Proton Exchange Membrane Fuel Cell Contamination

OBJECTIVE AND SIGNIFICANCE: The objective of this project is to develop an effective technique to mitigate or restore the performance loss caused by air contaminants in proton exchange membrane fuel cell (PEMFC) systems, especially the losses that cannot be restored by clean air operation alone. If successful, the technique would facilitate PEMFC systems meeting the U.S. DOE technical targets at performance and durability by inhibiting the degradations of membrane electrodes assembly (MEA) components and their performance. This program would help overcome the challenge of operating PEMFC systems in polluted or other harsh environments.

BACKGROUND: PEMFCs are considered a promising clean energy technology for transportation and stationary applications. Currently, Pt-based catalysts are used almost exclusvely in PEMFC due to the high electrochemical activity. Unfortunately, air pollution is a challenge for the PEMFC applications in the realistic atmosphere. There are more than 200 airborne pollutants, which may be introduced into the PEMFC cathode via the air stream with the potential to poison the Pt-based catalysts.

In past decades, PEMFC contaminants were studied with single cells or stacks using both accelerated and long-term tests. At HNEI, more than twenty potential contaminants have been studied in single cell tests. Most of these compounds are able to adsorb and react on Pt surface and compete with oxygen reduction reaction, a key reaction in PEMFC. While the effects from both unsaturated hydrocarbon and oxygen-containing hydrocarbon contaminants, could be mitigated by interrupting the explosure to contaminants for sulfur and halogen compounds degrade cell performance that does not recover with clean air operation. The contamination also accelerates the permanent degradation of Pt catalysts and electrolyte membrane. The contamination mechanisms of those compounds (e.g. bromomethane) are illustrated in Figure 1.

The contaminants permeate through the thin ionomer film and break down to adsorbates ($BrCH_3$ to Br^-, SO_2 to S and SO_4^{2-}) on the Pt catalyst surface. The adsorbates cannot be oxidized or desorbed under normal PEMFC operating conditions, and accumulate at the catalyst-electrolyte film interface. The anions even cannot be removed by cyclic voltammetry scanning alone due to Donnan exclusion by the ionomer. The catalyst surface then loses activities to the fuel cell reactions. For a long-term operation, the absorption of anions also causes permanent damages on the MEA, such as Pt dissolution and particle growth, and ionomer electrolyte decomposition.

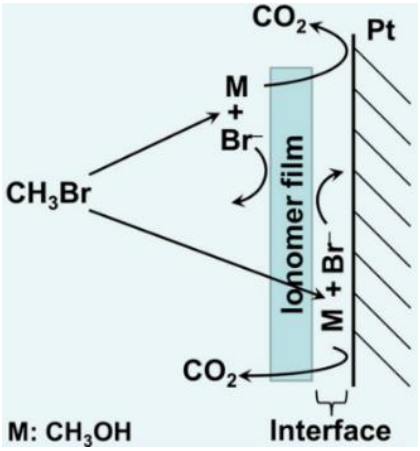


Figure 1. Contamination mechanisms of bromomethane in PEMFC cathode.

The possible solutions that have been proposed includes restoring the cell performance by in-situ potential scanning after the contamination and eliminating the contaminants with filter before reaching to the catalyst layer. However, the potential scanning is not applicable to stacks because the control of every cathode potential is required for multiplying electrical connections and equipment needs. On the other hand, chemical filter typically only last several months under realistic PEMFC vehicle operations.

PROJECT STATUS/RESULTS: Under this project, HNEI has developed performance recovery techniques that, in one case incorporates a combination of purging and flushing operations; and in other cases, uses an in-situ catalytically filtration method to eliminate the contaminants before it reaches the catalysts layer. The specific procedures are based on a comprehensive understanding on the contamination mechanisms of the selected air pollutants. The recovery method validated using single cells was shown to restore the performance losses and remove the adsorbates and anions after poisoning with bromomethane, hydrogen chloride, or sulfur dioxide.

Representative results are shown in Figures 2 and 3. The cell performance was restored to 100%, 97%, and 99% of its initial value, respectively for those contaminants.

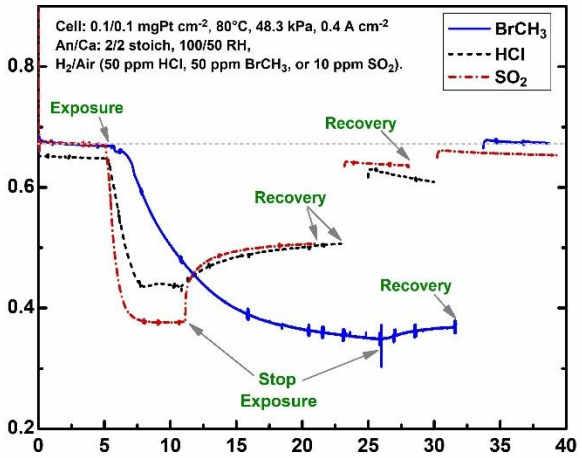
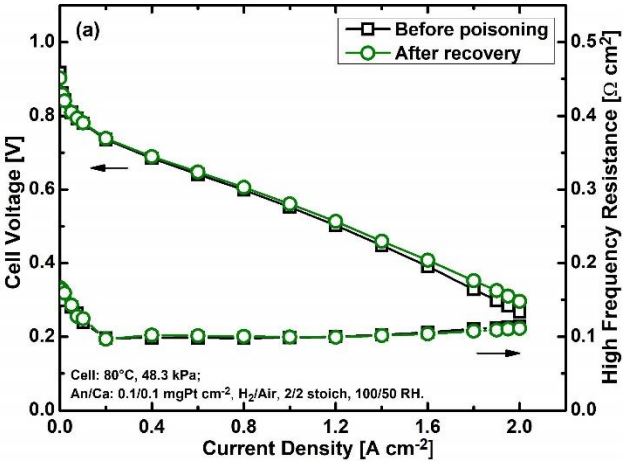


Figure 2. Cell performance responses to bromomethane, hydrogen chloride, and sulfur dioxide contamination and the subsequent recovery.



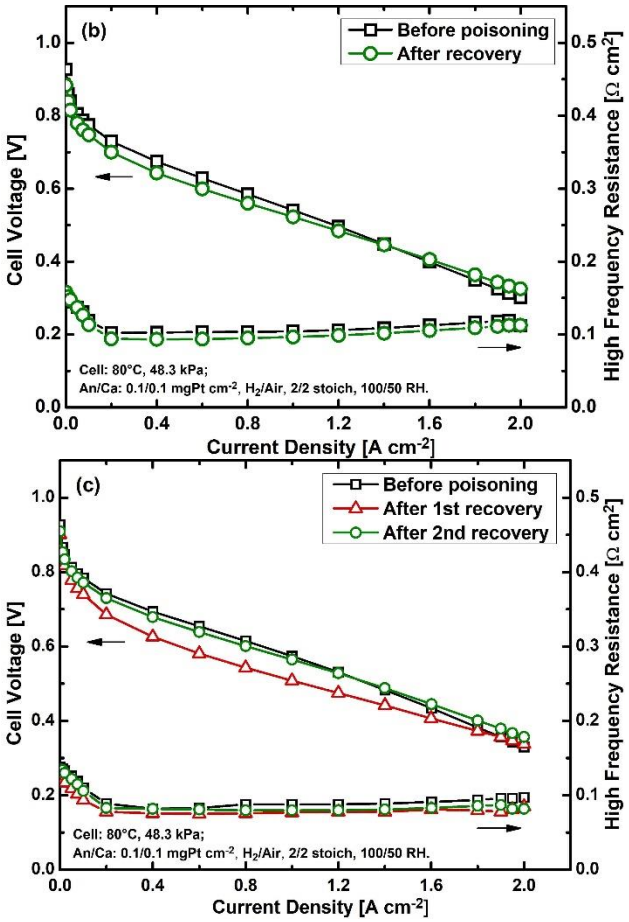


Figure 3. Cell polarization curves and high frequency resistance before poisoning and after recovery: (a) bromomethane, (b) hydrogen chloride, and (c) sulfur dioxide.

In summary, an effective recovery method has been developed and demonstrated that yields almost complete performance recovery after poisoning with bromomethane, hydrogen chloride, or sulfur dioxide. A provisional patent was filed. Collaboration with the PEMFC stacks manufactures, who are running fuel cell vehicle demonstrations, was sought to validate the efficiency of the method for contaminated PEMFC stacks.

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