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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 h, 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 h 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.
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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

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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^-, $(ClO_4)^-$ and $(SO_4)^{2-}$) 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.

Experimental

Nafion® membrane (NRE 211, Ion Power Inc.) was first treated with 500 mM Sulfuric acid solution at 80 °C for 6 h. 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 25 μm 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 h 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 1 cm below the gas inlet to the active area and all other electrodes (E2, E3, and E4) were placed approximately 1 cm apart from each other. In all electrochemical measurements, anode electrode was taken as the reference.

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 mg cm^{-2} loading. The whole arrangement shown in Fig. 1 was hot pressed at 130 °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

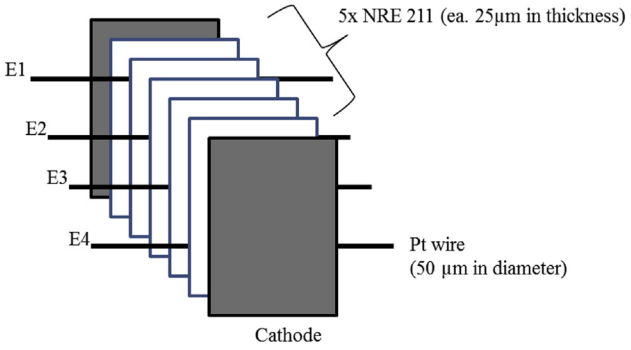

Fig. 1 – Simple schematic diagram of membrane electrode assembly (MEA). Four Pt wire (50 μm in diameter) electrodes (E1, E2, E3, and E4) were inserted between five layers of Nafion membrane (ea. 25 μm in thickness).

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 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 μL min 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 5 mA, which was small compared to the cell current (1000 mA) 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

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