



Effect of cationic contaminants on polymer electrolyte fuel cell performance



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HIGHLIGHTS

- Effect of cationic contaminants on polymer electrolyte fuel cell performance is investigated.
- Cause for cell performance degradation with the presence of cationic contaminants is studied.
- Mitigation method for cell performance degradation with the presence of cationic contaminants is given.

ARTICLE INFO

Article history:

Received 8 December 2014

Received in revised form

24 February 2015

Accepted 23 March 2015

Available online 24 March 2015

Keywords:

Polymer electrolyte fuel cell

Fuel impurity

Cationic contamination

Degradation

Mitigation

Recovery

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.

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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

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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 sulfate, $(\text{SO}_4)^{2-}$ 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 sulfate) 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 H_2/air : $80 \text{ }^\circ\text{C}/80 \text{ }^\circ\text{C}/73 \text{ }^\circ\text{C}$ (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 ($\text{Ba}(\text{ClO}_4)_2$, $\text{Ca}(\text{ClO}_4)_2$, $\text{Al}(\text{ClO}_4)_3$, or KClO_4) 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^+ , Ba^{2+} , Ca^{2+} , or Al^{3+}) 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 $80 \text{ }^\circ\text{C}$. 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 $0.05\text{--}0.8 \text{ V}$, respectively. The cell temperature was $80 \text{ }^\circ\text{C}$ and the anode and cathode humidification temperatures were 80 and $73 \text{ }^\circ\text{C}$, 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 represent the beginning of test and the end of test, respectively. As shown in Fig. 2, a baseline test with a flow rate of $130 \mu\text{L min}^{-1}$ DI water

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