OBJECTIVE AND SIGNIFICANCE: The objective of this project was to develop effective methods to restore the performance loss caused by air contaminants in proton exchange membrane fuel cell (PEMFC) systems, especially the losses that cannot be restored by interrupting the contaminant exposure. An effective recovery method would slow down the degradations of membrane electrodes assembly components and their performances, facilitate the system meeting with the U.S. DOE technical targets for PEMFC performance and durability, and overcome the air pollution challenges to the applications of PEMFC systems.

BACKGROUND: PEMFC is considered a promising clean energy technology for transportation and stationary applications. Currently, Pt-based catalysts are still extensively applied in PEMFC due to the high electrochemical activity. Unfortunately, more than 200 airborne pollutants can be introduced into the PEMFC cathode via the air stream. Air pollution is a challenge for the PEMFC application. In past decades, many 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 configurations. Most of these compounds adsorb and react on Pt surface and compete with oxygen reduction reaction, a key reaction in PEMFC. Fortunately, the effects from both unsaturated hydrocarbon and oxygen-containing hydrocarbon contaminants, could be mitigated by neat air operation. However, for sulfur and halogen compounds, the cell performance suffers a significant loss and does not recover with the neat air operation. The contamination also accelerates the permanent degradation of Pt catalysts and electrolyte membrane. The contamination mechanisms of those compounds, i.e. bromomethane, are illustrated in Figure 1. The contaminants permeate through the thin ionomer film and break down to adsorbates (BrCH₃ to Br, SO₂ to S and SO₄²⁻) on the Pt catalyst surface. The adsorbates cannot be oxidized or desorbed under normal PEMFC operating conditions, and accumulate at the catalyst layer 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.

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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, a performance recovery method has been developed by HNEI that incorporates a combination of gas purging and water flushing operations. Specific procedures are based on a comprehensive understanding on the contamination mechanisms of the selected air pollutant. The 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 1. Contamination mechanisms of bromomethane in PEMFC cathode.
Figure 2. (a) Cell performance responses to the bromomethane contamination and recovery; (b) Cell polarization curves before poisoning and after recovery.

In summary, an effective recovery method has been developed and demonstrated that yields an 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, is being sought for further validating the efficiency of the recovery method for contaminated PEMFC stacks.

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