Nuclear Instruments and Methods in Physics Research A 605 (2009) 119–122

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research A

journal homepage: www.elsevier.com/locate/nima

Probing water transport in polymer electrolyte fuel cells with neutron radiography

Kyu Taek Cho [a,b], Ahmet Turhan [a], Jong Hyun Lee [b], Jack S. Brenizer [a], Arthur K. Heller [a], Liang Shi [a], Matthew M. Mench [a,*]

[a] Department of Mechanical and Nuclear Engineering, Radiation Science and Engineering Center and Fuel Cell Dynamics and Diagnostics Laboratory, The Pennsylvania State University, USA

[b] Research & Development Division, Hyundai Motor Company, Yongin, 446-912, Republic of Korea

ARTICLE INFO

Available online 5 February 2009

Keywords:
Polymer electrolyte fuel cell
Gas purge
Neutron radiography
Heavy water
High frequency resistance

ABSTRACT

In this work, the characteristic water removal from a full-sized fuel cell is analyzed with coolant-controlled thermal boundary conditions. High frequency resistance (HFR) along with neutron radiography (NR) is used to elucidate the characteristic variation of water content in the membrane and in other components in the fuel cell during operation and purge, respectively.

During operation, the variation in stored water content was also investigated for different relative humidity (RH) and power conditions. The effect of purge was analyzed by shutting the current off and by holding the reactant flow rate constant during polarization, and the change of water content was investigated for the whole fuel cell and the membrane, respectively. Interestingly, it was determined that water removal from the membrane can be, to some extent, separately controlled from the flow field and porous media by utilizing proper purge conditions.

1. Introduction

Gas purge is normally applied to remove the residual water before shutdown and cooling to subfreezing temperature in a polymer electrolyte fuel cell. Durable operation under subfreezing temperature cycling cannot be guaranteed as long as the water remains in the cell after shutdown, due to potential damage of pore structure by volume expansion [1,2] as well as delamination of the electrodes by a frost heave mechanism [3,4].

Many studies have examined gas purge for removing water from the cell before freezing [5–7]. Cho et al. [6] observed no performance degradation after freeze/thaw cycling when the cell was purged with dry gas for 20 min. Guo et al. [1] found no apparent damage to the catalyst layer (CL) after 1 min dry purge, whereas the cathode CL was cracked in a non-purged cell. Hou et al. [8] observed no performance loss and no damage to the CL after 20 freeze/thaw cycles in a cell purged with RH 58% gas.

Several researchers found that cold start capability could be increased by some drying of the membrane prior to shutdown to provide additional water uptake capacity generated during cold start [5,7], which stimulated research focusing on achieving membrane dehydration. Sinha et al. [9] derived a simplified model of gas purge to understand water removal mechanisms, and Tajiri et al. [10] performed further gas purge experiments focusing on water removal from catalyst layer and membrane.

However, loss of membrane durability has been linked to excessive membrane dryout. Therefore, Ballard Power Systems Inc. described the optimal purge condition as occurring directly before the onset of a rapid increase in the resistance, which occurs in parallel with the onset of membrane dryout [11]. General Motors (GM) Corporation invented a method of removing free water (i.e. not contained within the membrane) with a vacuum pump [12]. Water removal from the cell was also observed to occur via water transport through the membrane electrolyte assembly (MEA) by temperature gradient [13–15]. Bradean et al. [13] showed evidence that, for a proper stack design, a temperature gradient could be developed that effectively drained the residual water during shut down, and thereby avoided subsequent freeze/thaw cycling damage.

Among the extensive studies on water removal, disagreement exists regarding how much the cell should be dried during shutdown. Cold start capability was found to be improved by achieving some membrane dryout before shutdown to a frozen state, and some believe purge should be performed to remove water from the membrane and catalyst layer to provide more space for water uptake [2,5,7,10]. However, others have indicated that membrane dryout, especially uneven dryout, can be damaging to the membrane electrode assembly, and should thus be avoided [11,16].

* Corresponding author. Tel.: +1 814 8650060; fax: +1 814 8634818.
E-mail address: mmm124@psu.edu (M.M. Mench).

0168-9002/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.nima.2009.01.144

Determination of the optimal purge can only be achieved by a more fundamental understanding of the effect of gas purge on water removal from the membrane, as well as from other components in fuel cell. In this study, characteristic water removal behavior was analyzed at a component level during operation and during purge, utilizing a full-sized automotive stack single fuel cell with realistic thermal boundary conditions controlled by coolant flow to understand the purge effect in an actual system.

2. Experiment

All the experiments were conducted with a full-scale fuel cell designed for neutron radiography (NR) analysis. The end plates were manufactured from aluminum to provide a low neutron attenuation of the fuel cell structure. The gas and coolant flow fields were constructed of fuel cell grade machined graphite and were assembled with a commercially available MEA (18 μm thickness, reinforced membrane type) and gas diffusion media (DM) (carbon felt type, 420 μm thickness 5 wt% polytetrafluoroethylene with microporous layer).

Water quantification was conducted with the neutron radiography system of the Breazeale Nuclear Reactor at Penn State University [17,18]. This facility is presently optimized for large cell testing. It has a maximum operating current of 1000 A with dual-level separate anode and cathode liquid coolant (D_2O) control. The scintillation screen is 25.4 cm × 25.4 cm in size, with a 12 bit Peltier cooled CCD camera. The fuel cell is mounted on a hydraulically actuated test stand used to remotely move the cell to precise locations and thus expand the effective imaging area. The theoretical minimum detectable water thickness achievable is 4 μm. Power normalization, beam flattening, and image averaging (averaged images over 54 s of exposure) are used to improve image quality and precision. As shown in Fig. 1, water calibration is achieved by using a liquid-filled wedge, and the neutron attenuation values recorded for these known liquid thicknesses are used to calibrate the pixel luminance recorded as described in Ref. [19]. A second polymer slip wedge with known equivalent water thickness was also used as a calibration standard to make sure that all software was functioning properly. The uncertainty in the calculated water amounts between the calibration and standard wedge was measured to be between 4% and 7%.

The total cell resistance was measured with a milliohm meter (Agilent, 4338B at 1 kHz). Due to its parallel electric connection to the cell as well as to the load bank, the results for this device are only stable in the open-circuit voltage (OCV—or zero current) condition. In this study, high frequency resistance (HFR) values were obtained for analysis after shutting the current off during purge, so this limitation did not affect the results.

The stoichiometric ratio of the anode and the cathode was 1.5 and 2.0, respectively, and pressure differences for anode and cathode sides were almost negligible, even at a maximum flow rate. Ultrahigh pure hydrogen and commercial air (79% N_2 and 21% O_2) were used for reactant gas. Humidification of each gas was controlled by a calibrated membrane-type humidifier, and the relative humidity of supplied gas was calculated based on the cell inlet temperature.

The effect of gas purge was simulated by shutting the current off after 15 min operation while holding constant the other conditions, such as type of gas, relative humidity, flow rate, and cell temperature. The water amount was measured every minute for 5 min (variation of water amount was significant in the initial 1 and 2 min of purge, and found to be negligible after 5 min purge, so purge for 5 min was applied in this study) with NR and HFR simultaneously to determine the transient behavior of water removal in the cell and in the membrane, respectively, during purge.

3. Results and discussion

3.1. Variation of water content in the fuel cell during operation

As shown in Fig. 2, the liquid water stored in the cell was maximum at low current density (0.16 A/cm^2), and then decreased with increasing current. This is despite a lack of significant evaporative forces at the fully humidified 100/100RH condition. This result indicates the drag removal from the channel and DM is responsible for the observed decreasing slope of stored water versus current (pressure loss effects are negligible in this case), which is consistent with previous NR imaging studies [20,21]. The drag force on the water slugs in the cell is proportional to the square of the velocity of supplied gas [22], and as the current (i.e. flow rate at constant stoichiometry, as is the case here) increases, the force to drag water out of the cell also increased, resulting in a net decrease of water amount in the cell as shown in Table 1.

The effect of evaporation was analyzed with different RH conditions on the anode and the cathode. As shown in Fig. 2, a dry condition on the cathode side (RH100/0) was very effective for water removal from the cell (40–45% water decrease with respect to RH100/100), whereas the dry condition on the anode

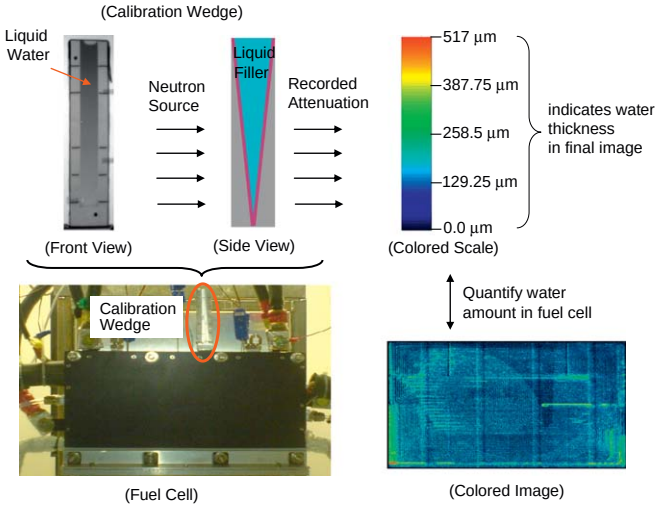

Fig. 1. Water quantification of fuel cell with NR.

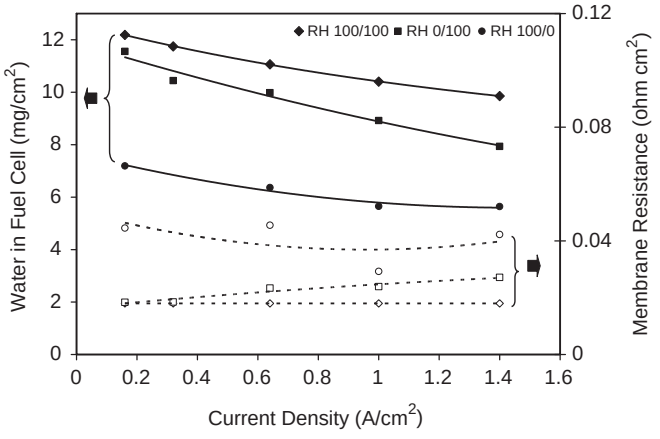

Fig. 2. Water content variation during operation at various RH conditions.

Table 1
Channel velocity of anode and cathode side.

Current density (A/cm^2)	Anode		Cathode	
	V_{CH}(m/s)	Re_{CH}	V_{CH}(m/s)	Re_{CH}
0.2	0.81	3.4	1.29	49.0
0.8	3.22	13.6	5.1	196.0
1.0	4.03	17.0	6.4	244.8
1.4	5.64	23.8	9.0	342.8

side (RH0/100) removed water nearly linearly with current (5.1–19.5% water amount decrease with respect to RH100/100).

Although the water level in the fuel cell decreases with flow rate in the fully humidified condition, the water level in the membrane remains almost constant in the non-evaporative 100/100 RH environment. For the case of RH0/100, membrane resistance increased almost linearly with current density, as shown in Fig. 2. For the case of RH100/0, membrane resistance increased significantly even at low current density (146% increase with respect to RH 100/100 condition at 0.16 A/cm^2) along with significant decrease of water amount in the cell. Membrane resistance fluctuated in this condition, which is typical when electrolyte water content has dry state, and slight additional humidity can dramatically impact resistance of the electrolyte.

3.2. Variation of water content in fuel cell during gas purge (RH-controlled purge)

The change of water was compared at the fixed flow rate condition of 1 A/cm^2 for the membrane and for the cell at each RH condition, as shown in Figs. 3 and 4, respectively.

The water amount was decreased by performing cell operation at different RH conditions before applying gas purge. As shown in Fig. 3, pre-purge operation at RH100/0 reduced the water amount significantly by 46% with respect to RH100/100, and the water amount was further reduced to 4.49 mg/cm^2 by 5 min purge. The condition of RH0/100 and RH50/50 showed similar water removal behavior during pre-purge operation (14% and 15% water removal, respectively), and the water amount was reduced to about 5.6 mg/cm^2 for both conditions by 5 min subsequent purge.

Variation in membrane resistance during purge is compared in Fig. 4. The resistance was increased to 63% by pre-purge operation at RH100/0, and significantly increased to 336% from subsequent 5 min purge. Purge of RH0/100 and RH50/50 showed different behavior of resistance change. The resistance was increased to 46% for purge of RH0/100, whereas it was increased to 158% for RH50/50 purge.

The different water removal behavior from the membrane in the RH0/100 and RH50/50 purge indicates selective control of water amount in the components in the cell is achievable by utilizing specified purge conditions. By performing a conditioned operation, the water amount could be reduced efficiently while maintaining a moist membrane, which is key to promoting durability.

4. Conclusions

To investigate the purge effect in actual conditions, a full-sized fuel cell was utilized with realistic coolant flow controlled boundary conditions. Water behavior was analyzed comprehensively during operation (current-on condition) and purge (current-off condition) for a wide range of flow rate conditions. HFR and NR combined analyses were used to elucidate that characteristic water removal behavior in the cell and in the membrane.

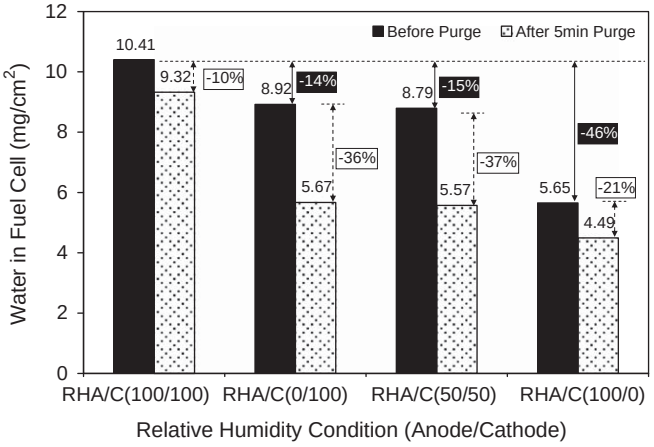

Fig. 3. Comparison of water amount before and after purge at 1A/cm^2 operation and purge flow rate equivalent for various RH conditions.

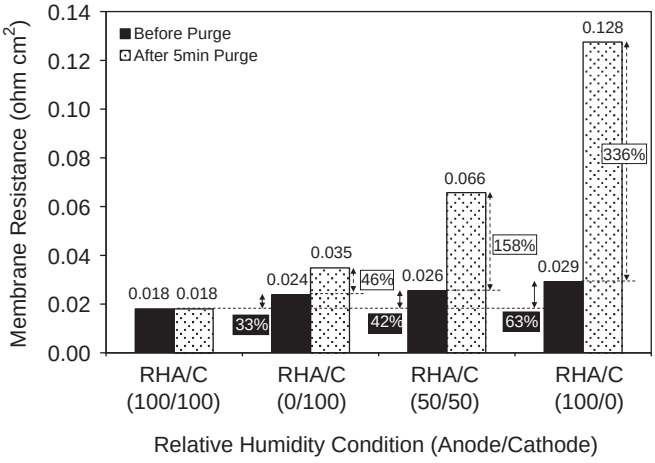

Fig. 4. Comparison of membrane resistance before and after purge at 1 A/cm^2 operation and purge flow equivalent for various RH conditions.

During the cell operation, effects of operating conditions were compared, and water amount was decreased with increasing current even with fully saturated conditions, due to the drag force removal of liquid water slugs from the flow field.

Purge effectiveness for water removal from the cell and from the membrane was compared for each RH condition. Purge with dry anode gas and fully humidified cathode gas (RH0/100) can remove water from the cell while maintaining adequate membrane hydration. However, purge with dry cathode gas and fully humidified anode gas (RH100/0) resulted in significant water removal from the cell, as well as from the membrane. This is due to the difference of amount of water supplied and removed with purge. By controlling the amount of water supplied on both sides of the anode and cathode, the water amount in the cell and membrane can be separately controlled, and result in far less membrane dehydration while reducing the overall cell water content to acceptable shut-down levels, a condition that is favorable for durability.

Acknowledgments

M.M. Mench wishes to thank the National Science Foundation CAREER award CBET #0644811 for partial funding of this work.

References

[1] Q. Guo, Z. Qi, J. Power Sources 160 (2006) 1269.
[2] M. Oszcipok, M. Sedda, D. Riemann, D. Geckeler, J. Power Sources 154 (2006) 404.
[3] S. He, M.M. Mench, J. Electrochem. Soc. 153 (2006) A1724.
[4] S. Kim, M.M. Mench, J. Power Sources 174 (2007) 206.
[5] M. Oszcipok, D. Riemann, U. Kronenwett, M. Kreideweis, M. Zedda, J. Power Sources 145 (2005) 407.
[6] E. Cho, J. Ko, H. Ha, S. Hong, K. Lee, T. Lim, I. Oh, J. Electrochem. Soc. 151 (2004) A661.
[7] S. Ge, C. Wang, Electrochim. Acta 52 (2007) 4825.
[8] J. Hou, H. Yu, B. Yi, Yu. Xiao, H. Wang, S. Sun, P. Ming, Electrochem. Solid-State Lett. 10 (2007) B11.
[9] P. Sinha, C. Wang, J. Electrochem. Soc. 154 (2007) B1158.
[10] K. Tajiri, C. Wang, Y. Tabuchi, Electrochim. Acta 53 (2008) 6337.
[11] J. Roberts, J. Pierre, M. Geest, A. Atbi, N. Fletcher, Ballard Power Systems Inc., US Patent no. 6,479,177B1, 2002.
[12] R. Fuss, General Motors Corporation, US.Patent no. 6,358,637B1, 2002.
[13] R. Bradean, H. Hass, K. Eggen, C. Richards, T. Vrba, ECS Trans. 3 (1) (2006) 1159.
[14] S. Kim, M.M. Mench, J. Membr. Sci. 328 (2009) 113.
[15] S. Kim, M.M. Mench, J. Electrochem. Soc. 153 (2009) B353.
[16] K. Cho, A. Turhan, J. Yoon, J. Lee, M.M. Mench, 213th Electrochem. Soc. Meet., Phoenix, AZ, May 2008.
[17] N. Pekula, K. Heller, P. Chuang, A. Turhan, M.M. Mench, J. Brenizer, K. Unlu, Nucl. Instr. and Meth. A 542 (2005) 134.
[18] A.K. Heller, M.S. Thesis, The Pennsylvania State University, 2007.
[19] J.S. Brenizer, K.W. Tobin, J.M. Hylko, D.D. McRae, R.W. Jenkins, Mater. Eval. 45 (1987) 1310.
[20] M. Hickner, N. Siegel, K. Chen, D. Hussey, D. Jacobson, M. Arif, J. Electrochem. Soc. 155 (2008) B294.
[21] A. Turhan, K. Heller, J. Brenizer, M.M. Mench, J. Power Sources 180 (2008) 773.
[22] E.C. Kumbur, K.V. Sharp, M.M. Mench, J. Power Sources 161 (2006) 335.