more robust than the control membranes (unmodified Nafion 115 and recast Nafion), which degraded after high operation temperature and thermal cycling.
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Recent advances have made hydrogen/oxygen proton-exchange membrane fuel cells (PEMFCs) a leading alternative to internal combustion and diesel engines for transportation. Cells of this type have also been suggested for power generation. These advances include the reduction of the platinum loading needed for electrocatalysis, and membranes with (*i*) high specific conductivity (0.1 Ω^{-1} cm^{-1}) (*ii*) good water retention, and (*iii*) long lifetimes.[1]

The advantages of PEMFCs over thermal engines are the ultralow or zero emissions of environmental pollutants (CO, NO, volatile organic compounds (VOCs), and SO_x), fewer moving parts, and higher theoretical efficiencies for energy conversion.[2] PEMFCs work at their optimum performance with pure H_2 and O_2 as the reactant gases. Unfortunately, the storage, transportation, and refueling of H_2 gas is nontrivial, particularly for the transportation application.[3] However, hydrogen for transportation can be produced by on-board fuel processing of liquid hydrocarbons or alcohols. Presently the most developed systems are steam reforming and partial oxidation methods with methanol or gasoline as the fuels, but in both of these cases, the CO level coming out of the processor can only be reduced to 50 or 100 ppm.[3]

CO is a major problem because trace amounts of CO (more than 10 ppm) poison the Pt anode electrocatalyst in the state-of-the-art PEMFCs operating at 80°C. CO-tolerant electrocatalysts (*e.g.,* Pt-Mo, Pt-Ru) have been investigated to enhance CO tolerance, 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*) their CO tolerance level is only about 50 ppm. Even at this level there is an increased overpotential for the anodic reaction.[4-6] An alternate approach to gain CO tolerance is to take advantage of the fact that the absolute free energy of adsorption of CO on Pt has a larger positive temperature dependence than that of H_2. Therefore, CO tolerance levels increase with temperature.[7-9] This effect is illustrated in Fig. 1, which shows the fractional coverages of CO and H on a Pt surface assuming competitive Langmuir-type adsorption. These adsorption isobars are computed for 100 ppm CO in 1 bar H_2, based on the adsorption equilibrium constants for CO and H_2 on Pt(111) surfaces. The hydrogen coverage increases from 0.02 monolayers at 350 K (77°C), to 0.39 monolayers at 450 K (127°C). Since the current density is proportional to the hydrogen coverage on the anode, a 50 K temperature increase from 80 to 130°C increases the current density by a factor of 20. This effect has been shown experimentally in commercialized phosphoric acid fuel cell power plants operating at 200°C, demonstrating a CO tolerance of about 1%.[10]

Other difficulties, encountered with PEMFCs, are the elaborate water and thermal management subsystems needed to achieve optimal performance. The ability of proton exchange membranes (PEMs) to conduct protons is proportional to their extent of hydration; 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 cause pinholes to form, leading to the crossover of the reactant gases. Increased operating temperature may raise the condenser load needed to maintain membrane hydration; however, the new conditions would also make the cooling system for the stack significantly simpler.

The concept of operating the cell at higher temperatures to alleviate the CO poisoning problem and simplify the water and thermal

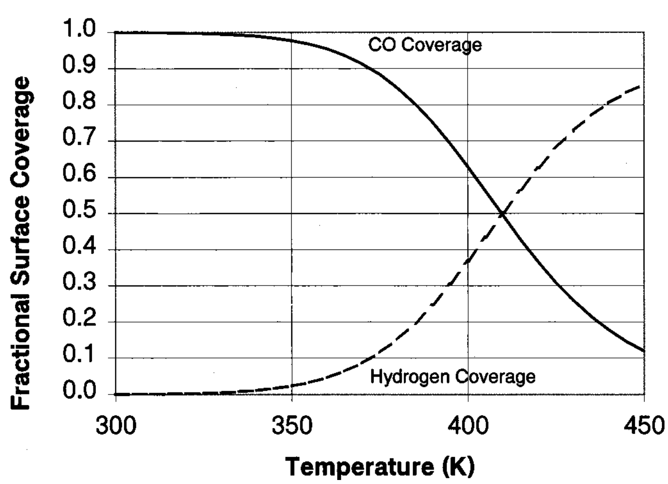

Figure 1. Langmuir-type adsorption of hydrogen and carbon monoxide on a smooth platinum surface as a function of temperature.

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management subsystems brings to surface another dilemma; keeping the membrane hydrated in order to maintain proton conductivity. Unfortunately, the vapor pressure of water increases very rapidly with temperatures above 100°C, and in order to maintain the needed hydration for the PEM and substantial partial pressures of the reactant gases, the total cell pressure has to be raised well above 1 atm.

The aim of this work is to identify PEMFC membrane materials which function above 100°C. Current perfluorosulfonic acid membranes are limited in performance under this condition because of the high evaporation rate of water. A fully hydrated membrane is vital for efficient proton conduction in the membrane, via the Grotthus mechanism. Previous efforts to enhance the water retention of Nafion and related membranes by incorporating hydrophilic metal oxide particles such as SiO_2 produced promising results; however, none were tested in a H_2/O_2 PEMFC above 100°C.[11,12] Mauritz *et al.* used a sol-gel technique to introduce silicon oxide into a perfluorosulfonic acid membrane. Using this method, it was shown that silicon oxide enters the fine hydrophilic channels (≅50 Å diam) of Nafion homogenously.[13] No PEMFC studies were conducted with these membranes. The incorporation of the silicon oxide via sol-gel into Nafion may benefit the hydrophilic properties of the membrane and thus maintain the proton conductivity for good PEMFC performance above 100°C. This approach was thus chosen for developing membranes for PEMFC operation at temperatures above 100°C.

To solve both the CO poisoning and water-thermal management problems, present state-of-the-art PEMs such as Nafion need to be modified in order to remain hydrated at higher operating temperatures. In this study, it is proposed that the water retention qualities of Nafion can be improved at temperatures above 100°C by impregnating its pores using the Mauritz method[13] with a hydrophilic siloxane polymer, a matrix of SiO_2/-OH/-OEt-silicon oxide. The main difference between our approach and that used previously is that the hydrating oxide is introduced as a sol-gel, allowing the incorporation of the silicon oxide within a preformed Nafion membrane as opposed to recasting silica particles with solubilized Nafion solution. This sol-gel process was found to reduce water loss from the membrane's nanopores and permit operation in a H_2/O_2 PEMFC above 100°C.

Experimental

Nafion 115 membranes (DuPont) were pretreated by refluxing them in a 50:50 mixture (by volume) of water and concentrated HNO_3 (70.8% HNO_3, Fisher) for 6-8 h to remove metal and organic impurities, followed by a 50:50 mixture (by volume) of water and concentrated H_2SO_4 (95-98% H_2SO_4, Fisher) for 6-8 h to remove trace metal impurities. The membrane was then refluxed in distilled H_2O until the pH of the H_2O was equal to or greater than 6.5 to remove any excess acid. After the membrane was dried for 24 hours in a vacuum oven at 100°C, it was immersed in a 2:1 mixture (by volume) of MeOH/H_2O for 5 min, followed by immersion in a 3:2 mixture (by volume) of tetraethoxysilane (98% TEOS, Aldrich)/MeOH for varied amounts of time. The duration of time varied according to the desired percent weight of silicon oxide. After the treatment, the membrane was placed in a vacuum oven at 100°C for 24 h.[13] The composite membranes were then refluxed in 3% by volume H_2O_2 for 1 h to remove organics, two times in distilled H_2O for 1 h, in 0.5 M H_2SO_4 for 1 h, and two times in distilled H_2O for 1 h.

Silicon oxide/recast Nafion membranes were prepared by mixing 5% commercial Nafion solution (DuPont) with double its volume of isopropyl alcohol and varying amounts of a silicon oxide solution. The silicon oxide solution was prepared by mixing 2 mL TEOS, 4.7 mL distilled H_2O, and 100 μL 0.1 M HCl for 3 h at room temperature.[14] The Nafion, isopropyl alcohol, and silicon oxide 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 silicon oxide/Nafion 115 membranes.

Electron microprobe (Cameca SX-50) was used to analyze the distribution of Si and O over the cross section of the composite membranes. Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) spectra were obtained using a BioRad 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 Nafion (dry weight) by applying 12 mg/cm^2 of 5% Nafion 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°C for 1 min in a Carver hot-press with no applied pressure, followed by increasing the temperature to 130°C for 1 min with no applied pressure, and finally hot-pressing the MEA at 130°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., model 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°C, respectively. During this period, the external load was maintained at a constant value of 0.1 Ω, to reach an optimal hydration of the membrane using the water produced in the single cell. After the single cell had reached stable conditions (*i.e.*, current density remained the constant over time at a fixed potential), cyclic voltammograms, (CVs) were recorded at a sweep range of 20 mV s^{-1} and in the range 0.1-1 V *vs.* reversible hydrogen electrode (RHE) for 1 h, in order to determine the electrochemically active surface area. Cell potential *vs.* current density measurements were then made under the desired conditions of temperature and pressure in the PEMFC. Identical procedures were followed for the PEMFCs with the unmodified and silicon oxide Nafion 115 and recast Nafion membranes. Most PEMFC experiments were carried out at the cell temperatures of 80, 130, and 140°C with the total pressure (reactant gas plus water vapor pressure) at 1 or 3 atm to maintain a relative humidity of 90-100%. The flow rates of gases were two times stoichiometric.

Results and Discussion

The electron microprobe data in Fig. 2 shows a homogeneous and uniform distribution of Si and O across the Nafion silicon oxide membrane cross section on a scale of 20 μm. FTIR-ATR spectra (Fig. 3) illustrate absorption bands corresponding to the stretching frequencies of Si-O, Si-OH, Si-OEt, Si-O-Si, and other forms of bonding. 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 Nafion. All controls and composites reported here produced identical results.

Typical CVs for the cathode with the unmodified Nafion membranes and silicon oxide Nafion membranes were acquired. By integrating the oxidation peak at 0.1 V *vs.* RHE and assuming a coulombic charge of 220 μC cm^{-2} for a smooth platinum surface,[1] an average roughness factor of 135 $cm^2\,cm^{-2}$ per geometric area for both the unmodified Nafion and the silicon oxide Nafion composite membranes were obtained.

The main objective of this study was to determine whether the incorporation of silicon oxide via sol-gel processing in Nafion 115 and recast Nafion 115 could enhance the current density obtained at a fixed potential at a temperature of 130-140°C. By limiting the total pressure to 3 atm, the maximum operating temperature investigated was 140°C, since the vapor pressure at water at this temperature is 3.5 atm.

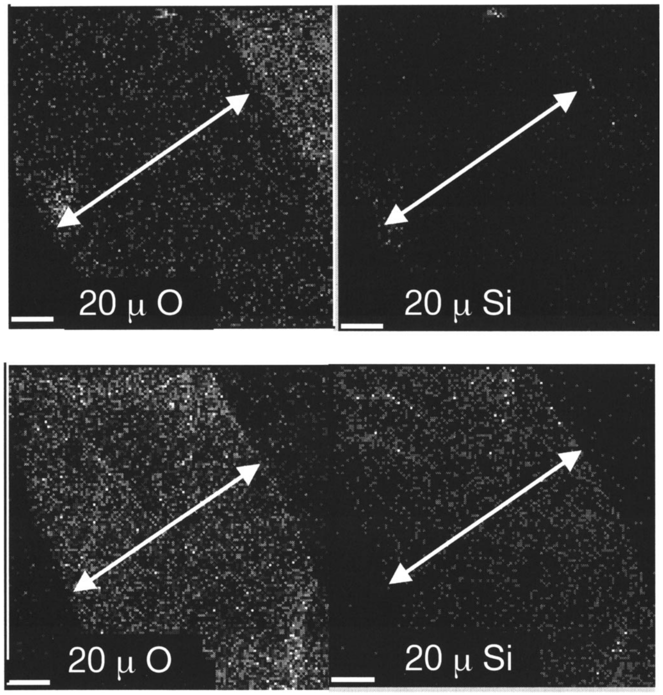

Figure 2. SEM photographs of (a, top) unmodified Nafion 115 (oxygen left, silicon right) and (b, bottom) silicon oxide/Nafion 115 composite membrane (oxygen left, silicon right). White two-headed arrow designates the membrane boundary.

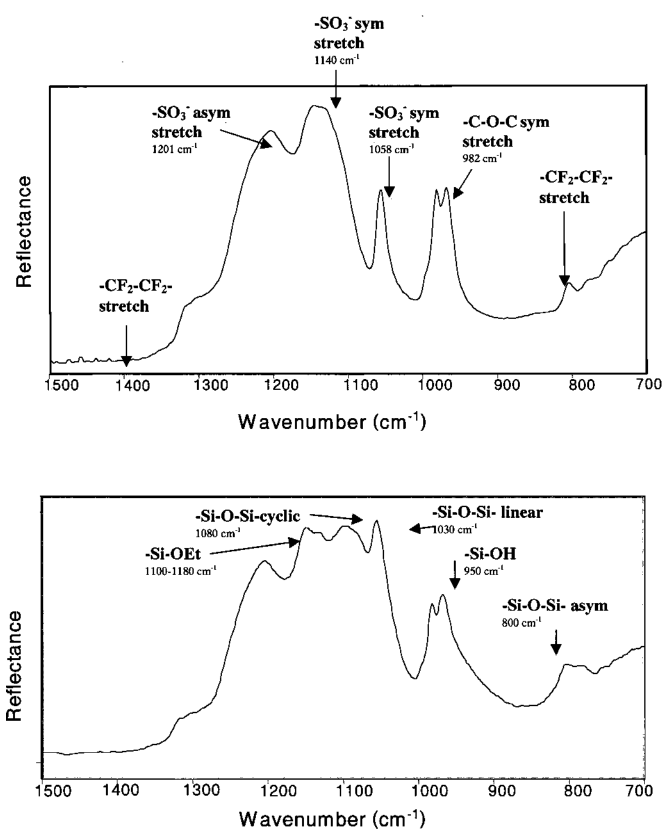

Figure 3. FTIR-ATR spectrum of (a, top) Nafion 115 and (b, bottom) silicon oxide/Nafion 115 composite membrane.

All cell potential (E) *vs.* current density (i) data was analyzed by fitting the PEMFC data points to Eq. 1

$$E = E_o - b \log i - Ri \quad [1]$$

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

$$E_o = E_r + b \log i_o \quad [2]$$

where E_r is the theoretical open cell potential.

Presented in Table I are the electrode kinetic parameters derived from Eq. 1 and 2 for both the unmodified and the silicon oxide Nafion 115 and recast Nafion membranes.

Preliminary PEMFC experiments were performed at 115°C with the silicon oxide/Nafion 115 composite and Nafion 115 membranes (Table I). Silicon oxide/Nafion 115 composite membranes with 6% silicon oxide content by weight showed the lowest membrane resistance, 0.23 Ω cm^2. The Tafel slopes for these membranes are approximately equal to 67 mV, indicating that it is not dependant on the weight percent of the silicon oxide within the Nafion 115 membrane. Maximum conductivity at elevated temperatures was attained at intermediate loadings of silicon oxide where the silicon oxide improved water retention without hindering the continuity of the Nafion.

The optimal loading of silicon oxide within the silicon oxide/recast Nafion composites appears to be greater than in the Nafion 115 film (Table I). At 130°C, the silicon oxide/recast Nafion composite membrane with 10% silicon oxide by weight showed the lowest membrane resistance, 0.26 Ω cm^2. In these three cases, the Tafel slopes are approximately equal to 70 mV, again indicating that it is not dependent on the weight percent of the silicon oxide within the recast Nafion membrane. Composites with a percent content higher than 10% silicon oxide by weight were mechanically unstable and not amenable to PEMFC experiments.

The difference in optimal silicon oxide loading in the Nafion 115 (6% by weight) and recast Nafion (10% by weight) films may be due to the phase-separated microstructure in the membranes. The hydrophilic regions in Nafion 115 where silicon oxide formed were preexistent. In the recast membranes, the silicon oxide polymer was formed at the same time the hydrophilic regions of Nafion could restructure, thus accommodating more silicon oxide.

At a cell temperature of 80°C, a pressure of 3 atm, and reactant gas temperature of 8-10°C above the cell temperature, the effect of silicon oxide in the membrane on the amount of current density was small, with the Tafel slopes all being within the same region of 88 mV (Fig. 4, Table I). The resistances (R) of the unmodified membranes at this temperature showed a lower value than the silicon oxide/Nafion membranes. This may have been due to the silicon oxide disrupting the continuity of the conduction paths in the Nafion membrane, thereby decreasing the efficiency of proton conduction at this particular temperature.

With both the humidified gases and the cell temperature at 130°C with a total cell pressure of 3 atm, the Nafion 115 and recast Nafion silicon oxide membranes showed a considerable improvement over the unmodified Nafion 115 and recast Nafion membranes in PEMFC performance, *i.e.*, increased current density and lower resistances (Fig. 5, Table I). The unmodified and modified Nafion 115 membranes had Tafel slopes of 92 and 93 mV, respectively, indicating that the silicon oxide did not affect this region of the polarization curve. The E_o values for both the unmodified and modified recast Nafion membranes were significantly lower than that of the Nafion 115 membranes, corresponding to flatter Tafel regions and very low effective exchange current densities (Table I). This may have been

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

Cells supplied with hydrogen/oxygen fuel

Membrane	Temperature (°C) H_2/cell/O_2	Pressure (anode/cathode)	E_o (mV)	b (mV/dec)	i_o (mA/cm^2)	R (Ω cm^2)	Current density (mA cm^{-2}) at 0.9 V	at 0.4 V
Control Nafion 115	90/80/88	1/1	991	63	1.7×10^{-4}	0.36	—	995
	90/80/88	3/3	1012	85	3.3×10^{-3}	0.17	24	1950
	130/130/130	3/3	1000	93	2.4×10^{-3}	1.3	8	280
	130/140/130	3/3	937	87	4.3×10^{-4}	2.1	8	200
	130/115/120	3.75/3	973	64	1.0×10^{-4}	0.38	70	1300
Control recast Nafion	90/80/88	3/3	985	88	1.7×10^{-3}	0.17	13	1938
	130/130/130	3/3	910	43	5.2×10^{-8}	0.5	1	770
	130/140/130	3/3	900	42	3.1×10^{-8}	2.4	—	207
2% Silicon oxide/Nafion 115	130/115/120	3.75/3	981	67	1.99×10^{-4}	0.28	80	1520
6% Silicon oxide/Nafion 115	130/115/120	3.75/3	969	70	1.93×10^{-4}	0.23	—	1745
10% Silicon oxide/Nafion 115	130/115/120	3.75/3	937	66	6.74×10^{-4}	0.26	—	1400
6% Silicon oxide/Nafion 115	90/80/88	3/3	1015	90	3.7×10^{-3}	0.21	18	1547
	130/130/130	3/3	932	92	6.9×10^{-4}	0.36	8.3	848
	130/140/130	3/3	930	96	8.7×10^{-4}	0.81	8.1	389
3% Silicon oxide/recast Nafion	130/130/130	3/3	941	67	5.03×10^{-5}	0.42	6	820
6% Silicon oxide/recast Nafion	130/130/130	3/3	946	69	7.9×10^{-5}	0.46	5	810
10% Silicon oxide/recast Nafion	90/80/88	3/3	979	87	1.6×10^{-5}	0.26	13	1191
	130/130/130	3/3	932	72	9.1×10^{-5}	0.33	4	969
	130/140/130	3/3	931	61	1.6×10^{-5}	0.78	3	471

Cells supplied with hydrogen/air fuel

Membrane	Temperature (°C) H_2/cell/air	Pressure (anode/cathode)	E_o (mV)	b (mV/dec)	i_o (mA/cm^2)	R (Ω cm^2)	Current density (mA cm^{-2}) at 0.9V	at 0.4V
Control Nafion 115	90/80/88	3/3	953	60	3.2×10^{-5}	0.38	5	989
	130/130/130	3/3	888	61	3.2×10^{-6}	1.59	—	217
	130/140/130	3/3	885	47	6.4×10^{-8}	2.62	—	145
Control recast Nafion	90/80/88	3/3	982	65	1.58×10^{-4}	0.27	6	945
	130/130/130	3/3	866	44	5.62×10^{-9}	1.18	—	343
	130/140/130	3/3	849	32	1.33×10^{-12}	3.55	—	133
10% Silicon oxide/recast nafion	90/80/88	3/3	954	46	1.05×10^{-6}	0.42	6	990
	130/130/130	3/3	926	52	1.49×10^{-6}	0.61	4	623
	130/140/130	3/3	891	60	2.33×10^{-6}	2.25	—	225
6% Silicon oxide/Nafion 115	90/80/88	3/3	938	89	6.3×10^{-4}	0.41	2	692
	130/130/130	3/3	896	49	2.1×10^{-7}	0.78	—	470
	130/140/130	3/3	891	38	1.83×10^{-9}	1.91	—	210

due to pinholes forming in the membrane, as they were not as mechanically stable as the preformed Nafion 115 membranes (Table I). A comparison of resistances and current densities at 80, 130, and 140°C for all the membranes studied (Fig. 4-6 and Table I) show increased resistances and decreased current density with elevated temperature. However, the reduction in current density at elevated temperature was substantially less for the silicon oxide Nafion membranes.

One reason the cell performance decreased for both the modified and unmodified Nafion membranes with increasing temperature was a reduction of the partial pressure of the reactant gases. When the total cell pressure was maintained at 3 atm and heated from 80 to

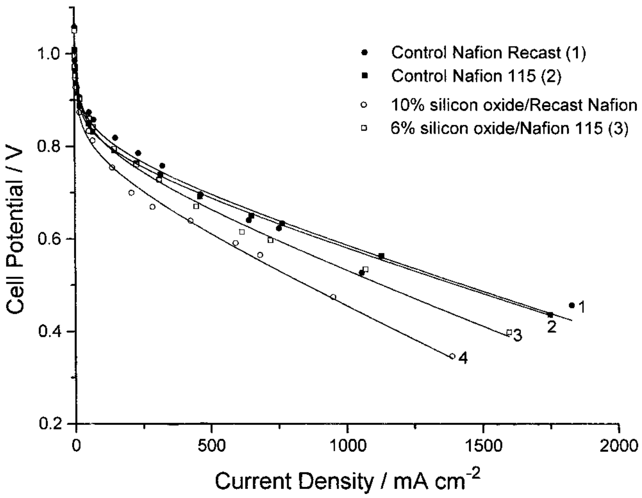

Figure 4. Cell potential *vs.* current density of (●) recast Nafion control, (■) Nafion 115 control, (○) 10% silicon oxide/recast Nafion, and (□) 6% silicon oxide/Nafion 115 membranes at a pressure of 3 atm. H_2 humidifier temperature 90°C; O_2 humidifier temperature 88°C; cell temperature 80°C.

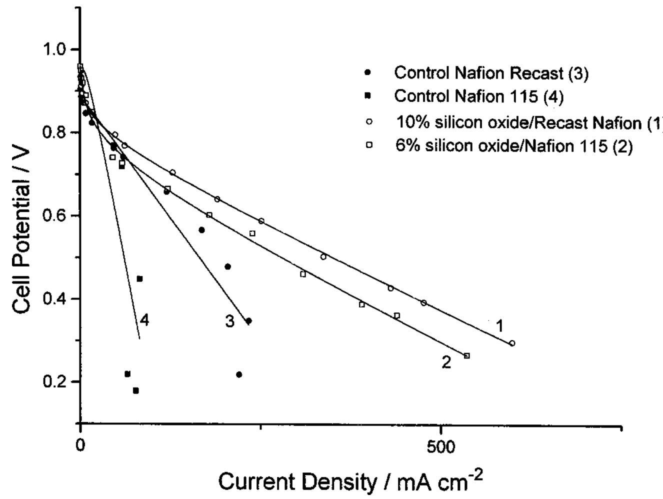

Figure 6. Cell potential *vs.* current density of (●) recast Nafion control, (■) Nafion 115 control, (○) 10% silicon oxide/recast Nafion, and (□) 6% silicon oxide/Nafion 115 membranes at a pressure of 3 atm. H_2 and O_2 humidifier temperature 130°C; cell temperature 140°C.

130°C, the water vapor partial pressure increased from 0.5 to 2.5 atm, decreasing the partial pressure of the reactant gases from 2.5 to0.5 atm. This drop in reactant gas partial pressure also negatively affected the open cell potential (E_o), as seen in Table I.

We also suspect the degree of membrane hydration decreased as the cell temperature increased. Membrane hydration state should depend on the relative humidity of the reactant gases. Direct measurements of the water vapor pressure were not available; however, mass-transfer limitation in the humidifiers resulted in water vapor pressures slightly below the saturation pressure. The difference between the actual vapor pressure and the saturation pressure increases with increasing temperature, resulting in lower relative humidity and hence, lower water content in the membranes at higher temperatures.

The silicon oxide Nafion membranes exhibited lower resistances and higher current densities at 130 and 140°C than the unmodified Nafion membranes. The silicon oxide essentially lowered the vapor pressure of the water in the membrane, *i.e.*, the hydrated silicon oxide provided better water retention than unmodified Nafion at reduced relative humidity. Also, the impregnation of the silicon oxide into the nanopores of Nafion caused the silicon oxide Nafion membranes to be less susceptible to high-temperature damage. Dehydration of the unmodified Nafion at elevated temperatures leads to the destruction of the pore structure as detected by a decrease in proton conductivity. The presence of the silicon oxide within the membranes apparently prevented these temperature-related structural changes, and conductivity is maintained even after thermal cycling above the observed dehydration temperature (130°C) of the unmodified Nafion membrane.

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

A time performance test was performed on the unmodified Nafion 115 membrane and the 6% silicon oxide/Nafion 115 membrane (Fig. 7). The unmodified membrane performance fell dramatically and failed within an hour, while after 50 h of operation at 130°C the performance of the composite membrane remained constant, indicating that the membrane's hydration was not transitional. More extensive time studies are currently underway.

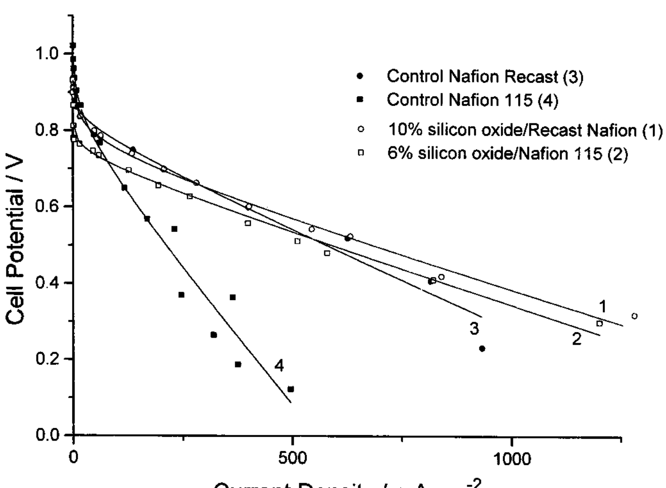

Figure 5. Cell potential *vs.* current density of (●) recast Nafion control, (■) Nafion 115 control, (○) 10% silicon oxide/recast Nafion, and (□) 6% silicon oxide/Nafion 115 membranes at a pressure of 3 atm. H_2 and O_2 humidifier temperature 130°C; cell temperature 130°C.

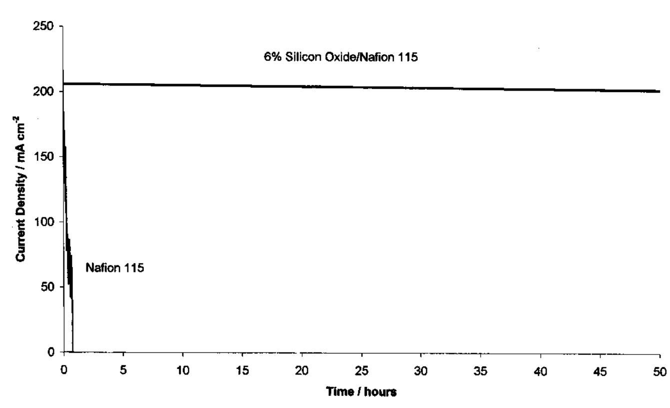

Figure 7. Time performance test of Nafion 115 and Nafion 115/silicon oxide at a pressure of 3 atm. H_2 and O_2 humidifier temperature 130°C; cell temperature 130°C. Potential 0.65 V.

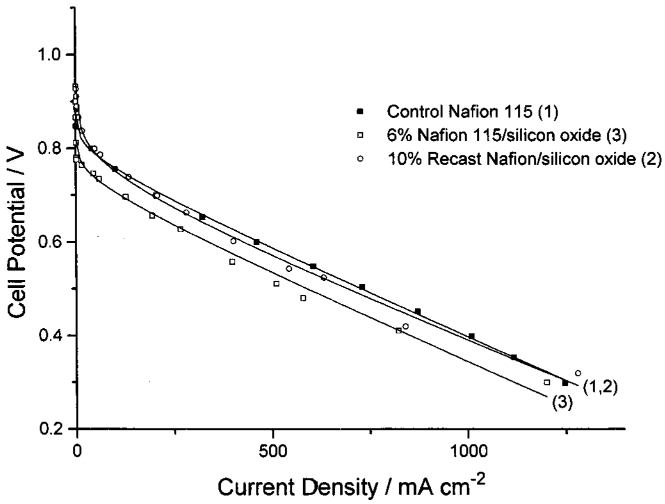

Figure 8. Cell potential *vs.* current density of (■) Nafion 115 control at a pressure of 1 atm. H_2 humidifier temperature 90°C; O_2 humidifier temperature 88°C; cell temperature 80°C. (□) 6% Nafion 115/silicon oxide and (○) 10% recast Nafion/silicon oxide membrances at a pressure of 3 atm. H_2 and O_2 humidifier temperature 130°C; cell temperature 130°C.

Figure 8 shows the cell potential *vs.* current density of unmodified Nafion 115 at 80°C and 1 atm, and the silicon oxide/Nafion 115 and recast composite membranes at 130°C and 3 atm of pressure. The three membranes demonstrated similar current densities and resistances. While the total operating pressure is 1 atm for the unmodified Nafion 115 membrane and 3 atm for the silicon oxide Nafion membranes, in both cases the partial pressure of the reactant gases is ~0.5 atm. The silicon oxide Nafion membranes gained 50°C in operating temperature without a significant decrease in current density; exhibiting approximately the same level of hydration at 130°C as the unmodified Nafion 115 membranes did at 80°C.

Conclusions

The method of sol-gel preparation of the polymeric silicon oxide and its impregnation into the preformed Nafion membrane or corecasting with solubilized Nafion produced a uniform, homogeneous distribution of the silicon oxide in Nafion's nanoporous structure. The water retention characteristics of the composite membranes were better than the unmodified Nafion membranes at temperatures above 100°C. This made it possible for PEMFCs with the composite silicon oxide Nafion membranes to be operated at 130°C, exhibiting desirable current density levels. Unmodified Nafion 115 and recast Nafion membranes both provided relatively poor performance above 100°C and suffered irreversible heat damage. The advantage of operating a PEMFC at 130°C, rather than at 80°C, is that the CO (from reformed fuels) level can be increased by about a factor of 20 from 10 to ~200 ppm. Additionally, elevated temperatures provide the basis for a more efficient and simpler water-management subsystem.

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