
V.G.13 Impurity Effects on Membrane-Electrode Assembly Components

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- 5,000 operating hours under load cycling at $\leq 80^{\circ}\text{C}$
- 2,000 operating hours under load cycling at $> 80^{\circ}\text{C}$

Accomplishments

- Determined the effect of chloride on the oxygen reduction kinetics of $\text{Pt}_3\text{Co}/\text{C}$ catalyst.
 - Determined that multiple oxidation-reduction cycles are necessary to remove adsorbed chloride from the platinum electrocatalyst.
 - Determined that oxygen reduction kinetics on $\text{Pt}_3\text{Co}/\text{C}$ are unaffected by 1 mM methylene chloride at 60°C .
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Objectives

- Determine the mechanisms for the degradation of polymer electrolyte fuel cell (PEFC) performance by impurities in hydrogen and in air.
- Predict the long-term effects of impurities on PEFC stack performance.
- Predict the effect of operating conditions and impurity concentrations on PEFC stack performance.
- Develop strategies to mitigate performance degradation and enhance stack durability.
- Develop strategies to recover stack performance after the impurity is removed from the fuel or air streams.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Component Durability
- (C) Electrode Performance

Technical Targets

This project focuses on fundamental studies of the effect of hydrogen and air contaminants on polymer electrolyte fuel cell performance. Insights gained from these studies will be applied to defining hydrogen and air quality specifications and to developing mitigation or recovery strategies for achieving the following 2010 technical targets:

Introduction

Contaminants in the ambient air and fuel hydrogen can adversely affect the performance of a polymer electrolyte fuel cell stack by various mechanisms. Cationic impurities or impurities converted to cationic species within the fuel cell can bind with the anionic sulfonate groups in the polymer electrolyte membrane and reduce its proton conductivity, thereby increasing the cell resistance. Contaminants may also adsorb on the electrocatalyst and block the active sites from adsorbing and dissociating hydrogen or oxygen. This decreases the effective catalyst active surface area and can decrease the power output of the fuel cell if a significant fraction of the catalyst sites is blocked. The adsorption of the impurity can be: irreversible and, thus, cumulative; reversible if, when the contaminant is removed from the reactant stream, then the impurity desorbs from the electrocatalyst surface; or reversible, by using a chemical or electrochemical clean-off mechanism (e.g., electro-oxidation of adsorbed carbon monoxide). Impurity testing on single membrane-electrode assemblies or stacks provides the ultimate result of the poisoning, but provides only an overall effect on the ionomer and electrocatalyst. This does not allow decisive determination of the degradation mechanism, nor does it help to develop a predictive model of fuel cell performance degradation due to the presence of the impurity.

Approach

In this project we are determining the effects of anticipated air and fuel impurities on the electrocatalyst and ionomer separately to determine the degradation mechanisms, the type of poisoning (irreversible or reversible), the effect of impurity concentration and

dose, and the effect of temperature. These data will be used to develop models of contaminant interaction with stack materials to enable prediction of the long-term effects of the impurities, the effect of stack operating conditions, and to provide insight for developing mitigation or recovery techniques.

The effects of air and fuel impurities on the ionomer are being determined using electrochemical impedance spectroscopy (EIS) of test samples of the membrane in a proton conductivity apparatus. The apparatus can be operated in the 10–120°C temperature range and from dry to 100% relative humidity conditions. The effects of contaminants on the ionic and electronic conductivity of the electrode layer are being determined using EIS on electrode inks with electron-blocking or proton-blocking electrodes. The effects of air and fuel impurities on the electrocatalyst are being determined by exposing inks of the electrocatalyst deposited on glassy carbon to electrolyte solutions containing the impurities. The decrease of the electrochemically active surface area is being determined using cyclic voltammetry and the effect of poisoning on the electrode reactions (i.e., hydrogen oxidation and oxygen reduction) is being determined using potentiodynamic rotating disk electrode measurements. These tests are being performed in a controlled-temperature cell over the temperature range of 10–80°C. The data acquired in these experiments will be used to develop a predictive model for the degradation of long-term stack performance.

Results

This year's research has focused on chloride and chloride-containing organics and their effects on oxygen reduction reaction (ORR) kinetics on a commercially-purchased Pt₃Co/C catalyst. As shown in Figure 1, hydrogen chloride has a dramatic effect on the ORR kinetics, shifting the half-wave potential by >100 mV, at 60°C. This is in agreement with published data on the

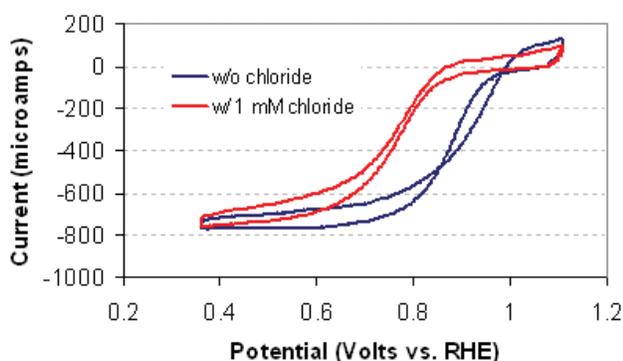


FIGURE 1. The effect of 1 mM chloride on ORR activity of Pt₃Co/C. Conditions: catalyst-coated glassy carbon rotating-disk electrode, 0.5 M HClO₄, 60°C, 1,600 rpm, 5 mV/s, curves not corrected for double layer charging.

effects of chloride on Pt/C [1]. In voltammetric cycles, the chloride was seen to block both the adsorption of hydrogen and the formation of oxide on the Pt₃Co surface, consistent with a site-blocking mechanism for the inhibition of oxygen reduction. It was also found that multiple oxidation-reduction cycles between hydrogen evolution and oxygen evolution potential regions were necessary to remove the adsorbed chloride from platinum.

As opposed to the chloride anion, the organic chloride, methylene chloride, was found to have minimal effect on Pt₃Co/C. As shown in Figure 2, the kinetic current at 0.9 V for ORR is unaffected by 1 mM methylene chloride. This minimal effect was also reflected during the cyclic voltammetry, which showed only a slight inhibition of oxide formation with the addition of methylene chloride.

Conclusions and Future Directions

Conclusions

- Chloride anion has a similar inhibiting effect on the ORR activity of Pt₃Co/C as has been observed for Pt/C [1].
 - Chloride anion is irreversibly adsorbed on Pt₃Co/C.
 - Methylene chloride does not inhibit oxygen reduction on Pt₃Co/C.

Future Directions (Remainder of FY 2006)

- Determine effect of temperature and concentration of chloride, chloride-containing organics, C7 aliphatics, C7 aromatics on:
 - Oxygen reduction reaction kinetics and selectivity.

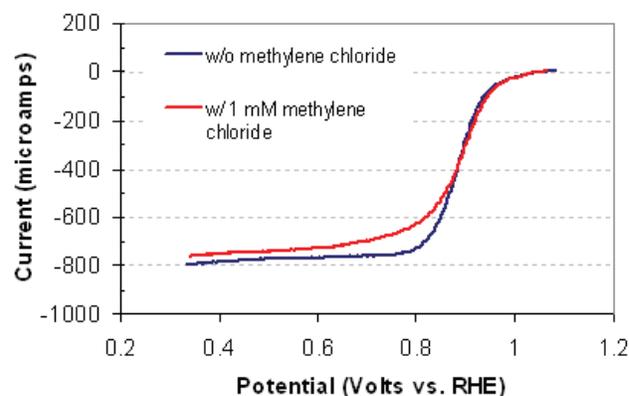


FIGURE 2. The effect of 1 mM methylene chloride on ORR of Pt₃Co/C. Conditions: catalyst-coated glassy carbon rotating-disk electrode, 0.5 M HClO₄, 60°C, 1,600 rpm, 5 mV/s, curves not corrected for double layer charging.

- Hydrogen oxidation reaction kinetics.
- Electrode layer conductivity.
- Membrane conductivity.
- Incorporate effect of chlorides into Argonne's stack performance model.

References

1. T. J. Schmidt, U. A. Paulus, H. A. Gasteiger, and R. J. Behm, *J. Electroanal. Chem.*, **508** (2001) 41.