Distributed Cation Contamination from Cathode to Anode direction in Polymer Electrolyte Fuel Cells

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Abstract

Distributed effects of cation contamination on polymer electrolyte fuel cells (PEFC) were investigated at a fixed concentration of 5 ppm of Ca^{2+} in the air stream of an operating fuel cell. A special purpose MEA was prepared using five layers of membrane, and four Pt wires (electrodes) were inserted between the membrane layers. These Pt electrodes were used to monitor the through plane potential due to the permeation of hydrogen and oxygen from the anode and the cathode, respectively as well as the resistance distribution across the membrane thickness. At the beginning of the test, oxygen permeated from the cathode to the first layer of the membrane. After 32 hours, oxygen continued to permeate from cathode to the other layers of the membrane. The cell performance deteriorated, when CaSO_4 solution was injected as a contaminant. Within 21 hours of contaminant injection, the cell voltage dropped to less than 200 mV. High frequency resistance (HFR) increased more than 50% in the individual membrane layer that was located close to the cathode.

Keywords: Polymer electrolyte fuel cell, Cation contamination, Through plane contamination, Multilayer membrane cell

1 Introduction

Due to their zero emission potential, polymer electrolyte fuel cells (PEFCs) are a promising source of clean energy in EVs and stationary power generation. But their vulnerability to cationic impurities is one of the key issues with PEFCs. Cationic impurities replace protons from the sulfonic acid sites in ionomer and cause performance degradation [1-3]. These cationic impurities may originate from the water in the humidifier, salt aerosols in the air or fuel stream, and the corrosion of fuel cell stack system components, such as bipolar plates, seals, inlet/outlet manifolds, humidifier reservoirs, and cooling loops [4-8].

Several modeling [9-13] as well as experimental studies have been conducted to investigate the effect of cationic contaminants, including soaking the membrane with various cations before test [1-3, 14-21] and injecting cations into the air or fuel stream of an operating fuel cell [6,22-25]. It is reported that when cations enter the ionomer, they reduce the ionic conductivity and the water content as well as lower the gas permeability through the ionomer [14-17]. Oxygen reduction reaction (ORR) is also reported to be suppressed by cation contamination either through lowered oxygen gas transport or through suppressed charge transfer reactions by cations [1,26]. Moreover, cations can act as a catalyst for peroxide radical formation resulting membrane degradation [6,27].

Our group investigated the effect of different cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ni^{2+} , Ba^{2+} , Al^{3+} , Cr^{3+} , Fe^{3+}) combined with different anions (Cl^- , $(\text{ClO}_4)^-$ and $(\text{SO}_4)^{2-}$) injected into the air stream of an operating fuel cell [22-25] as well as modeled the effects of cation contamination on PEFC performance [9,11]. When injected into the cell along with the air stream, we observed that cationic salts can deposit on the flow field and the GDL surface causing significant mass transport losses. Certain salt solutions can also penetrate

into the GDL and reached to the CCM, indicating a need for a study of the through plane distribution of cationic contamination on PEFC.

To study the effect of cationic contamination in the through plane, a special membrane electrode assembly (MEA) was prepared with five layers of membrane (NRE 211) equipped with four Pt wires. As the contaminant, CaSO_4 solution was introduced in the air stream of the fuel cell. A similar cell design was used by Watanabe *et al.* to measure through plane water content distribution [28-30], hydrogen and oxygen permeation [31], and the transient behavior of specific resistance during the load change [32]. According to our search of the open literature, this is the first time this type of MEA was used for the analysis of the contamination effect.

2 Experimental

Nafion® membrane (NRE 211, Ion Power Inc.) was first treated with 500 mM Sulfuric acid solution at 80°C for 6 hours. Then the membrane was thoroughly washed in DI water and kept in DI water for overnight. The membrane was thermally flattened with the following process: the membrane was sandwiched between 25µm thick Teflon films, and carbon plates and rubber sheets were placed on both side of the Teflon films. Then the membrane sandwich was placed in the hot press and kept for 1 hour at 80°C with no applied pressure. The nominal thickness of each membrane was 25 µm. Four Pt wire electrodes (diameter 50 µm, Alfa Aesar, USA) were inserted between five layers of treated Nafion® membranes and placed over the active area from the inlet to the outlet of the cell as shown in Fig. 1. The Pt wire electrode close to the anode (E1) was placed 1cm below the gas inlet to the active area and all other electrodes (E2, E3, and E4) were placed approximately 1cm apart from each other. In all electrochemical measurements, anode electrode was taken as the reference.

Fig. 1 Simple schematic diagram of membrane electrode assembly (MEA). Four Pt wire (50 μm in diameter) electrodes (E1, E2, E3, and E4) were inserted between five layers of Nafion membrane (ea. 25 μm in thickness).

The membranes equipped with Pt wires were sandwiched between two gas diffusion electrodes (GDEs) (FuelCellsEtc, College Station, TX, USA). The GDE (thickness of 410 μm) consisted of carbon cloth GDL/microporous layer (MPL)/catalyst layer. Catalyst layers were made of Pt black with 4 mgcm^2 loading. The whole arrangement shown in Fig. 1 was hot pressed at 130 $^{\circ}\text{C}$ for 50 min at a pressure of 4.5 MPa. After compression, total thickness of the MEA with GDEs was 900 μm .

The single-cell hardware consisted of an aluminum alloy anode flow field, an aluminum alloy cathode flow field, and two aluminum end plates. Both flow fields consisted of 5 straight flow channels with 1.0mm width, 1.0mm channel depth and 1.0mm landing. To prevent corrosion and contamination, all the aluminum parts were gold plated and before gold plating, a thin nickel adhesion layer was applied on aluminum parts. The active area of the cell was 5 cm^2 .

The details of the experimental setup and experimental procedures are mentioned in elsewhere [23,25]. Calcium sulfate (99.99% pure, Sigma-Aldrich[®], St. Louis, MO, USA) solution was injection into the air stream of the fuel cell as a contaminant through a nebulizer (ES-2005, PFA-400, Elemental Scientific Inc., Omaha, NE, USA) and a high resolution HPLC pump (Series III Pump, Scientific Systems Inc., State College, PA, USA). The flow rate of the Calcium sulfate solution was 65 μ Lmin with a concentration of 1.14 mM which corresponds to 5 ppm flow in air stream on mole basis.

An electrochemical impedance spectroscopy (EIS) test was carried out with a potentiostat/galvanostat (Solartron SI 1260). The EIS was measured from 100 kHz to 0.1 Hz with an AC amplitude of 5mA, which was small compared to the cell current (1000mA) to ensure that the response is linear. The real component of impedance (Re (Z)) at the high frequency region of EIS was taken as the high frequency resistance (HFR) where imaginary component of the impedance is zero (Im (Z) = 0).

After the test, the cell was disassembled and the contaminated MEA was characterized by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis (FEI Quanta 250, FEI, Hillsboro, OR, USA). Some analyses were also conducted with micro-computed tomography (Micro XCT, Xradia Ultra XRM-L400, Xradia, Inc. Pleasanton, CA, USA). Using Xradia's MicroXCT system, a tomography of the GDL with precipitated salts was obtained. This system utilized geometric and optical magnification in the region of interest in order to resolve the individual features of the carbon fibers and salt deposits. Exploiting the differences in the attenuation coefficients, the X-ray photon energy was optimized such that sufficient contrast between the individual components (air, carbon and salt deposits) was observed to segregate each material. Using the commercial software Avizo (FEI, Hillsboro, OR, USA), the reconstructed tomography data was imported and rebuilt. To separate the salt

voxels from carbon and air, analysis of the pixel histograms was used to resolve pixel values to determine the thresholds for individual constituents of the sample. Tertiary segmentation of the tomography using the previously obtained threshold values was used to visualize the salt deposits in the sample.

3 Results and discussion

3.1 Cell performance

Fig. 2 shows the cell voltage measured with time at a fixed current density of 200mAcm^{-2} . At first, the cell was run for 55 hours without contaminant injection. During this period, a voltage drop of 113 mV was observed. After 55 hours of baseline testing, CaSO_4 solution injection was started. During this period, the cell voltage decreased rapidly, and within 21 hours of contamination, cell voltage became less than 200mV. Then contaminant injection was stopped for recovery; however, the cell voltage did not recover and decreased further. When the cathode air flow was increased by 200 sccm, the cell voltage started to increase and at some point it suddenly dropped to zero. The reason behind the performance degradation is explained later. It should be noted that there were several discontinuities in the plot; EIS was measured at those times.

Fig. 2 Cell performance measured at 200mAcm^{-2} . Operating conditions: cell temperature: 80°C ; flow rate H_2/air : 348/332 sccm; A/C: 50/20 stoic, 25/125% RH, 0/0 kPag back pressure.

After the test, the cell was disassembled and postmortem analyses were done. A significant amount of white deposit was observed on both the cathode GDE and the flow field surface. Fig. 3 shows the secondary electron image of the cathode GDE surface which clearly shows the salt deposit on GDE. These salt deposits contained calcium, sulfur, oxygen, aluminum, and nickel as detected by EDX spectra and the elemental maps (Fig. 3). Since CaSO_4 solution was injected during the test, it is reasonable to detect Ca, S and O. Aluminum and nickel probably come from the sub-surface of gold coated aluminum alloy flow field, where there was a nickel adhesion layer on the surface under the gold coating. These results confirm that the aluminum flow field was corroded and also contaminated the cell. 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 [33]. Moreover, on the gold plated aluminum flow field, two dissimilar materials (Al and

Au) with a galvanic potential difference [34] were in contact in presence of calcium sulfate as the electrolyte which would allow a micro-galvanic cell on the surface of the flow field and galvanic corrosion. In either case, post-test inspection shows that the gold plated aluminum flow field was corroded in the presence of moist air (125% RH) and calcium sulfate solution. So, although no contamination was injected into the cell during first 55 hours of the test (Fig. 2), the cell was contaminated with the corrosion products of the gold plated aluminum alloy flow field corrosion resulting in a significant voltage drop during the baseline test. When the calcium sulfate solution was injected, the cell performance became significantly worse causing salt deposit which blocked some of the flow channels and barred air transport causing mass transport losses. As a result, the cell voltage became close to zero. When air flow was increased, mass transport loss was reduced and the cell voltage was started to increase. Finally, the cell failed due to high internal shorting between anode and cathode. Although the cell failed showing symptoms similar to internally shorted cell, this could also be caused by complete flow field blockage.

Fig. 3 Secondary electron image of cathode GDE surface with elemental spectrum of whole image and elemental mapping of Ca and Al.

The cross-section of the MEA was also analyzed using SEM/EDX. No cations were detected in the membrane; however different cations (calcium, aluminum and nickel) might have penetrated the membrane, but they were below the EDX detection limit. Even though the MEA was contaminated by three different cations, our qualitative findings (next section) are unaffected, since they are all positively charged and migrate similarly under the potential field.

Fig. 4a shows the 3D representation of a portion of cathode GDE which was obtained with micro XCT. In Fig. 4b, salt deposit was segmented from the fiber. Similar to our previous tests [23,25], salt deposited on GDE surface and entered into the GDE, but it was mostly concentrated on the top of the GDE.

Fig. 4 (a) 3D representation of cathode GDE and (b) salt deposit only.

3.2 Through plane contamination effect

Pt wires inside the membrane layers act as electrodes. Any presence of hydrogen or oxygen at the Pt electrode reacts very fast and gives the following reactions:

Fig. 5 shows the distribution profile of mixed potential along the membrane thickness at the beginning of the test (BoT) for different current densities. For all cases, electrode 4 (E4), which was closest to the cathode, shows similar to the cathode voltage as oxygen permeated from the cathode to the E4 region. So, in E4, potential was dominated by Eq. (1). In electrode 3 (E3), a very low voltage was observed probably due to the limited permeation of oxygen from cathode. Electrode 1 (E1) which was close to anode showed a zero potential. It can be expected that in E1 region, hydrogen permeated from anode, but oxygen permeated from cathode side was not enough to contribute to the mixed potential. So, E1 potential was dominated by Eq. (2). Similarly, Electrode 2 (E2) voltage was also close to zero. It should be mentioned that anode was taken as the reference electrode in all voltage measurement.

Fig. 5 Distribution profile of mixed potential along membrane thickness at BoT. Operating conditions: cell temperature: 80°C; flow rate H₂/ air: 348/332 sccm; A/C: 50/20 stoic, 25/125% RH, 0/0 kPag back pressure.

Fig. 6 shows the through plane voltage change with time. E4 voltage closely followed the cell voltage during baseline test. At the beginning of the contaminant injection, there was larger voltage drop in E4 compared to the cell voltage and in rest of the test, it maintained a gap with the cell voltage, but it followed the same trend. In case of E1, E2, and E3, voltages remained zero until 32 hours; hence, up to 32 hours, oxygen permeation from cathode to these electrode positions remained negligibly small. E1 voltage remained zero throughout the test. E2 showed a measurable voltage after 40 hours and then it followed the same trend as the cell voltage. In case of E3, after 32 hours voltage started to increase during baseline test. E3 was found broken after disassembly (Fig. 7); therefore we do not consider the voltage measurement for E3 very reliable. As a result, measurements from E3 were not shown in the plot. For other electrodes, membrane degradation might have started after 32 hours resulting in increased permeation of oxygen. As contaminant started to deposit on the GDE surface with time (Fig. 3), it impeded the oxygen transport. As a result, potential in all electrodes decreased with the cell voltage.

Fig. 6 Through plane voltage change with time when cell was exposed to CaSO_4 at 200 mAcm^2 . At each discontinuity in the plot, EIS was measured. Operating conditions: cell temperature: 80°C ; flow rate H_2/air : 348/332 sccm; A/C: 50/20 stoic, 25/125% RH, 0/0 kPag back pressure.

Fig. 7 Broken position of Electrode 3 (E3) (shown in circle).

Fig. 8 shows the distribution profile of mixed potential for various current densities at the end of the test (EoT). For all the cases, E1 voltage remained zero and for all other electrodes the potential increased linearly from the anode to the cathode. These again clearly represented permeation of oxygen from the cathode to the anode. Moreover, voltages are lower for the same locations at OCV and at 100 mAcm^2 compared to the

measurements at the beginning of the contamination test (shown in Fig. 5). The change in probe potential is mostly due to salt deposition on GDE and flow field surface that impede the oxygen transport. It can also be related to the change in water content induced by the presence of foreign cations. Generally, the presence of foreign cations decreases the membrane water content [1,14-17]. Additionally, gas permeability is also a function of water content as reactants usually follow the hydrophilic channels [35]. As a result of these two linked dependencies, the reactant permeability of cation contaminated membranes is less than the value for a proton form membrane [26], which may have affected the measured potentials as well.

Fig. 8 Distribution profile of mixed potential along membrane thickness at EoT. After disassembly, E3 was found discontinuous. So, potentials for E3 were not shown here. Operating conditions: cell temperature: 80°C; flow rate H₂/ air: 348/332 sccm; A/C: 50/20 stoic, 25/125% RH, 0/0 kPag back pressure.

Through plane cation contamination effect can also be visualized from high frequency resistance (HFR) changes. Kienitz et al found more than 200% increase in HFR for a contaminated membrane which was contaminated by soaking into the contaminant solution [2]. In our experiment, as contaminant was injected into the air

stream, it was expected that HFR would increase on the cathode side. Within 21 hours of contamination, HFR increased in all layers of membrane (Fig. 9). Between E3 and E4, 50% increase in HFR was observed. HFR increase between E2 and E3 was 17.6%, and 6.7% between E2 and E3. Although E3 was found broken after disassembly, HFR data related to E3 was considered, since E3 was found broken at the end of the wire which was used for voltage measurement, but the other end of the wire was intact which was used for HFR measurement (Fig. 7). It should also be mentioned that HFR measurements are not necessarily corresponding to the ohmic loss due to proton transport because all charged ions are excited by AC perturbation during EIS measurements [2].

Fig. 9 High frequency resistance (HFR) increase (%) between electrodes within 20 hours of contamination. Operating conditions: current density: 200mAcm^{-2} ; cell temperature: 80°C ; flow rate H_2/air : 348/332 sccm; A/C: 50/20 stoic, 25/125% RH, 0/0 kPag back pressure.

4 Summary and Conclusions

Effect of cationic contamination in PEFCs in the through plane was investigated using a multilayered membrane cell. The MEA was prepared using five layers of membrane, and four Pt wires were inserted between the membrane layers. Ca^{2+} (at a concentration corresponding to 5 ppm) was injected into the air stream of the fuel cell. Pt

electrodes were used to monitor through plane potential due to permeation of hydrogen and oxygen from the anode and the cathode, respectively, and the resistance distribution across the membrane thickness.

At the beginning of the test, the electrode closest to the cathode showed the same potential as the cell potential and other electrodes showed zero potential, as the potential of the electrode closest to the cathode was dominated by oxygen permeation from the cathode, while for the other electrodes, oxygen permeation from the cathode was negligibly small so the potential was dominated by hydrogen reduction reaction. After 32 hours, there was enough oxygen permeation from cathode to other layers of membrane symbolizing the membrane degradation, as oxygen permeation increased with time.

The aluminum alloy flow field was found to be corroded, as the aluminum originated due to corrosion (possibly nickel from the base layer as well) degraded the cell performance from the beginning of the test. When Ca^{2+} was injected with air, the cell performance degraded rapidly. Salt was deposited on the GDE and on the flow field surface causing mass transport losses. HFR was increased due to contamination, and in the membrane layer close to the cathode, HFR increase was more than 50%.

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