Large-scale current fluctuations in PEM fuel cells operating with reduced feed stream humidification

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Abstract

The effects of systematic dehydration of the fuel and oxidant feed streams on the performance of a proton exchange membrane (PEM) membrane electrode assembly (MEA) were investigated in an attempt to understand the effects of feed stream humidification on cell operation. A significant but expected performance loss was observed when the feed stream humidification was diminished. In addition, strong periodic fluctuations in current and cell resistance were also observed as the feed stream humidification was decreased. A cyclic mechanism is proposed that may offer a qualitative explanation for these unusual fluctuations.
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1. Introduction

Proper hydration of the membrane electrode assembly (MEA) in a proton exchange membrane (PEM) fuel cell is critical to maintaining membrane conductivity and mechanical stability, and MEA performance [1,2]. Most PEM fuel cells are tested and operated under highly humidified conditions such that the cell temperature (T_{cell}) is equal to or less than the feed stream humidifier temperatures (T_{anode} and $T_{cathode}$) in order that the membrane remains well hydrated. Under conditions of low water availability there is a tendency for most proton conducting ionomers, especially perfluorinated ionomers such as Nafion^{TM}, to dehydrate, which causes conductivity to drop precipitously thereby degrading cell performance [3]. In fact, the upper limit on operating temperature of most PEM fuel cells utilizing perfluorinated ionomers is dictated by the need to maintain membrane hydration [4]. A PEM fuel cell that does not require external humidification of the feed gas streams is highly desirable from an engineering standpoint. Eliminating the parasitic losses attributed to heating the gas humidifiers and maintaining a pressurized cell creates a more efficient system. Additionally, unhumidified gas streams are richer per unit volume in fuel or oxidant compared to the equivalent wet gas streams, which favors higher cell efficiency.

Stable performance has been reported for PEM fuel cells using dry or slightly humidified gas streams. Previous work by Buchi and Watanabe has shown that stable PEM fuel cell performance can be achieved without humidifying the gas streams through use of product water produced by the electrochemical cell reaction, or direct humidification of the membrane itself by wicking from an auxiliary water supply [5,6]. Membrane electrode assemblies using phosphoric acid-doped polybenzimidazole membranes have demonstrated stable performances at temperatures up to 150 °C with low gas humidification, however this is due to the unusual mechanism (nearly unique to phosphoric-acid-based electrolytes) involving site-to-site proton hopping in such materials [7]. However, cells operated in these manners show significantly decreased performance when compared to analogous well-humidified cells, and in some cases (e.g. phosphoric-acid-based electrolytes) they can be irreversibly damaged by exposure to liquid water.

In this paper the effects of systematic dehydration of the fuel and oxidant feed streams on cell performance for a particular configuration of a PEM fuel cell using perfluorinated ionomer electrolytes are described. The work was pursued in an attempt to understand the effects of feed stream humidification on cell operation. As expected, a significant loss in performance was observed when the feed stream humidification level was diminished. However, an unusual effect was also observed involving strong periodic fluctuations in current and cell resistance as the feed stream humidification

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level is diminished. Possible causes for this unusual observation are discussed.

2. Experimental

Fuel cell membrane electrode assemblies were prepared from Nafion membranes using the decal transfer method [8]. In brief, ink containing Pt/C and Nafion was prepared by mixing catalyst (20% Pt on Vulcan XC-72R, Alfa Aesar, Ward Hill, MA, USA) with solubilized Nafion ionomer (5% by weight solution, 1100 EW, Solution Technology, Mendenhall, PA, USA). The dry mass ratio of supported catalyst (Pt and carbon together) to ionomer (solvent free) was 5:2. After stirring for several hours, the proton form of the ionomer was converted to the tetrabutylammonium (TBA^+) form by the addition of TBAOH (1 M in methanol, Aldrich). The mixture was thickened by addition of glycerol. Additional changes in consistency were made by adding isopropanol or by allowing the evaporation of lighter alcohols. Once the desired consistency was achieved, the ink was applied by painting in thin layers onto PTFE-coated templates (area = $5\,cm^2$) onto which a PTFE-based release agent (6075 Dry Film Lubricant, Crown, Woodstock, IL, USA) had been applied. Catalyst loadings in the range of 0.3 mg Pt/cm^2 (determined gravimetrically) were achieved for both anodes and cathodes by a repetitive process of ink painting and drying steps.

Nafion 1135 membranes (CG Processing, Medenhall, PA, USA) in the sodium ion form were dried and flattened while heating at 120 °C on a vacuum table for 15 min. The painted catalyst templates were hot pressed onto the Nafion1135 membranes at 200–210 °C and 600 lb pressure for 5 min. Negligible catalyst remained on the templates when the pressing was complete and the templates were peeled away. Following pressing, the MEA was heated at 80 °C in 0.5 M sulfuric acid for 60 min to convert the ionomer back to the proton form. The MEAs were then soaked in the acid solution overnight at room temperature, rinsed several times with deionized water, then pulled dry and flat on a vacuum table at 60 °C for 20 min prior to being mounted in the fuel cell hardware for testing.

The testing hardware (Fuel Cell Technologies, Alberquerque, NM, USA) consisted of two nuclear-grade graphite blocks (Union Carbide) into which "single serpentine" gas flow channels had been machined. MEAs were mounted between the blocks. On each side of the MEAs was placed a piece of uncatalyzed gas diffusion backing (ELAT/NC, E-TEK, Natick, MA, USA). The current collectors for both the anode and cathode were gold-coated aluminum plates. The assembly was structurally supported by two electrically isolated aluminum blocks. The two blocks were fastened together using eight bolts tightened with 125 in. lbs of torque. The fixture was heated using integral cartridge heaters.

Heated and humidified fuel (H_2) and oxidant (O_2) streams were supplied to the test fixture by a test station (Globe Tech,

model 890, College Station, TX, USA). Gas humidification was accomplished using water-filled heated sparger bottles. Unless otherwise noted, the gas flow rates were linked to the current generated by the cells as follows: hydrogen flow consisted of a 60 sccm base rate + 14 sccm per ampere of cell current, and oxygen flow consisted of 60 sccm + 8 sccm per ampere of cell current. These parameters resulted in gas flows in the range of 4–6 times stoichiometric. The cells were operated with 2 atm of back-pressure (gauge) on both the anode and the cathode.

Water partial pressure values for the humidified gas streams were measured at 130 °C (to ensure the absence of liquid water) by replacing the usual fuel cell test fixture (see below) with a heated stainless steel Swagelock fitting into which a high-temperature hygrometer sensor (Rotronic, Huntington, NY, USA) was mounted. Hygrometer output values were reported as relative humidity at the measurement temperature of 130 °C, and converted to water partial pressures using standard steam tables [9]. Data points were collected approximately once per minute over a 60 min time span, and are reported here as average values over the 60 min time span. Fluctuations in hygrometer output were occasionally observed, particularly at the highest humidifier temperature of $T_{humidifier} = 115$ °C, and were found to correspond to the presence of liquid water in the gas stream. These fluctuations diminished as the humidifier temperature was lowered until disappearing completely at $T_{humidifier} = 80$ °C.

Cells were broken in overnight at a constant potential of 0.5 V at a cell temperature of 80 °C. Hydrogen at the anode and oxygen at the cathode were passed through sparger bottles heated to 105 and 90 °C, respectively prior to entering the cell. Once constant current was achieved, the cells were further tested by acquisition of a series of polarization curves to ensure normal performance. The effects of feed stream humidification were then tested by making systematic adjustments to the humidifier sparger bottle temperatures while monitoring cell current and resistance (measured by the current interrupt method) at constant cell potential over time to assess the response to the changes in feed stream humidification.

3. Results

The experiments described below follow a general protocol of monitoring cell current and resistance at a fixed cell potential (often 0.5 V) while changes are made to the humidification level of the feed gas streams. After a break-in period and verification of MEA operation by acquisition of polarization curves under typical humidification conditions ($T_{cell} = 100$ °C, $T_{anode} = 115$ °C, and $T_{cathode} = 110$ °C), MEAs were subjected to progressively more dehydrating conditions by lowering the temperature of the sparger bottles used to accomplish feed stream humidification.

Fig. 1 presents plots of cell current and resistance versus time for a $5\,cm^2$ Nafion 1135-based MEA subjected to
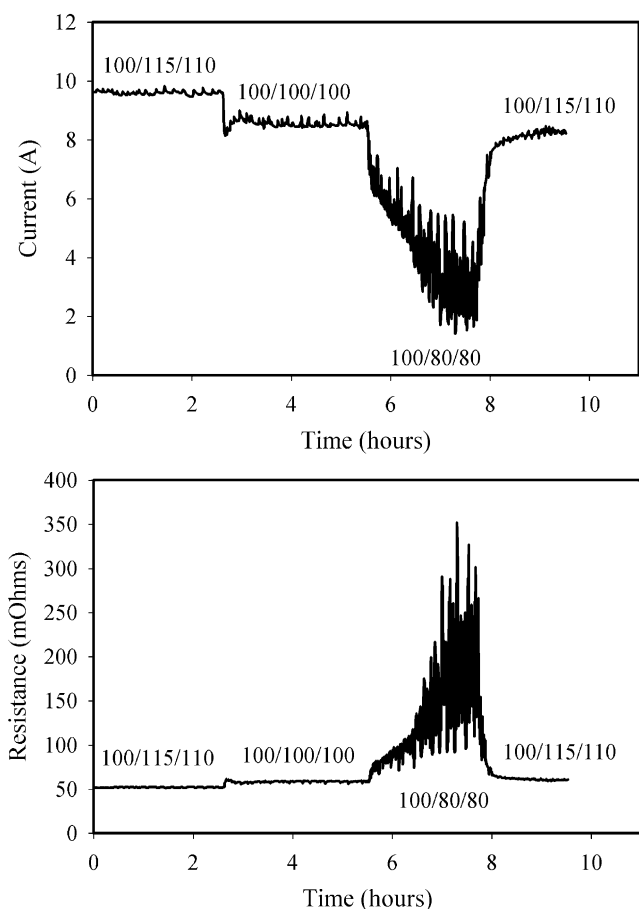
Fig. 1. Current and cell resistance as functions of time and temperature at 0.5 V load during desiccation for a $5\,cm^2$ Nafion 1135 (88 μm thick) MEA with Nafion 110 in the catalyst layers. Initial temperatures: $T_{cell} = 100\,°C$, $T_{anode} = 115\,°C$, and $T_{cathode} = 110\,°C$. Temperatures changed to $T_{cell} = 100\,°C$, $T_{anode} = 100\,°C$, and $T_{cathode} = 100\,°C$ at 2.6 h; $T_{cell} = 100\,°C$, $T_{anode} = 80\,°C$, and $T_{cathode} = 80\,°C$ at 5.5 h; $T_{cell} = 100\,°C$, $T_{anode} = 115\,°C$, and $T_{cathode} = 110\,°C$ at 7.8 h.

various levels of feed stream humidification. The first segment corresponds to operation under well-humidified conditions, for which current fluctuations were small (less than 0.15 A). The MEA was then subjected to two stages of
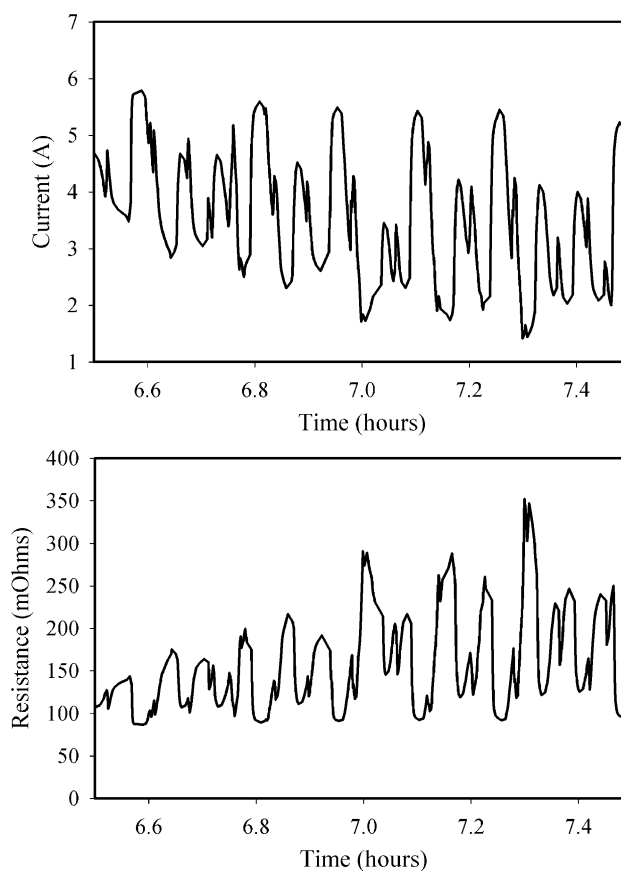

Fig. 2. Current as a function of time at 0.5 V load during desiccation for a $5\,cm^2$ Nafion 1135 (88 μm thick) MEA with Nafion 110 in the catalyst layers. $T_{cell} = 100\,°C$, $T_{anode} = 80\,°C$, and $T_{cathode} = 80\,°C$.

operation in which T_{cell} was kept constant while the humidifier temperatures (T_{anode} and $T_{cathode}$) were progressively decreased. From 2.5 to 5.5 h the temperature of the humidifier bottles were dropped from $T_{anode} = 115\,°C$ and $T_{cathode} = 110\,°C$ to $T_{anode} = T_{cathode} = 100\,°C$. As expected from previous conductivity studies on Nafion ionomers [2,4], cell performance (as indicated by cell current at a particular potential) diminished with decreasing humidification of the gas

Table 1
Water vapor pressure and relative humidities of gas feed streams

Humidifier temperature (°C)	Flow rate (sccm)	Water vapor pressure[a] (bar)	% Relative humidity at the humidifier temperature[b]	% relative humidity at the cell temperature[c]
80	60	0.214	45	21
80	100	0.221	47	22
80	175	0.253	54	25
100	61	0.593	58	58
100	100	0.520	51	51
100	175	0.668	66	66
115	61	1.151	68	114
115	100	1.490	88	147
115	175	1.709	101	169

[a] Measured at 130 °C; see Section 2.
[b] Assuming equilibrium water partial pressures of 0.473 bar at 80 °C, 1.014 bar at 100 °C, and 1.691 bar at 115 °C [9].
[c] 100 °C.

feed streams. Additionally, modest fluctuations in current (0.5 A in amplitude) and cell resistance (2 mΩ in amplitude) were observed. From 5.5 to 7.8 h the temperature of the humidifier bottles was further decreased to $T_{anode} = T_{cathode} = 80\,°C$. The relative humidity of both feed streams at the cell temperature of 100 °C thus decreased to less than 30% (see below, Table 1). Operation at these conditions resulted in further performance losses of greater than 65% relative to the original performance. Much larger fluctuations in current (4 A in amplitude) and cell resistance (250 mΩ in amplitude) were observed. In the final step of the experiment, the humidifier bottle temperatures were returned to their initial values of $T_{anode} = 115\,°C$, and $T_{cathode} = 110\,°C$. Cell performance returned to 90% of its original level as current fluctuations decreased.

Fig. 2 shows an expanded view of the cell current under the low-feed-stream humidification conditions of $T_{cell} = 100\,°C$, $T_{anode} = T_{cathode} = 80\,°C$. The repetitive nature of the fluctuations with periods of approximately 5 min is

evident. Despite the fluctuations, the baseline and peak currents were observed to stabilize following the change in feed stream humidification and the cell appeared to achieve a quasi-steady-state operation. While current and resistance fluctuations were observed as feed stream humidification was reduced for all of the cells studied, we note that the fluctuations were not always quantitatively reproducible. Both period and amplitude varied from one experiment to another even for nominally identical experiments.

It is useful to correlate the effects noted in Figs. 1 and 2 of changing feed stream humidification with independent measurements of feed stream humidification under different conditions. Table 1 presents a series of measured values for the water partial pressure and corresponding relative humidities at the humidifier and cell temperatures for feed streams at various humidifier temperatures and gas flow rates. Two things are especially notable about Table 1. First, relative humidity values calculated at the humidifier bottle temperatures are consistently less than 100%, particularly at the
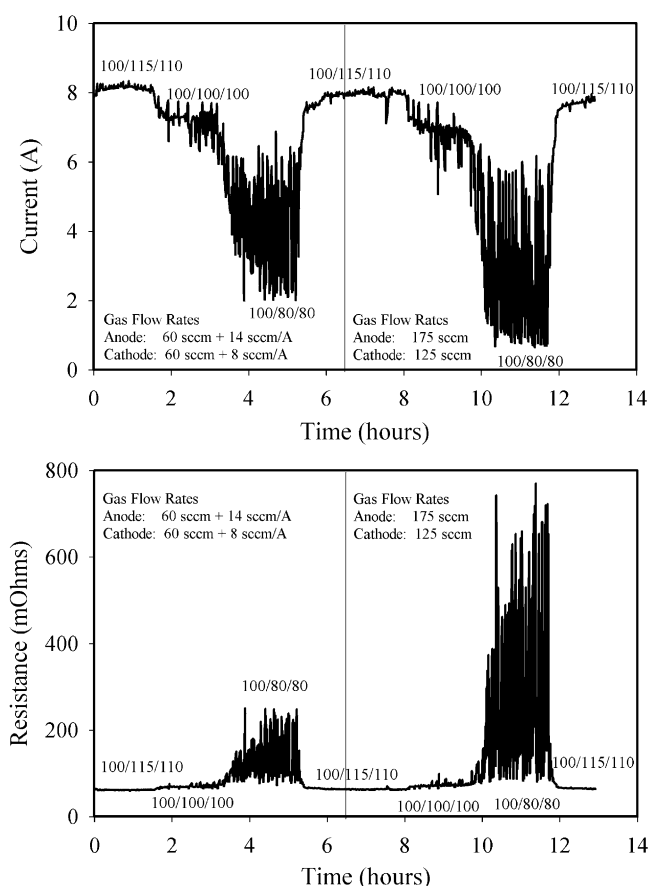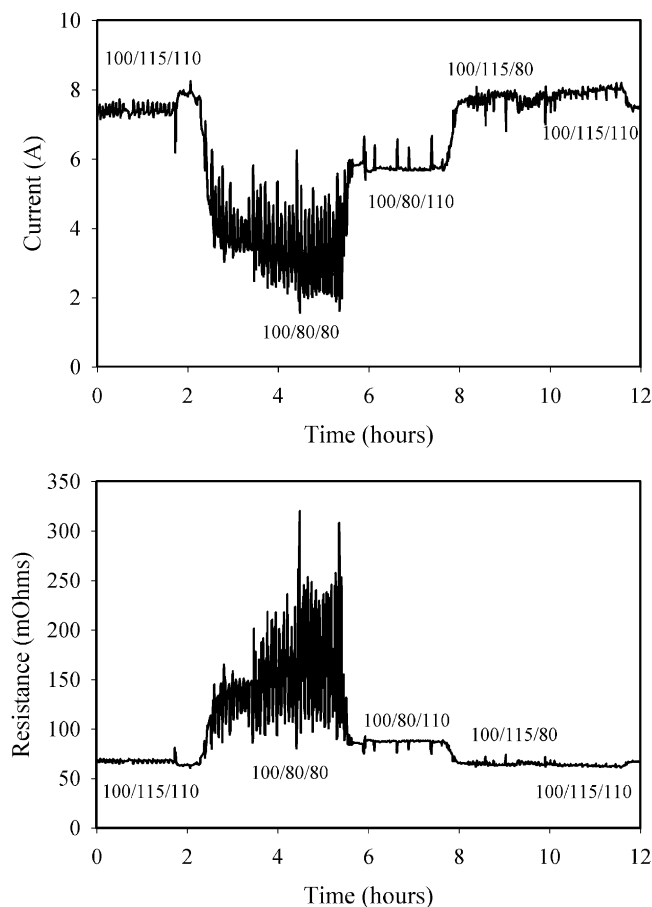

Fig. 3. Current and cell resistance as functions of time and temperature at 0.5 V load during desiccation for a 5 cm^2 Nafion 1135 (88 μm thick) MEA with Nafion 110 in the catalyst layers obtained with current based and fixed gas flow rates. Initial temperatures: $T_{cell} = 100\,°C$, $T_{anode} = 115\,°C$, and $T_{cathode} = 110\,°C$. Temperatures changed to $T_{cell} = 100\,°C$, $T_{anode} = 100\,°C$, and $T_{cathode} = 100\,°C$; $T_{cell} = 100\,°C$, $T_{anode} = 80\,°C$, and $T_{cathode} = 80\,°C$; $T_{cell} = 100\,°C$, $T_{anode} = 115\,°C$, and $T_{cathode} = 110\,°C$.

Fig. 4. Current and cell resistance as functions of time and temperature at 0.5 V load during desiccation for a 5 cm^2 Nafion 1135 (88 μm thick) MEA with Nafion 110 in the catalyst layers. Initial temperatures: $T_{cell} = 100\,°C$, $T_{anode} = 115\,°C$, and $T_{cathode} = 110\,°C$. Temperatures changed to $T_{cell} = 100\,°C$, $T_{anode} = 80\,°C$, and $T_{cathode} = 80\,°C$ at 2.0 h; $T_{cell} = 100\,°C$, $T_{anode} = 80\,°C$, and $T_{cathode} = 110\,°C$ at 5.5 h; $T_{cell} = 100\,°C$, $T_{anode} = 115\,°C$, and $T_{cathode} = 80\,°C$ at 7.7 h; $T_{cell} = 100\,°C$, $T_{anode} = 115\,°C$, and $T_{cathode} = 110\,°C$ at 9.3 h.
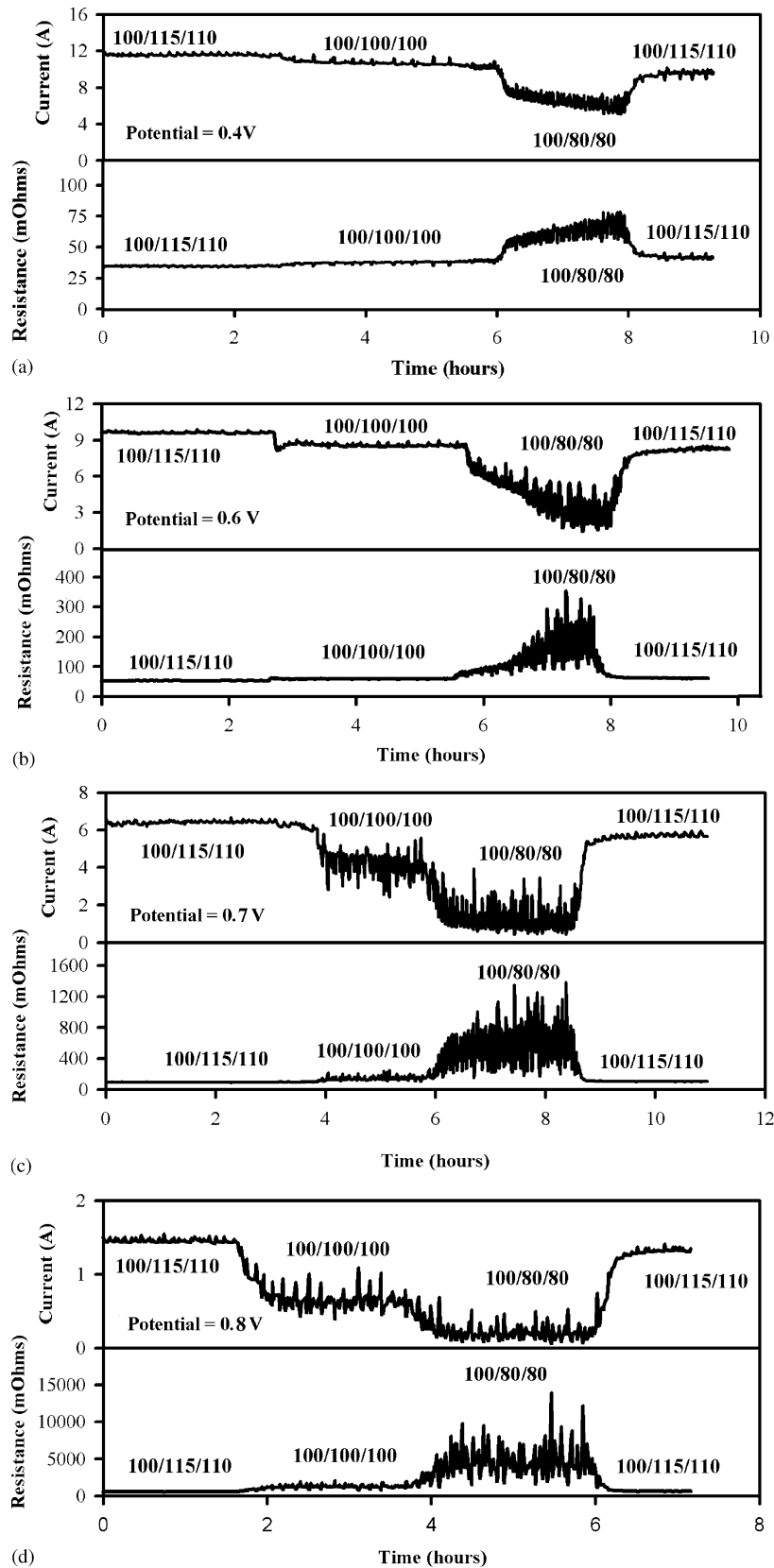
Fig. 5. Current and cell resistance as functions of time and temperature at (a) 0.4 V load, (b) 0.6 V load, (c) 0.7 V load, and (d) 0.8 V load during desiccation for a 5 cm^2 Nafion 1135 (88 μm thick) MEA with Nafion 110 in the catalyst layers. Initial temperatures: $T_{cell} = 100\,^\circ$C, $T_{anode} = 115\,^\circ$C, and $T_{cathode} = 110\,^\circ$C. Temperatures changed to $T_{cell} = 100\,^\circ$C, $T_{anode} = 100\,^\circ$C, and $T_{cathode} = 100\,^\circ$C; $T_{cell} = 100\,^\circ$C, $T_{anode} = 80\,^\circ$C, and $T_{cathode} = 80\,^\circ$C; $T_{cell} = 100\,^\circ$C, $T_{anode} = 115\,^\circ$C, and $T_{cathode} = 110\,^\circ$C.

lower bottle temperatures, indicating that the feed streams do not adequately equilibrate with the heated water as they pass through the bottle. This fact probably reflects an inadequate equilibration time and/or surface area for the gas stream with the heated water. Second, relative humidity values for the gas streams depend upon gas flow rate, but in a counterintuitive way, such that the relative humidities are highest at the highest gas flow rates, particularly at the higher humidifier temperatures. It is surprising that the relative humidity of the humidified gas stream increases with gas flow rate, although we note that there have been other prior reports of similar behavior with other sparger humidification systems in the literature [10]. It is thought to be due to an increase in carry-over of liquid water, either as aerosol or from splashing, with faster gas flow rates. Interestingly, the observed fluctuations in cell current and resistance shown in Figs. 1 and 2 are greatest under conductions where the gas feed streams are least humidified and where liquid water carry-over is minimal. Thus, we believe that the behavior in Figs. 1 and 2 cannot be attributed to variations in feed stream humidification associated with liquid water in the feed streams.

The fluctuations in cell current and resistance were not a strong function of whether the gas flow rates were linked to current or not. Fig. 3 presents data for a cell that was run under low-humidification conditions with both current-linked and fixed gas flows. Current-based flows were comprised of a base rate of $60 + 14$ sccm per ampere for the anode and $60 + 8$ sccm per ampere for the cathode. Fixed rates were set at 175 sccm for the anode and 125 sccm for the cathode. Fluctuations were seen under both sets of conditions, indicating that the observed oscillations are not a consequence of the current-based flow rates.

The effect of the diminished feed stream humidification levels on cell performance was observed to be reversed when either feed stream was rehydrated. Fig. 4 presents data from an experiment in which both feed stream humidification levels were lowered by adjusting as T_{cathode} and T_{anode} to 80 °C. At these low-humidification conditions large fluctuations were observed in both cell current (3 A) and resistance (200 mΩ). Cell performance was improved by selectively increasing T_{cathode} to 110 °C while maintaining $T_{\text{anode}} = $ 80 °C, with fluctuations in both current (0.7 A) and resistance (10 mΩ) being diminished. Selectively rehydrating the anode feed stream ($T_{\text{anode}} = 115$ °C and $T_{\text{cathode}} = 80$ °C) also improved cell performance, although slight fluctuations in cell current (0.6 A) and resistance (10 mΩ) still remained.

The results of several experiments involving variations in both cell potential (load) and feed stream humidification are presented in Fig. 5. Performance decreases (average cell current) and fluctuations in current and resistance were always observed with decreases in feed stream humidification at all cell potentials. However fluctuations in resistance grew larger at the higher cell potentials. For example, at the lowest humidification conditions ($T_{\text{cell}} = 100$ °C, $T_{\text{anode}} = T_{\text{cathode}} = 80$ °C), fluctuations of 20 mΩ were observed at

a potential of 0.4 V, which grew to fluctuations of 1100 mΩ at 0.6 V and to 10,000 mΩ at 0.8 V.

4. Discussion

While the cause of the observed fluctuations in current and resistance under relatively low-humidification conditions is not known for certain, it is likely related to water management issues in the cell. Figs. 6 and 7 present two possible cyclic schemes which could both offer qualitative rationalizations for the current fluctuations. The proposed scheme in Fig. 6 begins with a cell operating at high current. A combination of limited water available at the anode, electroosmotic drag transporting water from anode to cathode, and insufficient water back-diffusion from cathode to anode, causes the MEA to dehydrate, especially at the anode. The dehydration is manifested as an increase in cell ohmic resistance, which leads to decreased cell performance and low current output. While at diminished output level, the small amount of water available at the anode from the external humidification is enough to re-humidify the cell since the electroosmotic drag is also diminished at low currents. Consequently, the cell ohmic resistance decreases and the performance increases. Thus the whole cycle begins again.

A second possible explanation, presented in Fig. 7, involves flooding occurring at the cathode. At high currents,
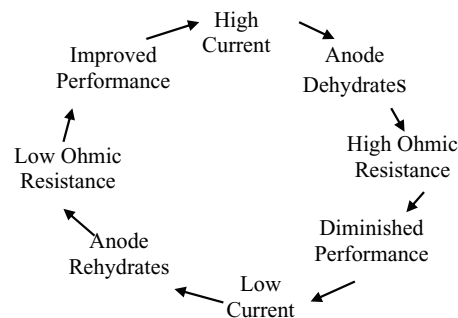
Fig. 6. Proposed cause of the observed fluctuations in current and resistance during operation of a PEM fuel cell under dry conditions involving dehydration of the MEA at the anode.
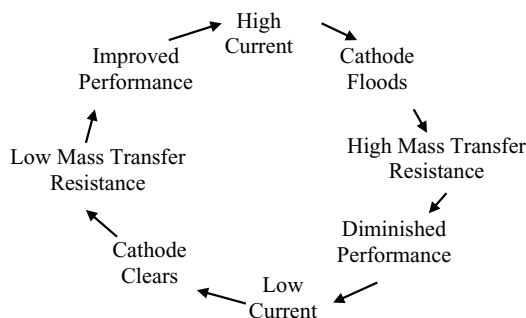
Fig. 7. Proposed cause of the observed fluctuations in current and resistance during operation of a PEM fuel cell under dry conditions involving flooding of the anode.

the greater production of water at the cathode hinders the mass transport of oxygen, increasing mass transfer resistance and diminishing cell performance. The decrease in current means that less water is produced, allowing the excess water to be removed from the cathode by the flowing gas stream. As a result mass transfer resistance decreases and cell performance increases.

A careful consideration of the data in Figs. 4 and 5 indicates that the scenario in Fig. 6 is the one most likely to be responsible for the observed current and cell resistance fluctuations. In Fig. 4 we note that rehydration of just the anode feed stream is highly effective in regenerating the cell performance, whereas rehydration of just the cathode stream is effective but less so. Also, in Fig. 5 we note that the performance losses (diminished current) and current and resistance fluctuations are greatest at the highest cell potentials (lowest loads) where water generation from the cell reactions is lowest and component dehydration is most likely. Neither of these observations would be consistent with the scenario in Fig. 7, where performance losses occur mostly at the cathode and are greatest when water availability is greatest.

5. Conclusions

Humidification of gas feed streams in PEM fuel cells has been found to play a large role in both cell performance and stability. Performance is greatest (currents are largest) and most stable when feed streams are highly humidified. As feed stream humidification levels are progressively diminished, large fluctuations in current and a significant decrease in overall cell performance (current) were observed. The fluctuations appear to be due to the process involving cyclic hydration/dehydration of the anode.

Acknowledgements

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