Proceedings of the 4th International Conference of Fluid Flow, Heat and Mass Transfer (FFHMT'17)
Toronto, Canada – August 21 – 23, 2017
Paper No. 136
DOI: 10.11159/ffhmt17.136

Transient Changes in Liquid Water Distribution in Polymer Electrolyte Membrane Fuel Cells

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Abstract **-** Water management is a critical factor in obtaining the highest performance and efficiency from polymer electrolyte membrane (PEM) fuel cells. The liquid water distribution in the individual layers of the PEM fuel cell has a strong impact on performance. The ionic conductivity of the membrane has a strong dependence on membrane hydration. The reactant gases in a PEM fuel cell are supplied through a humidification system to maintain appropriate levels of hydration in the membrane. However, the removal of the anode humidifier would significantly reduce the balance of plant costs and reduce the volume required for the fuel cell in an automotive setting. In this paper, the impact of lower anode humidification on the cell performance and the water distribution in the membrane and the cathode gas diffusion layer were studied. Synchrotron X-ray radiography was used to measure the changes in liquid water quantity in the individual layers. The impact of changing anode humidification on the water distribution is studied. The changes in membrane hydration levels have been measured by the radiographic technique and compared with the changes in membrane resistance.

Keywords**:** PEM fuel cell; membrane dehydration; synchrotron X-ray radiography; transient changes; anode humidification

1. Introduction

Polymer Electrolyte Membrane (PEM) fuel cells are considered as the most suitable candidate for replacing internal combustion engines for automotive applications [1]. Automotive powertrains have a dynamic power demand [2], [3]. Water management in PEM fuel cells is a topic of critical importance due to its impact on the performance and efficiency [4], [5]. Although water balance and the transport of water through the membrane has been studied extensively under steady state operation [5]–[10], it is important to investigate the dynamic changes in water content in the individual layers of the PEM fuel cell during transient operation. Banerjee and Kandlikar [11] presented a comprehensive review of the transient processes affecting fuel cell performance, and identified changes in membrane hydration as a process that undergoes transient changes over time periods of up to several minutes.

In a conventional fuel cell stack, both the anode and the cathode sides of the fuel cell are supplied with humidified reactant gases [12], [13]. However, removing the anode humidification system could significantly reduce the overall system cost [14]. In trying to remove the need for anode humidification from the fuel cell system, other works have focused at operating the cell with a dead ended anode setup [15]–[17]. The present work investigates the impacts of operating at lower reactant humidification at the anode on cell performance and membrane hydration. The time required for the hydration levels in the membrane to change as a result of changing current density has been investigated.

Changes in membrane hydration results in increased resistance to ionic transport, which contributes to the overall ohmic resistance of the cell. The changes in ohmic resistance can be measured through the high frequency resistance [18]. Friede et al. [19] measured the ohmic resistance of the cell, and reported that a significant increase in cell resistance was observed 50 seconds after the introduction of dry reactant gases, pointing to the time required for the membrane hydration to change for a significant impact on the cell resistance and potential. Yu and Ziegler [20] also demonstrated that change in

membrane hydration is predominantly observed when current density is increased, which is attributed to the increase in electro-osmotic drag with increase in current densities [21].

The membrane hydration can also be measured using visualization techniques. Hickner et al. [10] investigated the water distribution in the PEM fuel cell using neutron radiography and showed that losses in membrane hydration were evident at high temperature operation (at 80°C), even with fully humidified reactant gases. The loss in hydration was amplified at higher current densities. In the current work, the changes in membrane hydration were measured using synchrotron X-ray radiography. The changes in high frequency resistance were correlated to the changes in membrane hydration levels, resulting from operating the cell at different levels of anode inlet gas relative humidity.

2. Methodology

The experiments in this study were conducted with a custom-built fuel cell with an active area of 0.68 cm^2. A Nafion® 115 membrane was used in this study with a 0.3 mg/cm2 Pt/C catalyst coating. The GDL used in the study was SGL 25BC on both the anode and cathode sides. The flow field utilized channels of 0.5 mm width and 0.5 mm depth, separated by rib regions of 0.5 mm width.

The fuel cell operating conditions were controlled using a fuel cell test stand (Scribner 850e, Scribner Associates, North Carolina, USA). For this study, the fuel cell was operated at a temperature of 60°C at an outlet pressure of 200 kPa (absolute) and constant cathode inlet relative humidity (RH) of 100%. The anode relative humidity was varied from dry (RH = 0) to fully humidified (RH = 100%). The cell potential and the high frequency resistance are reported as performance metrics.

The radiography described in this study was performed at the Biomedical Imaging and Therapy – Bending Magnet (0505B1-1) beamline at the Canadian Light Source Inc. (CLSi) in Saskatoon, Canada [22]. X-ray radiographs were captured at an energy level of 24 keV, using an AA40 scintillator and an Orca Flash 4 Camera (Hamamatsu, Japan). The images were recorded with a pixel resolution of 6.5 µm/pixel and a temporal resolution of 0.33 frames per second (fps).

Test images were recorded during the operation of the fuel cell and compared against the dry (reference) images recorded at open circuit voltage (zero current), with the same flow conditions. The images were analysed using the Beer-Lambert law (equation 1) to obtain the liquid water thickness at each pixel location of the image. The images were also corrected for any imaging movements using an in-house developed algorithm [23], [24].

$$t_w = \frac{1}{\mu_{water}} \ln\left(\frac{I_{dry}}{I_{wet}}\right) \quad (1)$$

In equation 1, t_w is the measured thickness of water, and μ_{water} is the X-ray attenuation coefficient of water. I_{dry} is the reference image obtained when the cell was maintained at open circuit voltage (OCV), such that no water is produced as a result of the electrochemical reaction. I_{wet} is the test image with liquid water present, which is to be measured.

3. Results

Figure 1 shows the polarization curve of the fuel cell operated at a temperature of 60ºC with cathode inlet gas relative humidity of 100% and different levels of anode inlet gas relative humidity. It can be observed that the cell with dry inlet gases reached a much lower limiting current compared to the fuel cells operated with humidified inlet gases. The reduced performance is dominated by the ohmic resistance of the cell. The ionic resistance offered by the membrane contributes to the large ohmic resistance of the cell.

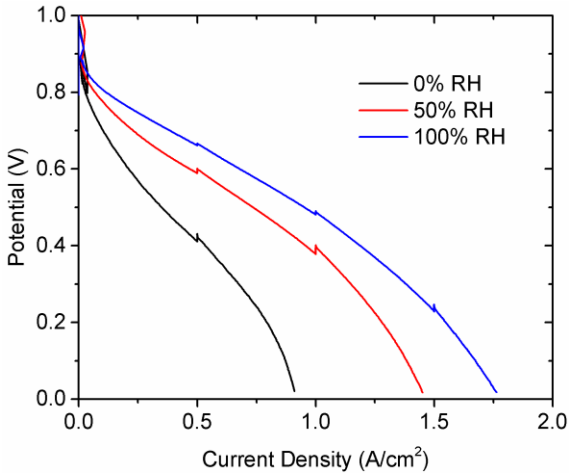

Fig. 1: Polarization curve of fuel cell operated at 60°C with three levels of anode inlet gas relative humidity.

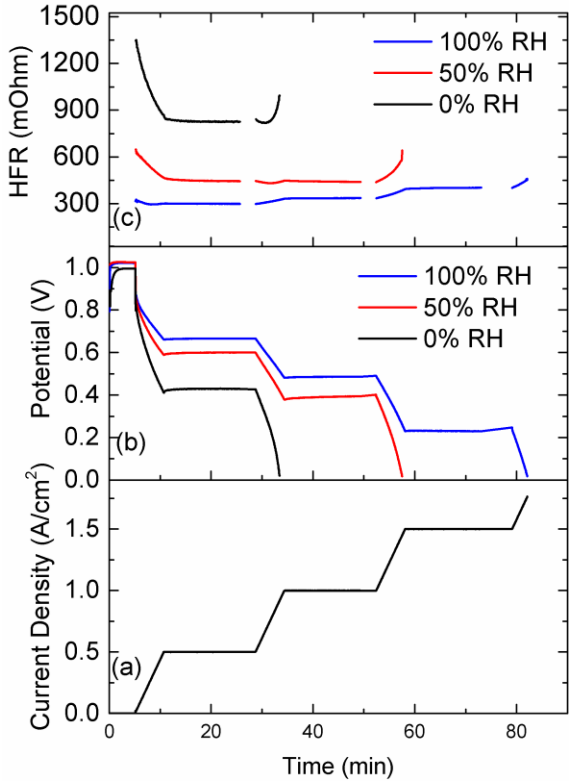

Fig. 2: Transient behaviour of fuel cell performance (a) current density changes (b) cell potential (c) high frequency resistance as a function of time.

Figure 2 shows the transient response of the fuel cell with changes in current density. Figure 2(a) shows the current density changes imposed on the cell as a function of time. These changes in current density act as the driving force for the changes in cell performance and the membrane resistance. Figure 2(b) shows the cell potential as a function of time and Figure 2(c) shows the high frequency resistance (HFR) measurement for the fuel cell operated at the three anode inlet relative humidity. The high frequency resistance is a measure of the ionic resistance offered by the cell and is a function of the hydration state of the membrane [5]. The fuel cell operated with dry anode inlet gases showed the highest membrane resistance (lowest membrane hydration). With the onset of current being drawn, water is produced as a result of the electrochemical reaction. The water generated from the reaction helps to rehydrate the membrane resulting in a decrease in membrane resistance. The decrease in membrane resistance is evident in the decrease in high frequency resistance of the

fuel cells operated with dry anode and 50% anode inlet relative humidity. However, the decrease in membrane resistance is not observed in the fuel cell operated with fully humidified (100% RH) anode.

Figure 3 shows the change in average water thickness in the membrane as a function of time. At OCV, the water thickness in the membrane remains steady. As the current increases to reach 0.5 A/cm^2, the membrane water quantity increases, and reaches a steady state. The increase is membrane hydration results in reduced membrane resistance as reported earlier (Figure 2(c)).

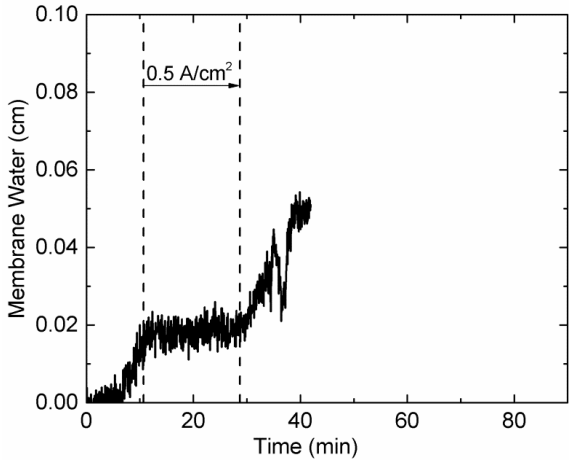

Fig. 3: Average water thickness in the membrane as a function of time.

Figure 4 shows the change in liquid water thickness in the cathode gas diffusion layer as a function of time. At a current density of 0.5 A/cm^2, the same quantity of water is produced as a result of the electrochemical reaction and the cathode reactant gases are fully humidified (100% RH) in both the cases. However, significantly lower amount of water is detected in the cathode gas diffusion layer, as observed in Figure 4. This shows that the difference in liquid water detected in this region is being taken up by the membrane to become rehydrated. This is reflected in the simultaneous increase in water detection in the membrane (see Figure 3) and a decrease in the membrane resistance (see Figure 2(c)).

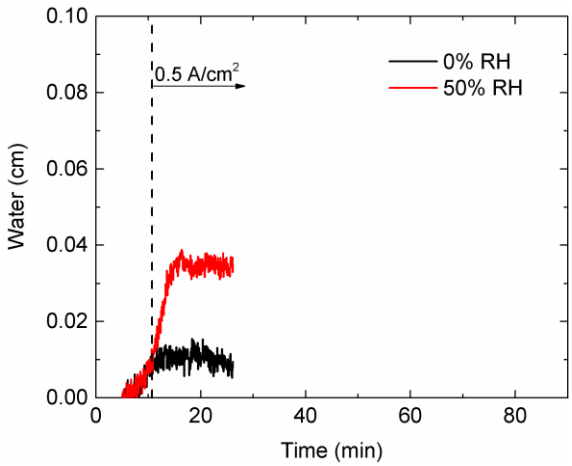

Fig. 4: Average water thickness in the cathode gas diffusion layer at current density of 0.5 A/cm2 for fuel cells operated with dry anode gases and with 50% anode inlet gas relative humidity.

From these results it is observed that the water distribution in the cathode gas diffusion layer and the membrane hydration levels are strongly affected by the anode humidification levels. The distribution is further affected by the changes in operational current density. As water is produced as a result of the electrochemical reaction, there is a redistribution of liquid water within the entire system. The membrane hydration levels increase, which can be detected through radiography as well as through changes in membrane resistance.

4. Conclusion

Synchrotron X-ray radiography was used to study the distribution of water within an operating PEM fuel cell. The water in the cathode gas diffusion layer and the membrane were reported independently as a function of time. The following conclusions can be drawn as a result of this study.

- The reduced cell performance is dominated by an increase in the membrane resistance as observed through the high frequency resistance measurements.
- The membrane resistance decreases steadily with water production resulting from current generation in the cell.
- Liquid water is detected in the membrane, and the quantity of water detected in the membrane increases with current density as the membrane hydration increases.
- Liquid water presence in the cathode gas diffusion layer is also impacted by the changes in anode humidification.

Acknowledgements

Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC), the NSERC Discovery Accelerator Program, the NSERC Canada Research Chairs Program, the Ontario Ministry of Research and Innovation Early Researcher Award, and the Canada Foundation for Innovation are gratefully acknowledged. Graduate scholarships to Nan Ge from the William Dunbar Memorial Scholarship in Mechanical Engineering, the Mercedes-Benz Canada Graduate Fellowship for Fuel Cell Research, and the Ara Mooradian Scholarship are gratefully acknowledged. NSERC Undergraduate Summer Research Award (USRA) to Chuzhang Han is also gratefully acknowledged.

Research described in this paper was performed at the BMIT facility at the Canadian Light Source, which is supported by the Canada Foundation for Innovation, Natural Sciences and Engineering Research Council of Canada, the University of Saskatchewan, the Government of Saskatchewan, Western Economic Diversification Canada, the National Research Council Canada, and the Canadian Institutes of Health Research. Authors acknowledge the receipt of support from the CLS Post-Doctoral and Graduate Student Travel Support Program. The authors would like to acknowledge Dr. George Belev, Dr. Adam Webb, Dr. Ning Zhu, Dr. Tomasz Wysokinski, and the BMIT group of the Canadian Light Source Inc. for their generous assistance.

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