Distributed Effects of Calcium Ion Contaminant on Polymer Electrolyte Fuel Cell Performance

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1. Introduction

Durability is a major issue for the commercialization of polymer electrolyte membrane fuel cells (PEFC) [1]; and cationic impurities presents a significant challenge, as they can decrease the protonic conductivity of the ionomeric membrane as a result of an ionic exchange with the protons from sulfonic acid sites [2]. For example, iron (Fe^{3+}) contamination originated from the stainless steel end plates causes Nafion® degradation as revealed by the fluoride loss [3]. 5 ppm level of Fe^{3+} in the air stream results in sudden and severe degradation due to the formation of a pinhole in the membrane [4]. Al^{3+} decreases cell performance by changing the kinetics and mechanism of the ORR [4]. Rodgers et al. [5] summarized the mechanism by which cationic impurities affect membrane durability and performance as (a) a reduction in proton conductivity, (b) a reduction of water content, (c) a catalyst for Fenton's reaction, and (d) a place where a crack can occur.

Our group experimentally investigated the effect of various cations (K^+ , Mg^{2+} , Ca^{2+} , Ni^{2+} , Ba^{2+} , Al^{3+} , Cr^{3+} , Fe^{3+}) combined with different anions (Cl^- , $(\text{ClO}_4)^-$ and $(\text{SO}_4)^{2-}$) being injected directly into the air stream of an operating fuel cell [6-11], and modeled the effects of cationic contamination on PEFC performance [12,13]. We down selected the list of cations for these studies depending on worldwide air and water filter samples, most likely to be encountered based on the usage and probable future usage, valence state, solubility, toxicity, availability, paucity of scientific or engineering data, and relevance in terms of materials of construction. After the screening studies, one contaminant (Ca^{2+}) that was prevalent in roadside particulates, abundant in the nature and not well investigated, was selected for more in-depth studies [7]. During our testing, we observed a cationic contamination mechanism that was not previously mentioned in open literature. Cationic salts were deposited on both the flow field and the GDL surface causing

serious mass transport loss. In our operating conditions, salt depositions was found mostly in the downstream of the cell [7], indicating a need for study the spatial performance change due to cation contamination.

There are many studies available on local performance distribution due to the influence of various parameters: flow field geometry, clamping pressure, operating conditions, types of membranes and GDL, and carbon monoxide (CO) poisoning [14]. To our knowledge, there is no such study related to cation contamination. This paper presents the effect of the cation contamination on spatial performance distribution under galvanostatic and potentiostatic load control of a segmented cell.

2. Experimental

The details of the experimental setup and procedures were described in our previous studies [7-10] where we used a conventional, single cell hardware. In this study, instead of the single cell hardware, a segmented cell hardware was used to observe spatial performance distribution. The segmented cell hardware consisted of an aluminum alloy (T6061-T6) anode flow field, a segmented cathode flow field, two gold-plated aluminum alloy end plates and one copper current collector. The cathode flow field was divided into eight segments. Eight pieces of equal size aluminum alloy current collectors were placed inside a PTFE block and continuous straight flow channels were machined through both the PTFE and the aluminum segments (Fig. 1). Both flow fields consisted of 5 straight flow channels with 1.0 mm width, 1.0 mm channel depth and 1.0 mm landing. To prevent corrosion and contamination, all the aluminum alloy parts were gold plated. Moreover, to prevent contamination from the end plates, a Teflon tube was used as a liner for the gas ports, passing through end plate into the flow field. To measure local performance distribution, 100m Ω shunt resistors were attached to each segment as shown in Fig. 1. The total

active area of the cell was 5 cm^2 . The MEA was prepared with a catalyst coated membrane (CCM) which was Gore[®] PRIMEA[®] Membrane Electrode Assemblies (GORE, PRIMEA and design are trademarks of W. L. Gore and Associates Inc., Elkton, MD, USA) and two Freudenberg C2 (Freudenberg FCCT SE & Co. KG, Germany) gas diffusion layers. Pt loading for the cathode and anode catalyst layers was 0.4 and 0.1 mg cm^{-2} , respectively.

In our previous study [7], we tested the cell galvanostatically with various concentration of CaSO_4 (1.14mM , 2.85mM , and 5.7mM). It was observed that high concentrations (2.85mM and 5.7mM) of CaSO_4 resulted in significant performance loss and caused salt precipitation which caused mass transport loss. Low current density (200mAcm^{-2}) operation caused more salt precipitation, which clogged gas channels and blocked the transport of reactants. In this study, 2.85 mM of CaSO_4 was selected to observe obvious performance degradation. The segmented cell was operated in two modes: galvanostatically and potentiostatically. A high air flow was maintained at the cathode to carry more water in the cathode that can help to prevent contaminant precipitation and a high hydrogen flow at the anode to limit the anode polarization overpotential and to make sure that performance degradation during the tests can be attributed to the contamination. All the operating conditions were listed in Table 1.

Similar to the previous studies (7-10), the cell was tested in Teledyne test station (Teledyne MEDUSA RD, TELEDYNE Energy Systems, Inc., MA, USA) interfaced with a Scribner 890C load box (Scribner Associates Inc. NC, USA). For injecting contaminant solution a micro flow nebulizer (ES-2005, PFA-400, Elemental Scientific, Inc., NE, USA) was used with a high performance liquid chromatography (HPLC) pump (Series III Pump, Scientific Systems Inc., PA, USA). In each test, the cell was conditioned using a constant voltage (0.6V) break-in

procedure and the cell was run with pure air for 24 hours. Then the contaminant was injected into the air stream for 96 hours. Finally, pure air was used for another 24 hours.

After the test, the cell was disassembled and the MEA was characterized by SEM/EDX (FEI ESEM Quanta 250, Hillsboro, OR, USA) analysis.

3. Results and discussion

Fig. 2 shows the polarization curves for all the segments at the beginning of the test. The segments upstream (close to the gas inlet) of the cell median have higher performance compared to the segments downstream (close to the gas outlet) of the cell, as a result the current density is not uniform throughout the cell. To minimize non-uniformity issue due to the reactants, very high stoichiometry of the reactants was used during contamination test. Other causes for the non-uniformity include non-uniform operating conditions (e.g. temperature), flow field design, non-uniform assembly pressure and microstructure of the gas diffusion electrode (thickness, structure, ionic and electronic conductivity, gas diffusion layer) [15].

Fig. 3 shows the average cell voltage and normalized current density distribution profile for each segment of the cell tested in galvanostatic mode at a constant overall cell current of 200mAcm^{-2} . The current density was normalized dividing by the average current density of last five hours (19h to 24h) of the baseline to facilitate easier comparison of all the segments. There was no change in the trend of curves due to this normalization.

During the baseline test of 24 hours, pure air was injected through the cathode. The voltage and the current density remained constant in all segments. Following the baseline test, the contaminant was injected in the air stream. After contaminant injection, the voltage in each segment started to decrease, and after 50 hours, voltages started to fluctuate. The voltage fluctuation was found to be mainly due to the mass transport loss. Similar to the previous study

(9), significant salt precipitation was observed (Fig. 4). As these deposits accumulate with time, they form a barrier for oxygen transport to the catalyst layer and act as a barrier for the water removal from the cell. Additionally, these deposits migrate into the GDL, and they may also affect the GDL wet proofing allowing water to accumulate locally. This water is free to move within the cell, and we believe that it has moved from cell inlet to the exit with the reactant flow. So when water accumulates in the cell, the voltage decreases and when water is removed voltage increased back.

From the current density profile in Fig. 3b, it was observed that the upstream segments were first affected by the contaminant, and the current density in the upstream segments decreased, while the downstream segments increased, although at the beginning of the test, in uncontaminated conditions, upstream segments have higher performance compared to downstream segments (shown in Fig. 2) which is typical in segmented cells. Since it was a constant current test, when the current in the segments closest to the gas inlet decreases, the current for the other segments must increase to maintain a constant total current. Segment 0 which was close to the gas inlet was first affected by the contaminant and the current density decreased and remained lower throughout the test. The other segments picked up that current, although all other segments were also contaminated later, and there was a sequence in current density distribution from the gas inlet to the gas outlet: segment 0 < segment 1 < ... < segment 7. So, from the galvanostatic test, it is certain that upstream portion of the cell is first affected by the contaminants, but it is not possible to make a decision about the downstream of the cell.

When the cell was disassembled after the test, salt deposit was found distributed over the entire flow field and the GDL surface (Fig. 4). So the entire active area was affected by the contaminants, but this was not clear from the distributed current density profile.

To get a clearer idea about the performance distribution, a new cell was assembled as described earlier and tested in potentiostatic mode with lower contaminant concentration in the air stream. Fig. 5 shows the average cell voltage, average cell resistance, and normalized current density distribution profile for each segment of the cell tested in potentiostatic mode. The cell was tested at a constant voltage (0.6V), and the cell resistance was measured by current interrupt, which includes the bulk membrane resistance, the GDL electronic resistance, and the contact resistance between fuel cell components. Since it was a galvanostatic test, there was no control on local current distribution. It was observed that all segments were affected by the contaminant, and current density in all segments decreased with time. The performance of the downstream segments was lower than the upstream segments which was completely opposite to the galvanostatically tested cell. It can be explained by our previous study [9] where it was reported that although Ca^{2+} was injected in the super saturated (125% RH) air stream, outlet of the cell became dry in our operating conditions causing more salt precipitation at the outlet of the cell. As a result, the performances of the downstream segments were lower than the upstream segments. At the end of 96 hour of test, the cell can no longer sustain any load, and even removing the contaminant injection did not recover the cell performance and the cell could no longer hold constant voltage. The cell voltage fluctuated similar to the potentiostatic test which can be attributed to the salt deposition inside the cell similar to the Fig. 4.

The cell resistance (as shown in Fig. 5a) did not get affected much by the contamination up to 80 hours and then it started to increase. During first 24 hour baseline, resistance increase rate was $0.3 \text{ m}\Omega\cdot\text{cm}^2\text{h}^{-1}$, from 24h to 80h resistance increase rate was $0.8 \text{ m}\Omega\cdot\text{cm}^2\text{h}^{-1}$ and after 80h, resistance increase rate was $26.6 \text{ m}\Omega\cdot\text{cm}^2\text{h}^{-1}$. We believe, the sharp resistance increase was

mostly due to salt deposition inside the cell that hindered the reactant transport in and out of the cell.

Postmortem analysis of both the cells was carried out with SEM/EDX. There was no significant difference between both the cells; hence the analysis for the cell tested in galvanostatic mode is presented.

Fig. 6 shows the SEM image of the cathode GDL surface. It shows a significant amount of salt deposit on GDL surface, which caused mass transport loss and voltage fluctuations. EDX results and elemental map show that salt contains calcium, sulfur, and oxygen. It also contains aluminum. During the test, CaSO_4 solution was injected, so it is reasonable to detect calcium and sulfur. In case of aluminum, we suspect that it came from the sub-surface of gold coated aluminum alloy flow field. After the test, inspection showed that some of the gold layer had lifted off of the flow field and there was some evidence of micro-cracks in the gold coating on aluminum flow field which were enough to allow the corrosion of aluminum [16]. Moreover, on the gold plated aluminum flow field, two dissimilar materials (Al and Au) with a galvanic potential difference [17] were in contact with the presence of calcium sulfate as the electrolyte which would allow a micro-galvanic cell on the surface of the flow field and galvanic corrosion.

Fig. 7 shows MEA cross section and elemental mapping of S and Ca. The SEM image of a portion of the cathode GDL is also shown, indicating the salt deposit inside the GDL. The elemental map of Ca clearly demonstrates that Ca is only detected inside the cathode GDL. Similar to the surface of the GDL, Al is also found inside the GDL. But no Ca/Al is detected in the CCM. These results conform to our previous findings [7, 8], which shows that highly

hydrophobic nature of the microporous layer (MPL) in GDL acts as a barrier to the transport of contaminant solution into the CCM [11].

4. Conclusion

In this study, distributed effects of the cation contamination on PEFC was studied by introducing Ca^{2+} solution in the air stream of an operating fuel cell that had segmented cathode flow field. The cell was operated both in galvanostatic and potentiostatic modes. In the galvanostatic test, segments upstream of the cell median were first affected by the contaminant and their current decreased. The segments downstream of the cell median demonstrated an increase in current, although salt deposit was observed throughout cathode flow field and GDL surface. In the constant total current test, when the cell current in the upstream segments decreased, downstream segments increased their current to maintain the constant total current. During contamination, the cell voltage decreased and fluctuated as a result of salt deposits on both the cathode flow field and the surface of the GDL, which caused mass transport losses.

In the potentiostatic test, all the segments were affected by the contaminants and the current density of all segments decreased with times. It was also observed that the segments downstream of the cell demonstrated lower performance than the segments upstream of the cell which conforms to our previous findings.

In this work, all the results were based on Ca^{2+} contamination as an air impurity in PEFC. For other cations which may be introduced to the cell through air/fuel stream or balance of plant components, the quantitative results may change, but change in observed trends is unlikely.

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References

- [1] R. Borup, J. Meyers, B. Pivovar, Y.S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, *Chem. Rev.* 107 (2007) 3904-3951.
- [2] T. Okada, in *Handbook of fuel cells – Fundamentals, Technology and Applications*, W. Vielstich, H. A. Gasteiger, A. Lamm, and H. Yokokawa, Editors, John Wiley & Sons, Ltd, (2010).
- [3] A. Pozio, R.F. Silva, M. De Francesco, L. Giorgi, *Electrochim. Acta* 48 (2003) 1543-1549.
- [4] H. Li, K. Tsay, H. Wang, J. Shen, S. Wu, J. Zhang, N. Jia, S. Wessel, R. Abouatallah, N. Joos, *J. Power Sources* 195 (2010) 8089-8093.
- [5] M.P. Rodgers, L.J. Bonville, H.R. Kunz, D.K. Slattey, J.M. Fenton, *Chem. Rev.* 112 (2012) 6075-6103.
- [6] J. Qi, X. Wang, U. Pasaogullari, L. Bonville, T. Molter, *J. Electrochem. Soc.* 160 (2013) F916-F922.
- [7] X. Wang, J. Qi, O. Ozdemir, A. Uddin, U. Pasaogullari, L.J. Bonville, T. Molter, *J. Electrochem. Soc.* 161 (2014) F1006-F1014.
- [8] M.A. Uddin, X. Wang, J. Qi, M.O. Ozdemir, L. Bonville, U. Pasaogullari, T. Molter, *J. Electrochem. Soc.* 162 (2015) F373-F379.

227 [9] J. Qi, X. Wang, O. Ozdemir, M.A. Uddin, L.J. Bonville, U. Pasaogullari, T. Molter, J.
228 Power Sources 286 (2015) 18-24.

229 [10] M.A. Uddin, J. Qi, X. Wang, M.O. Ozdemir, N.K.H. Dalasm, L. Bonville, U.
230 Pasaogullari, T. Molter, ECS Trans. 61 (2014) 37-48.

231 [11] M.A. Uddin, J. Park, X. Wang, J. Qi, L. Bonville, U. Pasaogullari, T. Molter, ECS Trans.
232 64 (2014) 537.

233 [12] M.F. Serincan, U. Pasaogullari, T. Molter, Int. J. Hydrogen Energy 35 (2010) 5539-5551.

234 [13] M.A. Uddin, U. Pasaogullari, J. Electrochem. Soc. 161 (2014) F1081-F1088.

235 [14] L.C. Pérez, L. Brandão, J.M. Sousa, A. Mendes, Renew. Sustain. Energy Rev. 15 (2011)
236 169-185.

237 [15] Z. Liu, Z. Mao, B. Wu, L. Wang, V.M. Schmidt, J. Power Sources 141 (2005) 205-210.

238 [16] A. Woodman, K. Jayne, E. Anderson, and M. C. Kimble, American Electroplaters and
239 Surface Finishers Society, AESF SUR/FIN '99 Proceedings, 6/21-24, (1999).

240 [17] M. G. Fontana and N. D. Greene, Corrosion Engineering, p. 31, McGraw Hill, New York
241 (1978).

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TABLE

Table 1. Contaminant and operating conditions.

Operation	Contaminant	Concentration	Concentration	RH	BP	H ₂ /Air flow	Nebulizer
mode		(mM)	in dry air	(A/C)	(A/C)	rate (slpm)	flow rate
			(ppm)	(%/%)	(kPag)		(μLmin^{-1})
Galvanostatic	CaSO ₄	2.85	21	100/125	10/100	0.35/0.33	110
(200 mAcm ⁻²)							
Potentiostatic	CaSO ₄	2.85	5	25/125	10/100	1.75/1.66	130
(0.6V)							

FIGURES

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.