## Effect of Ca<sup>2+</sup> as an Air Impurity on Polymer Electrolyte Fuel Cells

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Cationic contamination is a well-known phenomenon to cause performance degradation and decrease in lifetime in polymer electrolyte based electrochemical systems. Calcium is a significant cationic impurity due to its prevalence.

In this work, the role of calcium is investigated in-situ by injecting into the cathode of a single polymer electrolyte fuel cell (PEFC) through a nebulizer as a solution of calcium sulphate (CaSO<sub>4</sub>) in deionized (DI) water. Stability tests are conducted to determine the contaminant effects at different current densities with different Ca<sup>2+</sup> concentrations. The tested CaSO<sub>4</sub> concentrations are 1.14 mM, 2.85 mM and 5.7 mM which correspond to 2 ppm, 5 ppm and 10 ppm Ca<sup>2+</sup> in cathode air respectively under our experiment conditions. Constant current densities of 0.2 A/cm<sup>2</sup>, 0.6 A/cm<sup>2</sup> and 1 A/cm<sup>2</sup> are employed to run the experiments.

Figure 1 shows the contaminant effects of different  $Ca^{2+}$  concentrations at the same current density (1 A/cm<sup>2</sup>). The cell degradation rates increase with the rise of injected  $CaSO_4$  concentrations at the same current density. 10 ppm  $Ca^{2+}$  in air, i.e. the highest concentration, shows the highest performance loss as expected. 5 ppm  $Ca^{2+}$  also shows significant voltage degradation. However 2 ppm  $Ca^{2+}$  only has minor effects on the cell performance.

Besides the concentration, the current density also plays an important role on the effect of the Ca<sup>2+</sup> cation. Figure 2 shows the stability test results of different current densities with the same Ca<sup>2+</sup> concentration (5 ppm in dry air). The cell running at current density of 0.6 A/cm<sup>2</sup> shows the lowest performance loss among all the three tested current densities. At 0.2 A/cm<sup>2</sup>, heavy plugging occurs near the outlet of the cathode after cells run with CaSO<sub>4</sub> for approximately 40~50 hours. At this low current density, the water loss from cathode to anode causes CaSO<sub>4</sub> to precipitate in the cathode, and causes increased mass transport losses by plugging the pores of the diffusion media and the gas channels.

From the hydrogen crossover (CO) and cyclic voltammetry (CV) data shown in Table 1, higher concentrations of  $Ca^{2+}$  may lead to larger degradation of the membrane when cells are tested at the same current density. ECA loss varies with current densities and  $Ca^{2+}$  concentrations. Higher current densities with lower  $Ca^{2+}$  concentrations result in higher ECA loss than lower current densities with higher  $Ca^{2+}$  concentrations.

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Figure 1. Performance compare for PEM fuel cells operating at 1 A/cm<sup>2</sup> with different Ca<sup>2+</sup> concentrations. Testing conditions: cell temperature: 80C; flow rate A/C: 1.75/1.66 SLM; RH A/C: 25%/125%; back pressure A/C: 1.5/15 PSIG



Figure 2. Performance compare for PEM fuel cells operating with 5 ppm  $Ca^{2+}$  in air and at different current densities. Testing conditions: cell temperature: 80C; flow rate A/C: 1.75/1.66 SLM; RH A/C: 25%/125%; back pressure A/C: 1.5/15 PSIG

Table 1. Hydrogen crossover and cyclic voltammetry

Cell	H <sub>2</sub> crossover at BOT, mA/cm <sup>2</sup>	H <sub>2</sub> crossover at EOT, mA/cm <sup>2</sup>	ECA loss, (BOT- EOT)*100/ BOT
$1 \text{ A/cm}^2 \text{ with } 2$	2.68	2.93	24.5
ppm CaSO <sub>4</sub> in air			
$1 \text{ A/cm}^2 \text{ with } 5$	2.75	>80	45.9
ppm CaSO <sub>4</sub> in air			
$1 \text{ A/cm}^2 \text{ with } 10$	2.94	>80	N/A
ppm CaSO <sub>4</sub> in air			
$0.6 \text{ A/cm}^2 \text{ with } 5$	2.56	8.68	16.4
ppm CaSO <sub>4</sub> in air			
$0.2 \text{ A/cm}^2 \text{ with } 5$	2.89	3.55	10.1
ppm CaSO <sub>4</sub> in air			