Chapter 36

Membrane/electrode additives for low-humidification operation

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1 BACKGROUND

One of the technical difficulties in the commercialization of proton exchange membrane (PEM) fuel cells is the requirement that the fuel and oxidant within the fuel cell be saturated with water vapor. If this is not done, the water content of the currently used Nafion® electrolyte is lower than that desirable for good cell performance. This loss in water content in the membrane has several harmful effects. One effect is a decrease in the ionic conductivity of the membrane with lower water content, which causes an increase in the cell internal resistance. During cell operation, due to the electroosmotic drag of water from the cell anode to the cell cathode, the water content becomes even lower on the anode side of the cell resulting in even a further reduction in the electrolyte ionic conductivity. Within the electrodes, the loss in water content decreases both electrolyte conductivity and gaseous reactant permeability. The kinetics of the oxygen reduction reaction is also slowed by the loss of water. These effects caused by low water content increase the electrode polarizations.

Reactants may be saturated with water vapor before they reach the cell or they may be saturated within the cell. Both of these approaches result in a more complex system with increased cost, volume, and weight. The saturation requirement also limits the conditions under which a cell can operate. If a cell is to operate at a temperature above 80 °C, pressurization above 1 atm is required to maintain adequate reactant pressures because of the high water vapor pressure. Pressurized operation results in a large loss in system efficiency because of the energy needed to compress the oxidant air. For operation at 1 atm pressure, the required low operating temperature results in a complex fuel cleanup system if carbon monoxide is a component in the fuel. Carbon monoxide can be present as a result of the production of hydrogen from a hydrocarbon and is a severe poison for the anode reaction. A low operating temperature does not produce useful waste heat from the fuel cell and increases the size, weight, and cost of heat exchangers to reject that heat. The absence of free liquid water within the cell should also reduce corrosion of cell components caused by that water's acidity. The development of a PEM cell that can operate at low humidification would result in a major advancement in cell technology and enhance commercial viability.

The ability of a PEM cell to operate with low water content is also the key to the development of a more efficient direct methanol fuel cell. Two obstacles in the development of the direct methanol cell are the slow kinetics for the direct methanol oxidation reaction, which severely increase the anode polarization, and the migration of methanol through the membrane from the anode to the cathode. Migrating methanol is oxidized at the cathode, which lowers system efficiency, and increases the cathode polarization. Since Nafion® requires water to maintain its desirable properties, it also takes up much methanol permitting methanol to migrate to the cathode. If a membrane could be developed that is ionically conductive at low water contents, that membrane would probably contain little

Handbook of Fuel Cells – Fundamentals, Technology and Applications, Edited by Wolf Vielstich, Hubert A. Gasteiger, Arnold Lamm. Volume 3: *Fuel Cell Technology and Applications*. ISBN: 0-471-49926-9.

methanol. This membrane would permit higher temperature operation where the kinetics for methanol oxidation would be better and have a reduced crossover of methanol to the cathode.

Approaches that have used lower humidification of the reactants have centered on the addition to the Nafion® membrane of components that retain product water from the electrochemical reaction. Materials that have been evaluated for the retention of water are solid oxides such as silica.[1–10] Platinum catalyst has also been added to the membrane in some of these same references, to nonelectrochemically react the hydrogen and oxygen diffusing into the membrane from the fuel and oxidant sides, respectively. This reaction produces water within the membrane.

Other membranes that allow low-humidification operation are prepared by impregnating acids such as sulfuric acid,[11, 12] phosphoric acid[13, 14] or phosphonic acid[15] into membranes such as Nafion®, polybenzimidazole or other composite membranes. These composite membranes can operate at elevated temperature ($>100\,^{\circ}\mathrm{C}$) under ambient pressure. However, the liquid acid electrolytes might be lost during long-term operation.

At elevated temperature, the acids have considerable volatility that would lead to cell failures during long-term operation. Instead of using aqueous acids as impregnants, solid acids with negligible volatility can be used as additives into Nafion® or other proton exchange ionomers. Heteropoly acids[7, 16, 17] and zirconium (hydrogen) phosphate[18–23] are suitable ionic conductive solids for low-humidification operation. The chemistry of heteropoly acids has been investigated extensively.[24, 25] Properties such as conductivity[26–31] and structure[32] have been widely characterized. The conductivity of heteropoly acids such as phosphotungstic acid[33] in its 29 water molecule hydrate form ($H_3PO_4(WO_3)_{12} \cdot 29H_2O$) is about $0.17\,\Omega^{-1}\,\mathrm{cm}^{-1}$ which is similar to that of Nafion®. Since heteropoly acids are soluble in water, membranes with heteropoly acid should be used at elevated temperature ($>100\,^{\circ}\mathrm{C}$) and low water saturation. Under these conditions, no liquid water is present and leaching out of the additives can be avoided. Zirconium (hydrogen) phosphate was first used in the direct methanol fuel cell.[20] It was incorporated into the porous structure of the Nafion® membrane by in situ reaction between zirconyl chloride and phosphoric acid to reduce the methanol crossover by reducing the pore size of Nafion®–zirconium phosphate composite membrane. Both heteropoly acids and zirconium (hydrogen) phosphate are hygroscopic and ionically conductive solids. These solids would help retain the water and ionic conductivity in the membrane at low water content.

Although operating the fuel cell at low humidification has some advantages such as a simplified system (lower capital cost), better CO poisoning tolerance (elevated temperature), and better waste heat recovery (elevated temperature), several harmful effects, as described previously, occur. Membranes for low-humidification operation have been reported in the literature, especially membranes that allow operation of the cell at elevated temperature under ambient pressure. Unfortunately, little detailed discussion about technical challenges such as electrode polarizations for the cell operated under low humidification is available. In this section, discussion is focused on some of the critical technical issues to prepare high performance membrane-electrode assemblies (MEAs) that operate under low-humidification conditions.

2 EXPERIMENTAL

In addition to the general review, many laboratory results have been presented to explain important issues. Procedures to prepare composite membranes and MEAs as well as test conditions are presented here.

The composite membranes (Nafion®–Teflon®, Nafion®–Teflon®–$Zr(HPO_4)_2$, Nafion®–Teflon®–phosphotungstic acid) were prepared by impregnation of a matrix made of Teflon®. Nafion®solution (Solution Technologies, Inc.) or Nafion® solution containing proton conductor ($Zr(HPO_4)_2$ or phosphotungstic acid) was applied into the porous structure of a Teflon® matrix (Tetratec). The resulting membrane was then heated to crystallize the Nafion in the composite membrane. The thickness of the composite membranes was about 1 mil ($25\,\mu\mathrm{m}$).

The MEAs ($5\,\mathrm{cm}^2$ active area) were prepared by applying the catalyst Nafion® inks directly to the surfaces of the composite membranes. The catalyst (E-TEK) loading for anode (Pt/Ru/C) and cathode (Pt/C) was about $0.4\,\mathrm{mg\,cm}^{-2}$. Single-sided diffusion substrates (E-TEK) were used for cell tests.

Hydrogen and air (or oxygen) were fed to the cell through anode and cathode humidifiers, respectively. For nonhumidification experiments, dry gases were fed into the cell directly. The flow rates of gases were controlled by mass flow controllers (MKS) that matched the desired gas stoichiometry to the current density. The temperatures of the fuel cell, anode humidifier, and cathode humidifier were controlled by temperature controllers (Omega®) with K-type thermocouples. Temperature controllers, mass flow controllers, fuel cell load and data acquisition were done using a test stand manufactured by Scribner Associates. All tests were performed at ambient pressure.

3 LOW TEMPERATURE FUEL CELL MEMBRANES

To reduce the cost and simplify the system, low temperature (<80 °C) fuel cells should be operated under low humidification or even nonhumidification conditions, especially for portable applications. To reach this goal, first, proton exchange ionomers should be able to maintain good ionic conductivity below saturation conditions. In the development of PEM fuel cells a variety of membrane materials such as poly(styrenesulfonic acid) and sulfonated phenol-formaldehyde have been explored. However, these membranes are limited due to their degradation under fuel cell operating conditions. A breakthrough was achieved with the introduction of Nafion®, a perfluorosulfonic acid (PFSA). Nafion® and its relatives have become the state-of-the-art membranes in PEM fuel cells. They have high chemical stability and ionic conductivity under water-rich environments, which often occur under PEM fuel cell operation.

A variety of membranes material that have been employed in PEM fuel cells contain poly(tetrafluoroethylene)-like backbones with perfluorocarbon sulfonate side chains that facilitate ionic conductivity. Due to their strong acid characteristics (sulfonate groups), the proton conductivity of PFSA membranes is strongly dependent on membrane water content. Water uptake in ionomeric membranes has been investigated intensively.[34–36] There are significant differences in water uptake by membranes from gas or liquid phases. The difference in water uptake can be explained by the less favorable sorption from the vapor involving capillary condensation of water vapor into the membrane compared to filling with liquid water due to liquid surface forces. This characteristic has been demonstrated by contact angle experiments.[37] The effect of water activity (relative humidity) and temperature on proton conductivity of Nafion® 117 membrane is shown in Figure 1.[38] The conductivity of the membrane is strongly dependent on relative humidity and slightly affected by the temperature.

A schematic diagram of water sources and water flux within a PEM fuel cell is shown in Figure 2. The concentration profile of water can be quite steep through the membrane thickness dimension, depending on membrane thickness, reactant water content, and the operating cell current density. Water is produced at the cell cathode and carried into the cell by humidified fuel and oxidant. Water is transported from the cell anode to cathode by electroosmotic drag. A water drag coefficient of 1.0 H_2O/H^+ was found to be nearly independent of membrane water content when Nafion® or other PFSA membranes were equilibrated with water vapor.[39] This suggests that the migrant species might be the hydronium ion (H_3O^+). When the Nafion® membrane is equilibrated with liquid water, the drag increases from 1 to between 2 and 3 and increases with increasing temperature.[40] Water is carried back toward the anode by diffusion caused by a water concentration gradient and capillary forces caused by the opening of pores in the membrane.

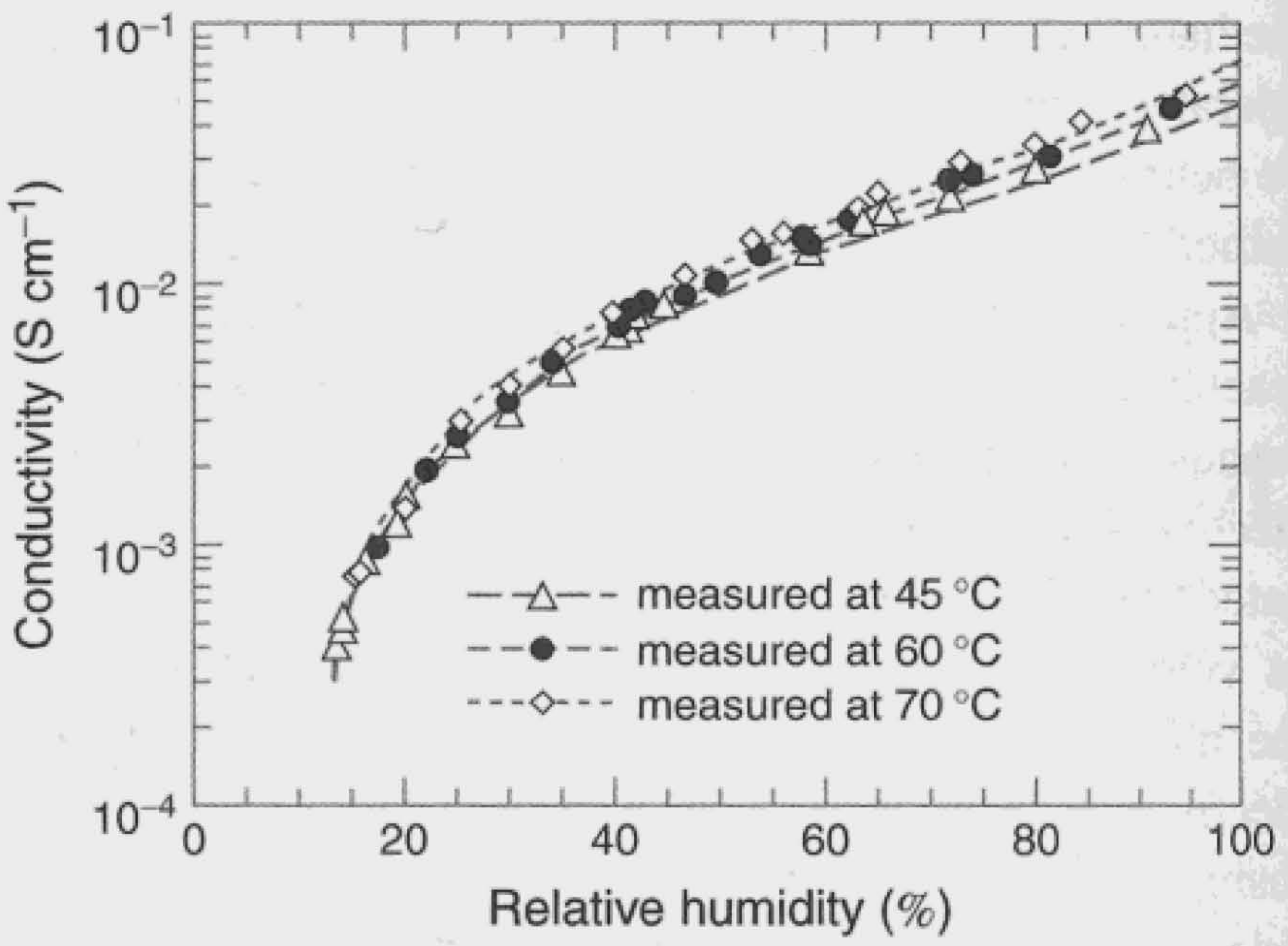

Figure 1. Effect of relative humidity and temperature on conductivity of Nafion® 117 membrane (E-Form). (Reproduced from Sone *et al.* (1996)[38] with permission of The Electrochemical Society Inc.)

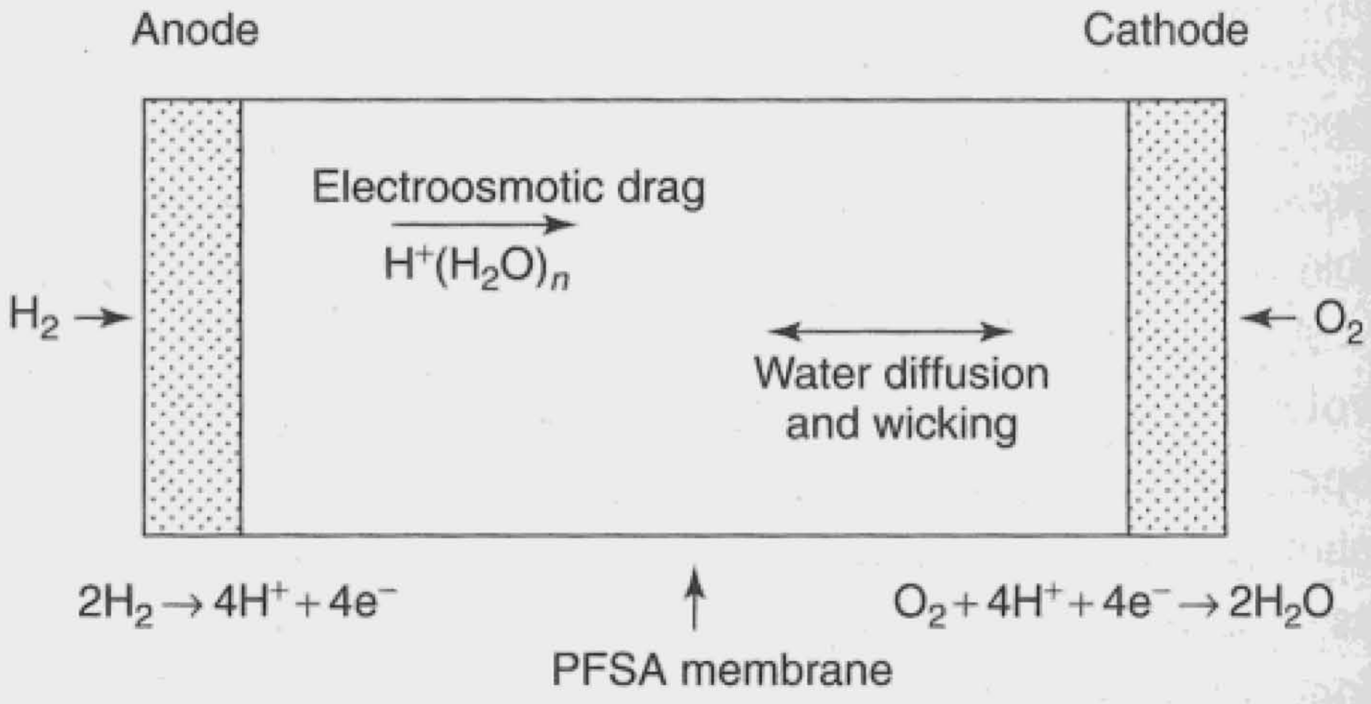

Figure 2. Schematic diagram of water source and water flux within a PEM fuel cell.

For fuel cells operated under low humidification or nonhumidified conditions, water management becomes extremely important. For nonhumidification operation, the only water source for the system is from the production of water at the cathode and a slight amount from reactant crossover. Thinner membranes are preferred for low humidification or nonhumidification operation because the water concentration change across the thinner membrane will be less than that for a thicker membrane. For a thicker membrane, the water content can become extremely low on the anode side of the cell, resulting in a severe reduction in the membrane conductivity.

Under low humidification or nonhumidified operation a technique for retention of water to prevent the membrane from drying out is needed to improve the membrane for operation under such conditions. Zirconium (hydrogen) phosphate is a hygroscopic and proton conductive solid which has been tested as an additive to Nafion®. Nafion® and the proton conducting solid can be impregnated into a porous structure of Teflon® that serves as a host for maintaining strength while allowing the membrane to be thin for fuel cell applications.[41]

The effect of cell temperature on the internal resistance of Nafion®–Teflon®–zirconium (hydrogen) phosphate (NTZr) membranes operating with no reactant humidification is shown in Figure 3. The resistance in all membrane electrode assembly performance experiments was measured by the "current interrupt" technique. Since the resistance measured is from the leads to the single cell, then through the carbon plates, through the gas diffusion layers and then through the MEA, the measurement does include contact resistance. Although the internal resistance of the membrane increases with increasing cell temperature indicating that membrane dries out at higher temperature, comparison between the Nafion®–Teflon® (NT) and NTZr membrane shows that the reduction in the internal resistance is due to the additive. The internal resistance of the NTZr membrane at 60 °C under nonhumidified conditions is below $0.2\,\Omega\,\text{cm}^2$. This membrane resistance value is comparable with that of a Nafion® 117 membrane under full hydration. Figure 3 also shows the effect of flow rate on the internal resistance, illustrated by different oxidant (air or oxygen) with same stoichiometry ($V_{air}/V_{oxygen} = 4.76$). Since the primary water produced in this system is from the cathode reaction, higher flow rates (here the air stream) aggravate the dry-out of the membranes, indicating that good flow distribution within the cell and a good diffusion substrate are needed for low-humidified or nonhumidification operation.

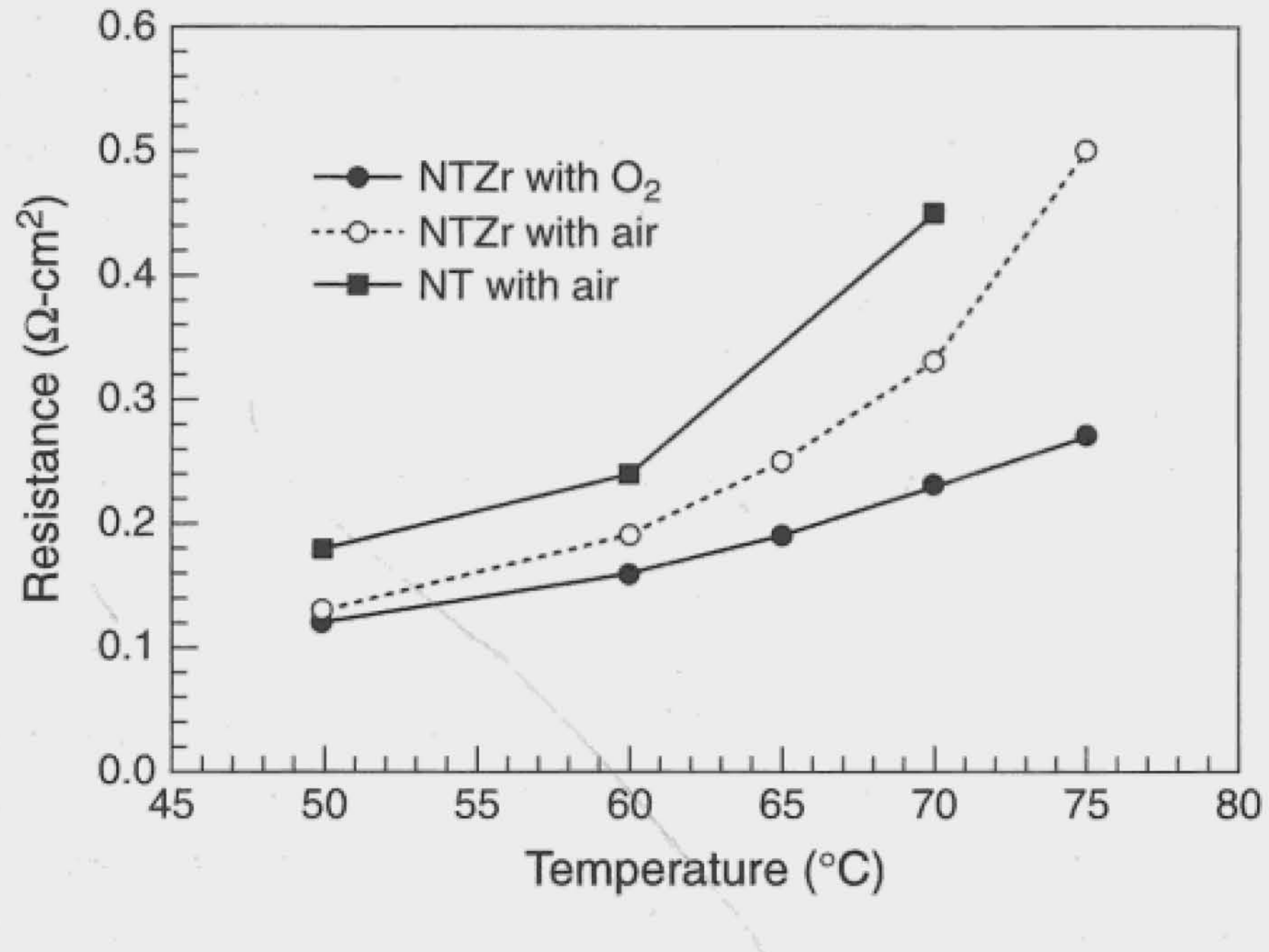

Figure 3. Effect of cell temperature on internal resistance of NTZr membrane under nonhumidification conditions (membrane thickness, 25 μm; anode, 1.5 stoichiometric hydrogen; cathode, 2 stoichiometric air/O_2; resistance measurement taken at $400\,\text{mA}\,\text{cm}^{-2}$).

4 PERFORMANCE OF FUEL CELLS AT LOW TEMPERATURE WITH LOW HUMIDIFICATION

The performance loss of the fuel cell is the contribution of anode and cathode polarization and ohmic drop from the membrane. When operating on pure hydrogen the fast reaction of hydrogen oxidation causes the anode to exhibit a negligibly small polarization compared to the cathode. As a result, the IR-free cell voltage is almost equal to the cathode potential relative to a hydrogen electrode in the same electrolyte under normal conditions. Decrease in thickness of the proton exchange membrane leads to a decrease in the internal resistance (IR) not only by the direct effect of a reduced ionic conduction length, but also by the increase in the average ionic conductivity in the thinner membrane from more effective back-diffusion of water from the cell cathode side to the anode side. Under low humidification or nonhumidification, the anode polarization increases slightly from dryout of that electrode. The reduced thickness of the membrane can alleviate this harmful effect due to more effective back-diffusion of water. For a cell with water-saturated reactants, liquid water flooding the cathode side of the cell can occur due to inadequate back migration and exit from the gas-side of the cathode.

5 HIGH TEMPERATURE FUEL CELL MEMBRANES

Composite membranes containing solid proton conductors have been fabricated to operate at low levels of humidification under conventional PEM cell temperatures, but also at elevated temperatures for ambient pressure cell operation. A higher cell temperature (> 100 °C) alleviates carbon monoxide poisoning on the anode, facilitates water management, and increases the quality to waste heat to further increase the overall efficiency. Most PEM fuel cell developers use Nafion® membranes which meet requirements in terms of mechanical strength, chemical stability, and ability to provide a relatively high-performing electrode. However, Nafion® loses ionic conductivity dramatically at temperatures above 100 °C at the lower water vapor partial pressures involved in cell operation at atmospheric pressure.

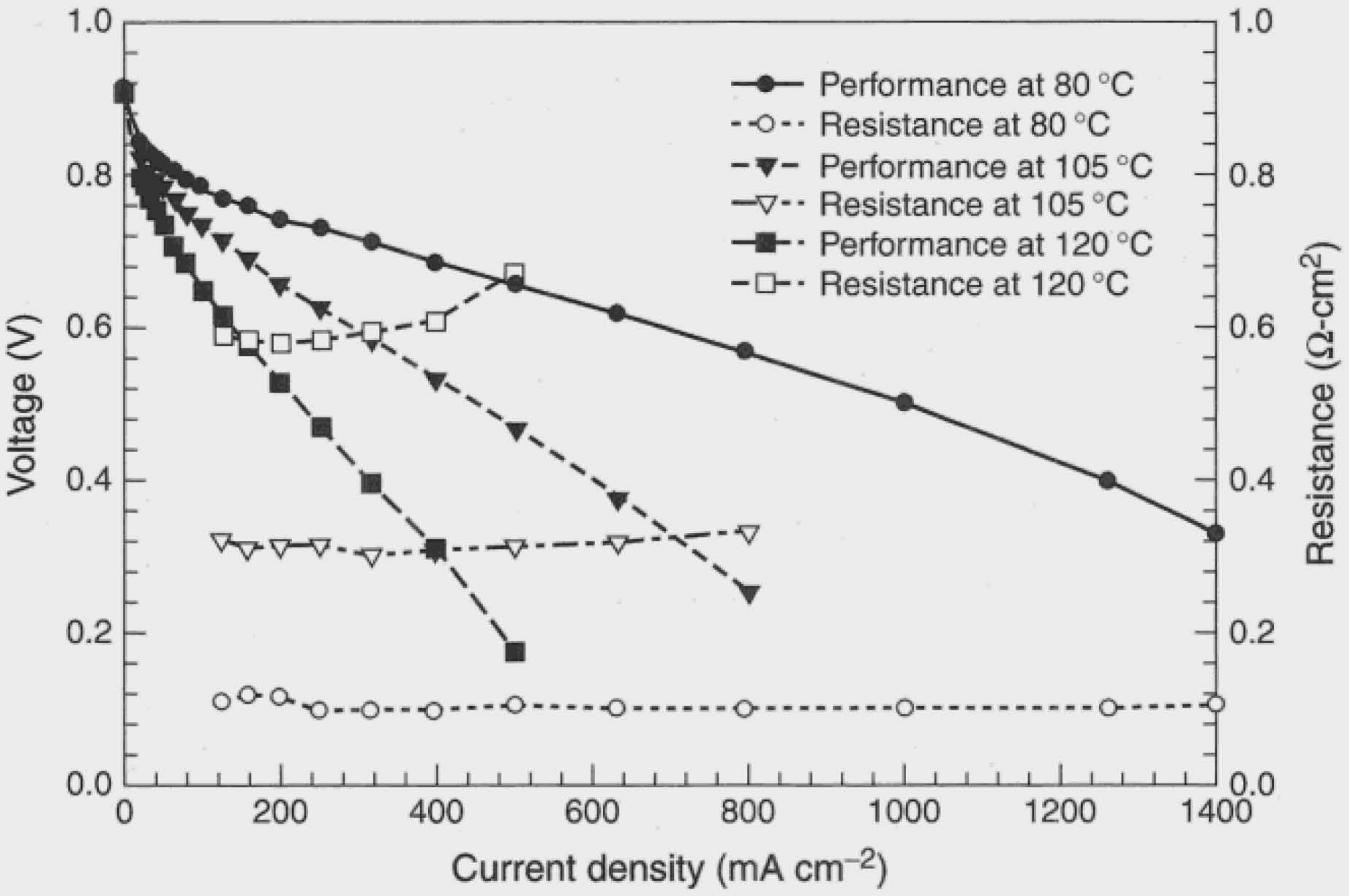

Figure 4. Effect of temperature on performance and resistance of commercial Gore MEA for pure hydrogen (ambient pressure; catalyst loading, 0.4 mg cm^{-2}; anode, 3.4 stoichiometric H_2; cathode, 4 stoichiometric air; humidifier temperature, 80 °C).

A commercial Gore MEA based on a Nafion®-like membrane of 25 μm thickness was tested at various cell temperatures with reactants saturated at constant temperature. The effect of temperature on performance of that MEA using ambient pressure hydrogen/air with both reactants saturated at 80 °C is shown in Figure 4. The Tafel slope of the commercial MEA at 80 °C is about 70 mV decade^{-1}, which is close to the value of $2.3RT/F$ based on the anticipated rate-determining step for the oxygen reduction reaction (ORR). Although the MEA shows excellent performance at 80 °C, a severe drop-off in performance and increase in resistance with increasing temperature are observed. At elevated temperature (120 °C), internal resistance increases slightly with increasing current density. This is a consequence of the drying out of the anode face of the membrane because the back diffusion of water is not sufficient at elevated temperature. Membranes that maintain good ionic conductivity at elevated temperature and low saturation are needed to obtain better cell performance.

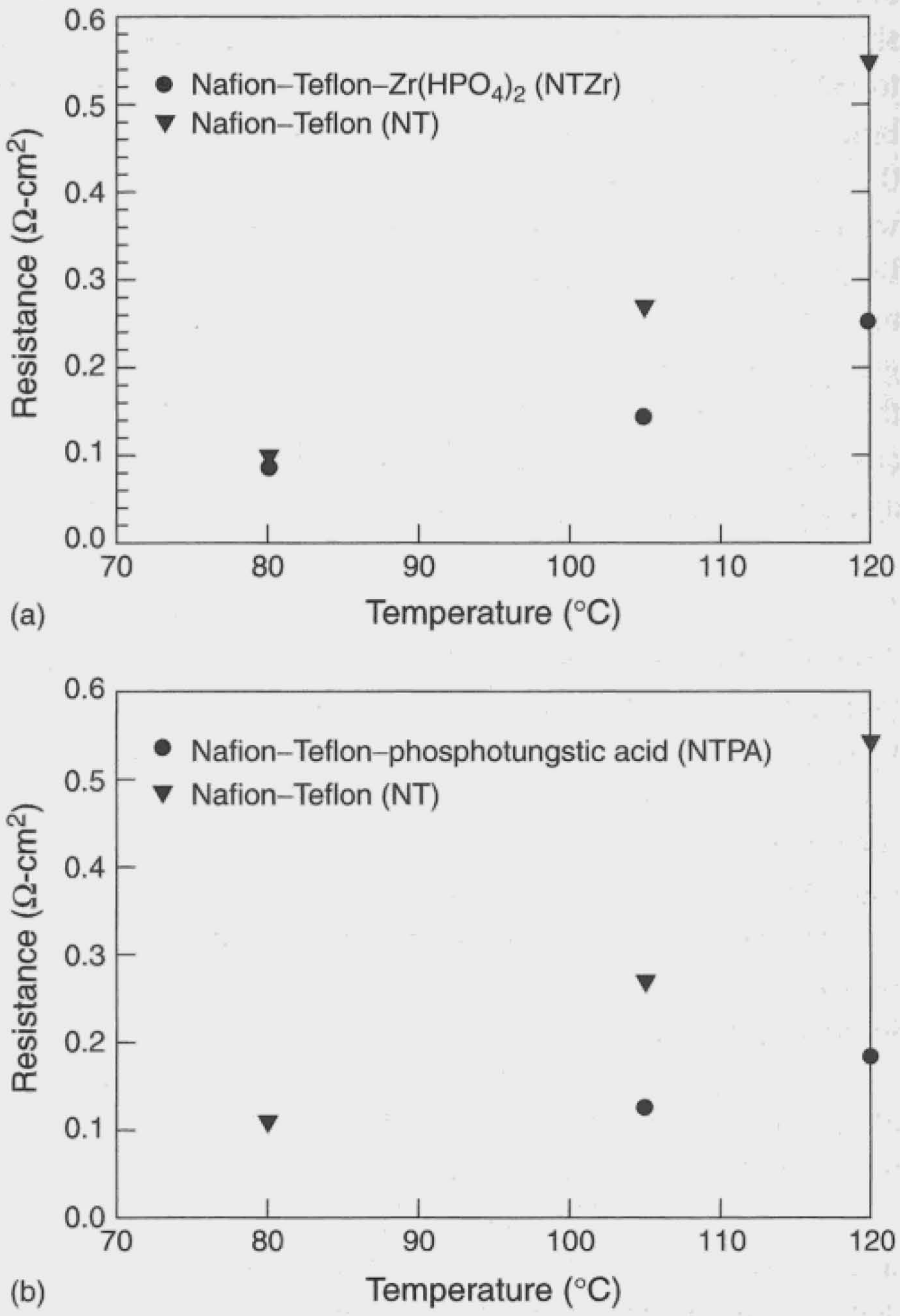

Figure 5. Effect of temperature on internal resistance of (a) NTZr and of (b) NTPTA at 400 mA cm^{-2}. Humidifier temperature, 90 °C.

Discussion of the numerous efforts that have been made in preparing high temperature membranes can be found in other sections of this handbook. The addition of ionically conductive solids such as heteropoly acids and zirconium (hydrogen) phosphate to PFSA membranes shows a promising reduction in the membrane resistance. The effects of temperature on the membrane resistances of Nafion® containing these additives are compared with membranes without additives in Figures 5(a) and (b). Large reductions in the membrane resistances are observed due to the addition of ionic/conductive solids. All of the data were

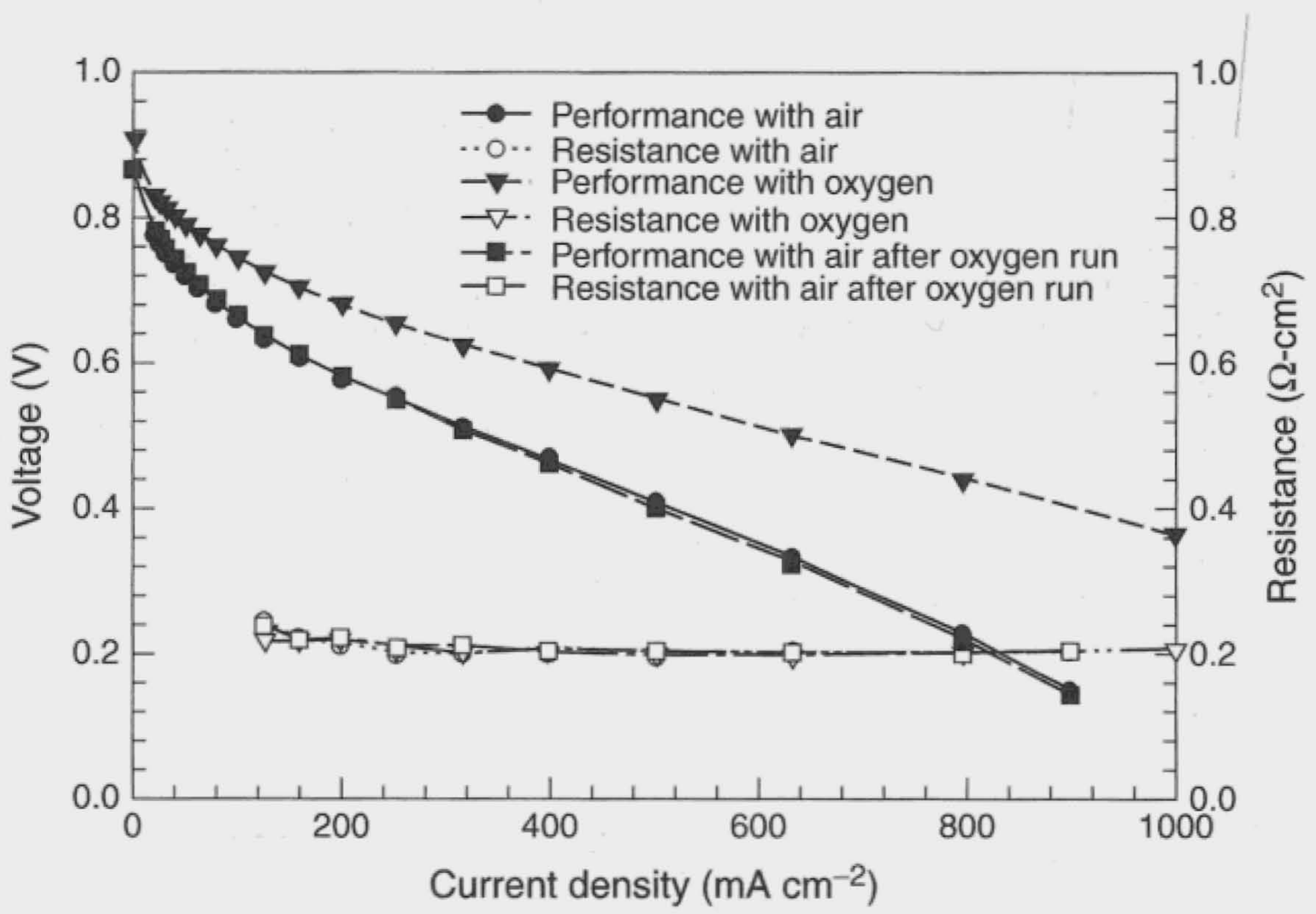

Figure 6. Performance and resistance data of NTPTA MEA at 120 °C (ambient pressure; anode, 3.4 stoichiometric H_2 saturated at 90 °C; cathode, 4.0 stoichiometric air or 19.0 stoichiometric oxygen saturated at 84 °C).

obtained at 400 mA cm^{-2} using the current interruption technique. However, the resistance for these membranes is independent of current density as, for example, the data plotted in Figure 6. A matrix made of Teflon® was used here to maintain good strength at a membrane thickness of 25 μm. Detailed discussion about these membranes can be found in the literature.[17, 22]

6 PERFORMANCE OF FUEL CELLS AT HIGH TEMPERATURE WITH LOW HUMIDIFICATION

The performance and internal resistance data of Nafion®–Teflon®–phosphotungstic acid (NTPTA) under ambient pressure (reactant dew points of 90 °C) at 120 °C using hydrogen as the fuel and oxygen or air as the oxidant are shown in Figure 6. Data using air as the oxidant were obtained both before and after oxygen data to make sure that the differences in performance between using air and oxygen as the reactants were accurately determined. The cell performances using air for the two cases were very close, indicating that no decay occurs in a short period of time.

A semilogarithmic plot of the IR-free performance data at 120 °C is shown in Figure 7. The Tafel slope on oxygen is about 83 mV decade^{-1}, which is close to the expected Tafel slope of 78 mV decade^{-1}. The level of polarization at low current density shows that the cathode catalyst is quite active. The current ratio between oxygen and air is below 4.8 : 1 (a ratio of 4.8 : 1 is expected for the first order oxygen reduction reaction) over the entire range. At 20 mA cm^{-2} for air, the current ratio was 4.0 : 1 decreasing to 3.2 : 1 at 100 mA cm^{-2}. This low current ratio is due to high ionic resistance present in the cathode catalyst layer. The cathode polarization increase at elevated temperature due to reduced ionic conductivity can also be seen in the commercial Gore MEA by re-plotting the performance data of Figure 4, using IR-free data. Since protons in the cathode behave both as a conductor and reactant, low proton activity in the electrolyte in the cathode can lead to large polarization (low reaction rate), resulting in poor cell performance.

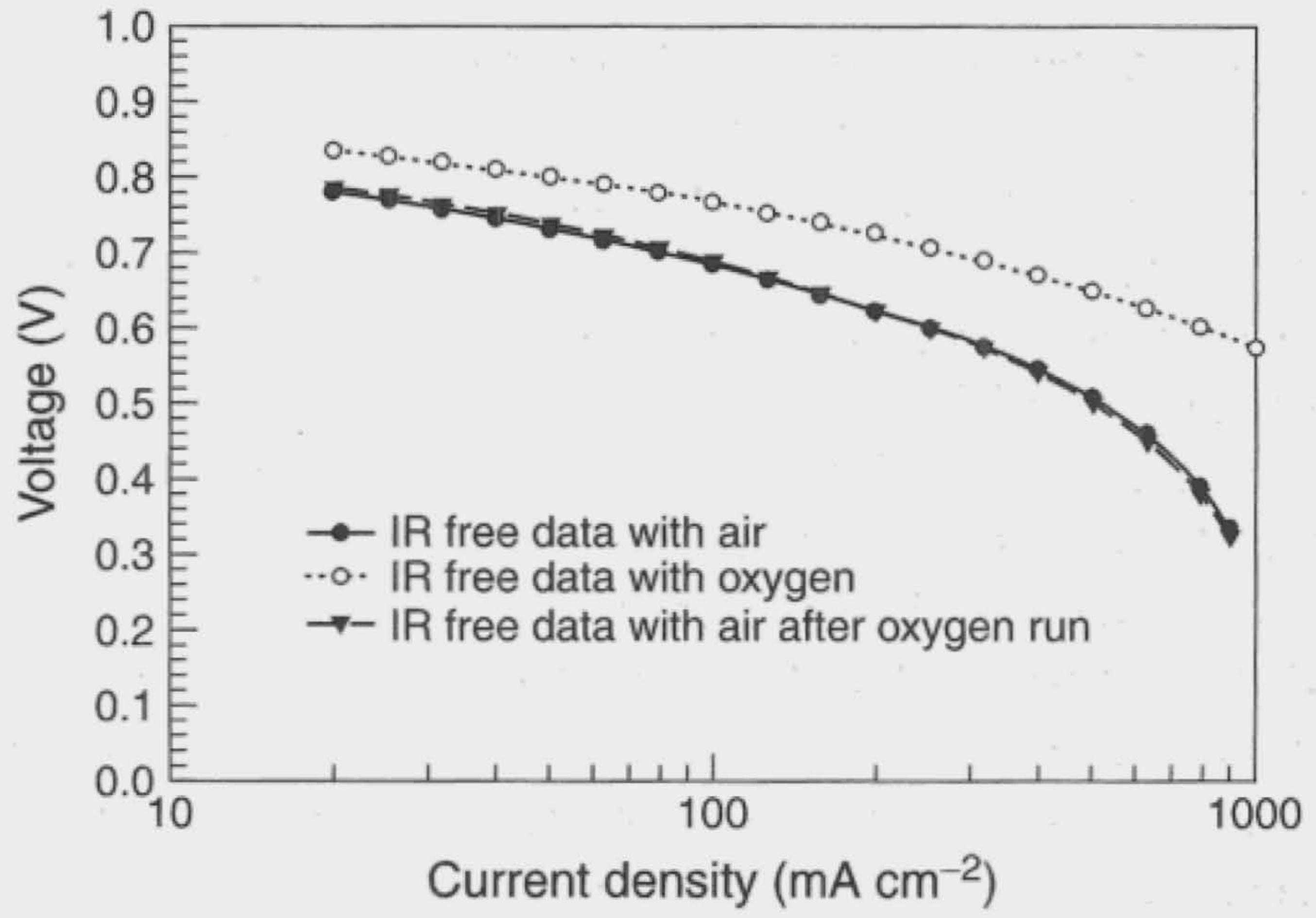

Figure 7. IR free performance data of NTPTA MEA at 120 °C (ambient pressure; anode, 3.4 stoichiometric H_2 saturated at 90 °C; cathode, 4.0 stoichiometric air or 19.0 stoichiometric oxygen saturated at 84 °C).

As a measure of cathode catalyst activity, the current at 0.8 V (IR free) on oxygen was 50 mA cm^{-2} for the NTPTA MEA of Figures 6 and 7 at 120 °C. The cathode catalyst activity measured on oxygen as a current at 0.8 V (IR free) for the NTZr MEA of Figure 5(a) was $49\,\mathrm{mA\,cm^{-2}}$ and $148\,\mathrm{mA\,cm^{-2}}$ at 120 °C and 80 °C, respectively.

This reduction in current at a constant cell voltage as temperature increases is largely due to the change in reactant pressure. The oxygen pressure decreases with the temperature increase resulting in a loss of current for the first order oxygen reduction reaction. The reduction of hydrogen pressure and increase of water vapor pressure also result in a reduction of the theoretical open circuit voltage with increasing temperature. A small reduction of theoretical open circuit voltage also results from a decrease in the free energy change.

7 SUMMARY

Single cell testing results indicate that the performance drop at low humidification conditions is due to the combination of membrane internal resistance loss and electrode polarization mainly from the cathode. Preparation of membranes with low resistance under low humidification conditions at ambient pressure is a first step in developing high performance PEM fuel cells. Fabrication of MEAs with small cathode polarization under low-humidification condition is the main challenge. PEM fuel cells have been developed for operation in a saturated environment. As a result, technical knowledge of optimal electrode structures under low-humidification conditions is lacking. More efforts in research are required to make PEM fuel cells successful under water-lean environments.

ACKNOWLEDGEMENTS

Some of data presented here are from Mr. Yongchao Si's Ph.D. work at the University of Connecticut. The authors appreciate his contribution.

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