Effect of Cationic Contaminants on Polymer Electrolyte Fuel Cell Performance

Jing Qi^{a,b}, Xiaofeng Wang^{b,c}, M. Ozan Ozdemir^{a,b}, Md. Aman Uddin^{a,b},
Leonard Bonville^b, Ugur Pasaogullari^{*,a,b}, and Trent Molter^{b,c}

^aDepartment of Mechanical Engineering, ^bCenter for Clean Energy Engineering, and
^cDepartment of Material Science & Engineering, University of Connecticut, 44 Weaver
Rd. U-5233, Storrs, CT 06269, United States

* Corresponding author. 44 Weaver Rd. U-5233, Storrs, CT 06269, United States. Tel.: +1 860 486 2332; Fax: +1 860 486 5088; E-mail:ugurpasa@engr.uconn.edu (U. Pasaogullari).

Abstract

The effect of cationic contaminants on polymer electrolyte fuel cell (PEFC) performance is investigated via in-situ injection of dilute cationic salt solutions. Four foreign cations (K^+ , Ba^{2+} , Ca^{2+} , Al^{3+}) are chosen as contaminants in this study due to their prevalence and chemical structure (e.g. valence), however contaminants that have already received extensive coverage in the literature like sodium and iron are excluded. It is found that the cells with $Ba(ClO_4)_2$ and $Ca(ClO_4)_2$ injection exhibit little cell performance change during the current hold test, and the cells with $Al(ClO_4)_3$ and $KClO_4$ injection show larger cell performance changes, i.e. decreasing cell voltage and increasing cell resistance. These cells with in-situ contaminant injection have a tendency to recover a portion of the lost performance after the recovery test when switched back to supersaturated air. The degradation in cell performance with the presence of cationic contaminants is mainly due, in addition to the membrane resistance increase associated with replacing protons on the sulfonate groups, to the increase in mass transport resistance and decrease in electrochemical surface area.

Keywords

polymer electrolyte fuel cell; fuel impurity; cationic contamination; degradation; mitigation; recovery.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are among the promising candidates for future automotive applications. However, the performance can be significantly decreased by the presence of cationic contaminants [1–3]. The source of cationic impurities includes the air stream, humidifier reservoirs, as well as the corrosion of stack and balance of plant components [4]. Extensive studies have been carried out to identify the potential impacts of cationic contamination in PEFC operations [5], investigating the effect of cationic impurity on the polymer electrolyte (perfluorosulfonic acid, PFSA) membrane (PEM) [6, 7], as well as modeling the effects of cationic contamination on PEFC performance [8–11]. In addition to replacing protons on the sulfonate groups in the ionomer, cationic contamination has several other major effects on PEFC performance: i) a decrease in limiting current, i.e., maximum current allowed by mass transport; ii) an increase in activation overpotential; and iii) a change in apparent working membrane conductivity that does not match high frequency resistance (HFR) data [8]. The degradation that is due to the replacement of protons attached to the sulfonate groups in the ionomer phase by foreign cations [3,12], can be measured by an increase in ohmic resistance. Explanations for the effects of the replacement of protons have been investigated, most notably by Okada et al. [13,14]. Compared to protons, most cations have a stronger affinity to the sulfonic acid groups and displace protons in the PEM in accordance with the normal ion exchange processes [13]. Substitution for protons with cations decreases the proton conductivity of the PEM, and this decrease in conductivity leads to increased ohmic losses [13].

In our previous studies, the effects of Al^{3+} [15] and Ca^{2+} [16] contaminants on PEFC performance were studied, where sulphate, $(\text{SO}_4)^{2-}$ was selected as the anion due to its compatibility with the catalyst coated membrane (CCM). It was found that the acid site

occupation in the CCM increased and the cell performance decreased with increased Al ion concentration in the solution [15]. 5 ppm CaSO_4 (calcium sulphate) in air (defined based on a dry air molar basis) was sufficient to lead to high cell performance loss at 1 A cm^{-2} as well as severe membrane degradation [16].

In order to identify important contaminants and quantify performance loss, four foreign cations (K^+ , Ba^{2+} , Ca^{2+} , Al^{3+}) were chosen as the contaminants in this study due to their prevalence and their chemical structure (e.g. valence). The ClO_4^- anion was selected based on high solubility and low/no toxicity of the compounds. Cations that were studied extensively in the literature (e.g. Na^+ , Fe^{2+}) were excluded.

2. Experimental

2.1. Materials and Components

CCMs were GORE® PRIMEA® Membrane Electrode Assemblies (MEA) (GORE and PRIMEA are registered trademarks of W. L. Gore and Associates, Elkton, MD). Pt loading of anode and cathode catalyst layers was 0.1 and 0.4 mg cm^{-2} , respectively. All of the chemicals used were of analytical grade: Potassium perchlorate (KClO_4), barium perchlorate ($\text{Ba}(\text{ClO}_4)_2$), calcium perchlorate tetrahydrate ($\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$), and hydrated aluminum perchlorate ($\text{Al}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$) were obtained from Sigma-Aldrich Co., St. Louis, MO. Ultra high purity hydrogen (99.999%), ultra high purity nitrogen (99.999%), and ultra zero purity air (99.8%) were used. All gases were purchased from Airgas, Inc.

2.2. Fuel Cell Tests

The CCMs (active area: $5 \text{ cm} \times 5 \text{ cm}$) were assembled in single cell hardware (Fuel Cell Technologies, Albuquerque, NM) using single pass anode and triple pass cathode flow fields, with SGL Carbon 25BC (Ion Power Inc., New Castle, DE) used as the gas

diffusion layer (GDL). A fuel cell test station (890B, Scribner Associates, Inc., Southern Pines, NC) was used to control the current load, flow rates, relative humidity, gas and cell temperatures, as well as to measure cell voltage and resistance. Resistance was measured using the built-in current interrupt technique.

The polarization curves were obtained under H₂/air: 80 °C/80 °C/73 °C (cell temperature/ anode humidifier temperature/ cathode humidifier temperature), which corresponded to 100% (anode)/ 75% (cathode) relative humidity at the inlets. The flow was controlled at a stoichiometry of 2 with a minimum of 0.2 slpm for both anode and cathode. These operating conditions were used from our predefined baseline for all PEFC tests conducted in our lab.

Schematic diagram of the experimental setup for in-situ injection of cationic contaminants is shown in Fig. 1. The injection system consisted of a micro flow nebulizer (ES-2005, PFA-400, Elemental Scientific Inc., Omaha, NE) and a high-resolution micro pump (Series III Pump, Scientific Systems Inc., State College, PA). The nebulizer was used to introduce either a finely dispersed contaminant solution or DI Water into air stream. It was placed just prior to the cathode inlet (shown in Fig. 1). In order to have consistent test conditions, the liquid flow rate from the nebulizer was maintained the same during the entire test processes (baseline test, contamination test, and recovery test). During the baseline test, DI water with a flow rate of 130 $\mu\text{L min}^{-1}$ was injected through the nebulizer. During the contamination test, the 100 mM contaminant (Ba(ClO₄)₂, Ca(ClO₄)₂, Al(ClO₄)₃, or KClO₄) in DI water at a flow rate of 130 $\mu\text{L min}^{-1}$ was injected into the cathode of the PEFC with dry air through a nebulizer, this corresponds to 175 ppm of the selected cation (K⁺, Ba²⁺, Ca²⁺, or Al³⁺) in the mixed inlet air on a dry air basis. Dry air was used as the carrier gas for the atomized droplets. The concentration was selected to represent an accelerated test along with operating conditions designed to

maximize the transport of cations into the MEA. After switching to the recovery test, the contaminant solution was replaced by DI water and the flow rate was kept the same. During all the test stages, the cell was run with a constant current density of 1 A cm^{-2} and maintained at 80°C . A high relative humidity was maintained at the cathode (125%) compared to the anode (25%) in order to facilitate the transport of the cationic impurities in the liquid phase into the MEA, and to force a net water flow from the cathode to the anode. For the same reason, a high back pressure was maintained at the cathode (15 psig) compared to the anode (1.5 psig). The flow was held at 1.75 slpm and 1.66 slpm for anode and cathode, respectively, corresponding to a 10 (anode) and 4 (cathode) stoichiometry. Cathode air came from two sources. The first source was humidified by the test station with a flow rate of 1.26 slpm. The other source was from the nebulizer with a flow rate of 0.4 slpm, which was used as the carrier gas for the atomized droplets as mentioned above. The relative humidity of the cathode was achieved by controlling the amount of water from the humidifier as well as from the nebulizer. A high air flow was maintained at the cathode (4 stoichiometry) to carry more water into the cathode in order to help to prevent contaminant precipitation, and a high H_2 flow at the anode to ensure that the performance degradation during these tests can be attributed to the contamination [16].

2.3. Cyclic Voltammetry (CV)

A potentiostat/galvanostat (Solartron SI 1287) was used to perform the cyclic voltammetry tests. The fuel cell cathode purged with humidified N_2 with a flow rate of 250 sccm was employed as the working electrode. Humidified H_2 with a flow rate of 250 sccm was passed through the counter electrode, which was also used as the dynamic hydrogen reference electrode. The scan rate and range were 20 mV s^{-1} and 0.05–0.8 V,

respectively. The cell temperature was 80 °C and the anode and cathode humidification temperatures were 80 °C and 73 °C, respectively.

Polarization scans and CVs were obtained at our conventional conditions in order to obtain a clear comparison between our historical uncontaminated cells and the contaminated cells.

2.4. SEM/EDX Analysis

After the fuel cell test was finished, the cell was disassembled and the contaminated CCM was examined using both a scanning electron microscope (SEM, FEI ESEM Quanta 250) and energy dispersive X-ray spectroscopy (EDX). The cross-section sample of the CCM was prepared using the procedure provided in our previous work [15]. The accelerating voltage for the SEM image and the EDX analysis was 5.0 and 15.0 kV, respectively.

3. Results and discussion

Fig. 2 shows the cell voltage and resistance of the contaminated cells during the current hold test (1 A cm^{-2}). BOT and EOT represents the beginning of test and the end of test, respectively. As shown in Fig. 2, a baseline test with a flow rate of $130 \text{ }\mu\text{L min}^{-1}$ DI water injected from the nebulizer has been carried out without any exposure to contaminants over 96 h. Comparing to the baseline, the cell voltages with $\text{Ba}(\text{ClO}_4)_2$ and $\text{Ca}(\text{ClO}_4)_2$ injection decayed slowly with time. However, as shown in our earlier work, only 5 ppm CaSO_4 in air was sufficient to lead to high cell performance loss at 1 A cm^{-2} [16]. This difference is thought due to lower solubility of CaSO_4 ($0.205 \text{ g} / 100 \text{ g H}_2\text{O}$) than that of $\text{Ca}(\text{ClO}_4)_2$ ($188 \text{ g} / 100 \text{ g H}_2\text{O}$). CaSO_4 precipitation was found at the contact regions between the GDL and flow plate of the cathode, causing mass transport issues [16], while no $\text{Ca}(\text{ClO}_4)_2$ salt deposits were detected in this study. Compared with the

$\text{Ba}(\text{ClO}_4)_2$ and $\text{Ca}(\text{ClO}_4)_2$ cells, the cells with $\text{Al}(\text{ClO}_4)_3$ and KClO_4 injection showed a sudden and fast cell voltage drop. An earlier and faster cell voltage drop was observed for the cell with the KClO_4 : 0.5 V drop within 4 h of the beginning of KClO_4 injection. Due to faster cell voltage drop, the $\text{Al}(\text{ClO}_4)_3$ and KClO_4 injection was stopped earlier than that of $\text{Ba}(\text{ClO}_4)_2$ and $\text{Ca}(\text{ClO}_4)_2$ injection. After the recovery test by switching back to non-contaminated supersaturated air as in the baseline test, the contaminated cells showed a tendency to recover a portion of the lost performance. The cell with $\text{Al}(\text{ClO}_4)_3$ exhibited the greater performance loss compared with the cells with $\text{Ba}(\text{ClO}_4)_2$ and $\text{Ca}(\text{ClO}_4)_2$, which might be due to the larger valence for Al^{3+} . As investigated by Okada et al. [6], the trivalent cations had more affinity to the sulfonic acid groups in the PEM than divalent cations, and larger valence cations caused a larger water content decrease in the PEM. It should be noted that the cell with KClO_4 injection exhibited severe performance degradation. This seemed to contradict the results above, however it must be taken into account that the larger affinity of cations to the sulfonic acid groups would result in the smaller cationic mobility as reported in ref [13]. Considering that the multivalent cations had more affinity to the sulfonic acid groups than monovalent cations, it is expected that the monovalent cations would have the higher mobility. In our case, K^+ would have a higher mobility than other cations, leading to earlier and faster performance decay. As shown in Fig. 2, comparing with the baseline, cell resistances with $\text{Ba}(\text{ClO}_4)_2$, $\text{Ca}(\text{ClO}_4)_2$ and $\text{Al}(\text{ClO}_4)_3$ injection increased gradually with time. The cell with $\text{Al}(\text{ClO}_4)_3$ injection showed a higher resistance increase compared with the cells with $\text{Ba}(\text{ClO}_4)_2$ and $\text{Ca}(\text{ClO}_4)_2$ injection; however, the cell resistances with KClO_4 injection increased sharply with injection time. The increase of the cell resistance could be explained by the effect of cation substitution for protons which reduced the proton conductivity and increase the ohmic loss as reported by T. Okada [13]. It should be noted that the zero

readings that were seen in the resistance curve for KClO_4 at approximately 26 h is due to a test equipment limitation where the current interrupt circuitry is not able to measure resistance at this low current.

Fig. 3 shows the polarization curve and resistance of the contaminated cells at BOT and EOT. Cell resistance was measured and recorded at current densities higher than 200 mA cm^{-2} using the built-in current interrupt technique. Resistance values at the current density lower than 200 mA cm^{-2} were not recorded, because the voltage loss in that small current range was too small to be accurately measured. Regarding the analysis of the activation overpotential, the polarization curve was plotted on semi-logarithmic scale (Tafel plot) to allow a more quantitative analysis. As shown in Fig. 3, the voltage losses for all the cells were due to: i) Activation polarization, dominant at the low current density region; ii) Ohmic polarization, dominant in the mid-current density range, i.e. the pseudo-linear portion of the polarization curve; and iii) Concentration polarization, dominant at high current densities, as described in ref [17]. All the cells in Fig. 3 showed a large cell voltage loss after the contaminant injection test. Among the above cells, the performance degradation of the cell with KClO_4 injection was the worst even though its contamination test time was shorter and recovery time was longer than those of the other cells (see Fig. 2). For each cell, the cell performance degradation got worse in the concentration polarization dominant region. Similar to the constant current tests shown in Fig. 2, the cell with KClO_4 injection showed a higher resistance increase compared with the other cells. Kienitz et al. found that the maximum power for the contaminated cells decreased proportionally to the percentage of protons that were replaced, then they investigated the transport of protons and contaminant ions to show why these limitations occurred [2,3,8]. Their results showed that this decrease was due to a decrease in electrode kinetics, cell thermodynamics, and limiting current of the system. When current

was drawn in a contaminated system, the cationic contaminants would accumulate at the cathode side of the membrane. This would slow the cathode electrochemical kinetics since fewer protons were available for reaction. This would also decrease the thermodynamic cell potential since a concentration gradient forms across the electrodes. Finally, the fuel cell limiting current would decrease because the fuel cell would become limited by the transport of protons to the cathode electrode. In our case, substitution of protons with cations in the CCM would hinder the electrode kinetics, cell thermodynamics, and limiting current, which resulted in increased activation and concentration polarizations, and consequent cell performance degradation. The decrease in electrochemical surface area (ECSA) and the SEM/EDX results discussed later also supported this conclusion.

Cathode CV curves were measured at BOT and EOT. The fuel cell anode was used as the counter electrode/ reference electrode with the inherent assumption that polarization of the anode was small relative to the polarization imposed on the cathode. The currents obtained in CVs in Fig. 4 were small and justified this assumption. To diminish the measurement error, CV was recorded with 4 cycles and the stable/repeatable curve was chosen for analysis. As shown in Fig. 4, the hydrogen adsorption and desorption peaks were reduced for all the cells with contaminant injection.

By integrating the charge (Q_H) associated with the peak area in the hydrogen desorption region (0.05–0.4 V), with the amount of charge corresponding to the double layer charging deducted, the ECSA ($\text{m}^2 \text{g}^{-1}$) for CCM was obtained using the following equation [18]:

$$ECSA = \frac{Q_H}{m \cdot Q_{Href}}$$

where m was the Pt loading in the electrode. Q_{Href} denoted the amount of charge of a homogenous H_{upd} monolayer on Pt, and was assumed to be 0.21 mC cm^{-2} [18]. We used hydrogen desorption region for the ECSA analysis not only because hydrogen adsorption on Pt changed with the temperature, but also because hydrogen adsorption region on CVs shown in Fig. 4 was deteriorated by hydrogen evolution. Table 1 shows the cathode ECSA values for BOT and EOT estimated from CV data. As shown in Table 1, compared with the cells with $Ba(ClO_4)_2$ and $Ca(ClO_4)_2$ injection, the cells with $Al(ClO_4)_3$ and $KClO_4$ injection showed a larger decrease in ECSA. The ECSA losses for these groupings showed the same trend as the cell voltage drop. We discuss this in detail in the next paragraph combined with the characterization of SEM/EDX for CCM cross-section of the cell at the EOT. In addition to the increase in Ohmic resistance as discussed for Fig. 2, the reduction in apparent ECSA was another cause for the cell performance degradation.

Higher valence cations were expected to have a larger effect on fuel cell performance; however, during fuel cell operation, the cations with a higher charge, did not seem to penetrate into the PEM. In order to investigate the cationic contaminant distribution, SEM/EDX of the CCM cross-section at the EOT was obtained as shown in Fig. 5. The accelerating voltage for the EDX analysis was 15.0 kV to achieve the best resolution without damaging the membrane. ACL and CCL represent the anode catalyst layer and the cathode catalyst layer, respectively. For the cell with $Al(ClO_4)_3$ injection, Al was found throughout the CCM. Chlorine (Cl) was also detected in the CCM (The EDX spectrum for Cl was not shown here). The presence of Ca, Ba, and K was found at the same locations as Al, however no Cl signal was detected. Efforts are currently underway to understand why Cl was found only in the presence of aluminum. The atomic percentage of Al, Ca, Ba, and K in the CCM at the EOT were obtained from the EDX

spectrum As shown in Fig. 6, the abscissa shows the cell with $\text{Al}(\text{ClO}_4)_3$, $\text{Ba}(\text{ClO}_4)_2$, $\text{Ca}(\text{ClO}_4)_2$, and KClO_4 injection. The ordinate shows the atomic percentage of Al, Ca, Ba, and K in the CCM, including ACL, membrane, and CCL. The experimental errors relate to the accuracy of the EDX spectrum. The atomic percentage of Al, Ca, Ba, and K in the CCM was estimated to be 0.9 at.%, 0.6 at.%, 0.2 at.%, and 1.7 at.%, respectively. The result confirmed that K^+ had the highest occupation in the CCM and Al^{3+} showed the next highest occupation in the CCM, followed by Ca^{2+} and Ba^{2+} , following the same trend as the cell voltage drop and ECSA loss. As discussed above with Fig. 3, the Al, Ca, Ba, and K substitution for protons in the CCM decreased the H^+ ion transport, which resulted in the concentration polarization and then the cell performance degradation. Based on the SEM/EDX results, a possible reason for the ECSA loss could be the cationic ions occupying the sulfonic acid groups in the CCM. It was discovered by Okada et al [14] that the impurity cations hindered the rate of the charge-transfer step at platinum covered with PFSA ionomer, indicating that the effect was specific to the Pt electrode-ionomer membrane interface. The presence of Cl in the CCM reduced the H_2 desorption and adsorption peaks as reported by Li et al. [19], which could be another reason for the reduced ECSA for the cell with $\text{Al}(\text{ClO}_4)_3$ injection.

4. Conclusions

The cells with $\text{Ba}(\text{ClO}_4)_2$ and $\text{Ca}(\text{ClO}_4)_2$ injection exhibited little cell voltage change during the current hold test, and the cells with $\text{Al}(\text{ClO}_4)_3$ and KClO_4 injection showed a larger cell performance change, i.e. decreasing cell voltage and increasing cell resistance. The cell with KClO_4 injection experienced a large voltage loss very quickly, while those with $\text{Ba}(\text{ClO}_4)_2$ and $\text{Ca}(\text{ClO}_4)_2$ injection showed a very slow voltage decay. The cell with $\text{Al}(\text{ClO}_4)_3$ injection showed an intermediate decay rate. The SEM/EDX

results showed that K^+ had the highest occupation in the CCM, which could explain why the performance degradation of the cell with $KClO_4$ injection was the worst in this study. The degradation in cell performance with the presence of cationic contaminants was mainly due, in addition to the membrane resistance increase associated with replacing protons on the sulfonate groups, to the increase in mass transport resistance and decrease in ECSA. The cells with contaminant injection had a tendency to recover a portion of the lost performance after the recovery test by switching back to supersaturated air.

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Cell	ECSA at BOT $\text{m}^2 \text{g}^{-1} \text{Pt}$	ECSA at EOT $\text{m}^2 \text{g}^{-1} \text{Pt}$	ECSA Loss (BOT-EOT)/BOT
$\text{Al}(\text{ClO}_4)_3$ injection	43.2	27.9	35.4%
$\text{Ca}(\text{ClO}_4)_2$ injection	46.3	32.2	30.5%
$\text{Ba}(\text{ClO}_4)_2$ injection	45.2	31.8	29.6%
KClO_4 injection	44.1	28.4	35.6%

Table 1. Cathode ECSA values for BOT and EOT estimated from CV data.

Figure captions

Fig. 1. Schematic diagrams of experimental setup and test procedure.

Fig. 2. Cell voltage and resistance during constant current hold (1 A cm^{-2}). Cell temperature: 80°C ; anode/cathode relative humidity: 25%/ 125%; flow rates (anode/cathode) 1.75 / 1.66 slpm (corr. stoichiometry 10/4) back-pressure (anode/cathode) 1.5/15 psig.

Fig. 3. Polarization (I-V) and resistance curves at BOT and EOT. Cell temperature: 80°C ; anode/cathode relative humidity: 100%/ 75%; flow rates: 2 stoichiometry (0.2 slpm minimum); back-pressure 0/0 psig.

Fig. 4. Cathode CV curves measured at BOT and EOT. The scan rate and range were 20 mV s^{-1} and 0.05–0.8 V, respectively. Cell temperature: 80°C ; anode/cathode relative humidity: 100%/ 75%; back pressure: 0/0 psig.

Fig. 5. SEM image and elemental mapping for CCM cross-section of the cell at EOT. (A) $\text{Al}(\text{ClO}_4)_3$ injection; (B) $\text{Ca}(\text{ClO}_4)_2$ injection; (C) $\text{Ba}(\text{ClO}_4)_2$ injection; (D) KClO_4 injection.

Fig. 6. Cation atomic percentage obtained from EDX for CCM cross-section of the cell at EOT.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.