

Impurity Effects on Membrane-Electrode Assembly Components

*Deborah Myers, Rajesh Ahluwalia,
and Romesh Kumar*

Argonne National Laboratory

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Overview

Timeline

- Start date: October 2005
- Project end date: open
- Percent complete: n/a

Budget

- FY'06 first year of project
- Funding for FY '06: \$250 K

Barriers

- This project addresses the following DOE Fuel Cell Component barriers:
 - A. Component Durability
 - C. Electrode Performance

Interactions

- Regularly providing updates to, and soliciting feedback from, the FreedomCAR Fuel Cell Technical Team

Objectives

- Determine the mechanisms for the degradation of 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 concentration 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

Approach

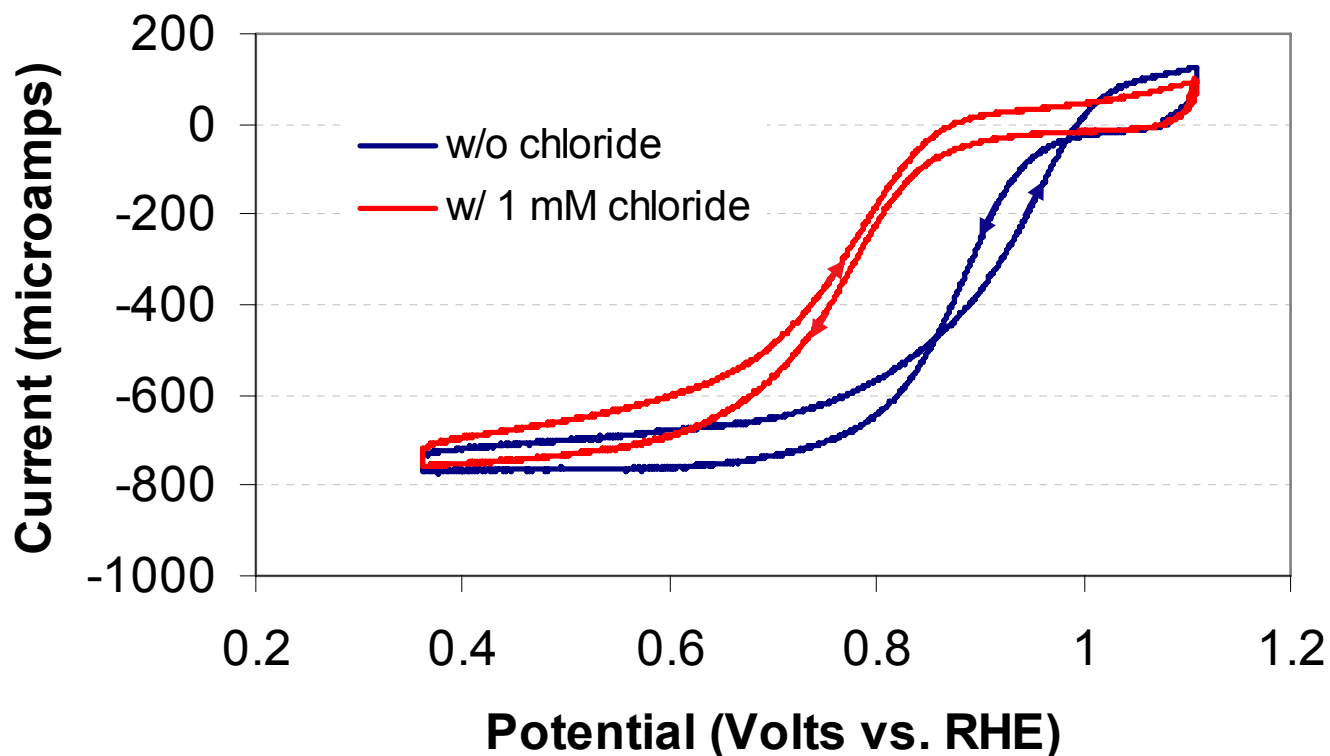
- Determine the mechanisms of the degradation of stack performance for anticipated air and fuel impurities by determining
 - the effects of anticipated air and fuel impurities on the
 - *Electrocatalyst activity*
 - *Proton conductivity of electrode layer*
 - *Electronic conductivity of electrode layer*
 - *Membrane conductivity*
 - the type of poisoning (irreversible or reversible)
 - the effect of temperature (10 to 120°C)
- Develop models of contaminant interaction with stack materials to predict the long-term performance degradation caused by air and fuel impurities

Progress vs. FY'06 Milestones

- Determine effects of chloride and chloride-containing organics (07/06)
 - Established the capability to determine the effect of impurities on the reaction kinetics of high surface area carbon-supported catalysts as a function of temperature
 - Determined the effects of millimolar concentrations of hydrogen chloride and methylene chloride on the oxygen reduction kinetics of Pt₃Co/C catalyst, at 60°C
- Determine effects of selected paraffinic / aromatic hydrocarbons (09/06)
 - To be initiated shortly

Hydrogen chloride has a dramatic effect on oxygen reduction kinetics of $\text{Pt}_3\text{Co}/\text{C}$

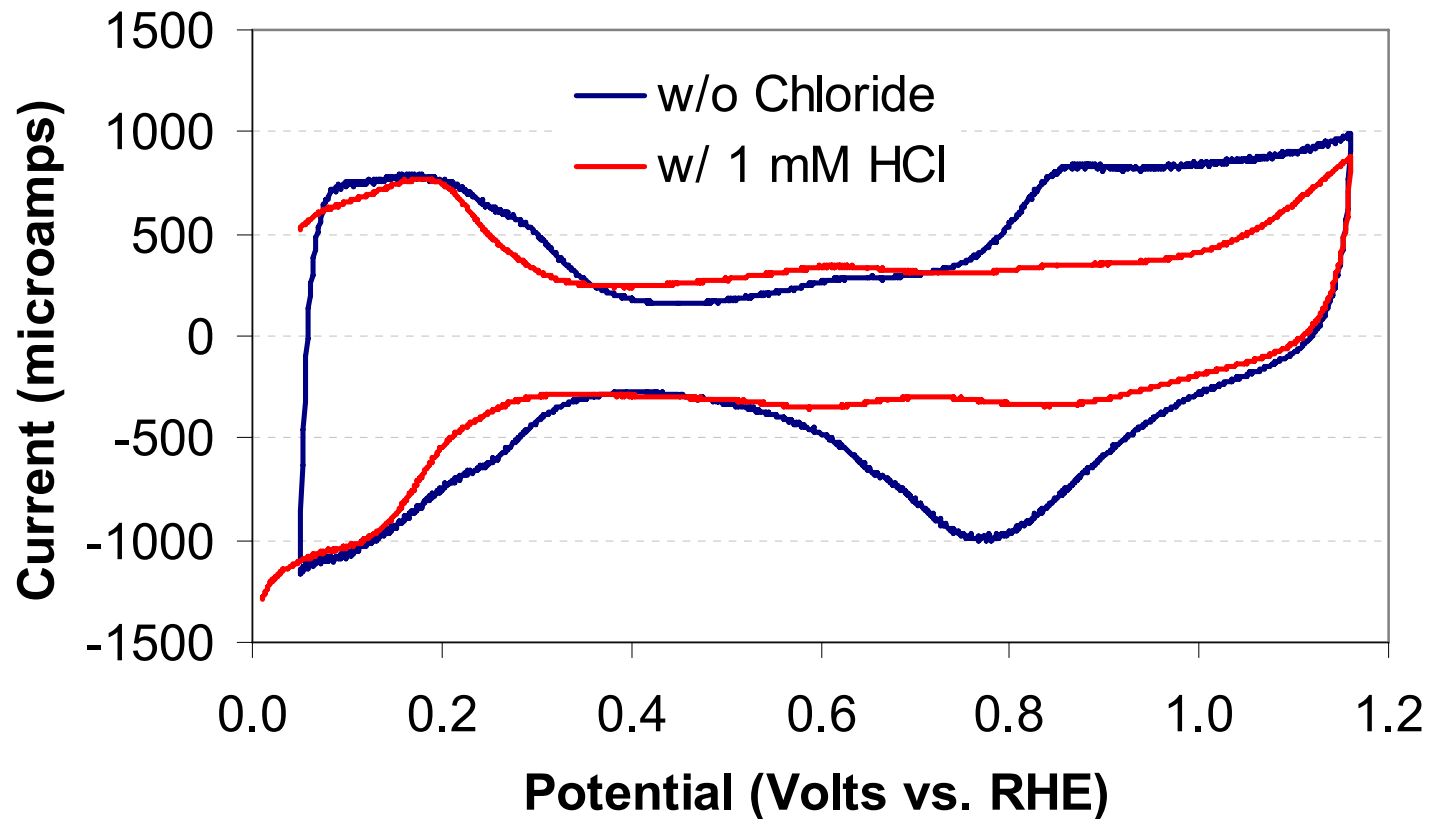
- Half-wave potential for ORR reaction is shifted by >100 mV by 1 mM chloride



- Catalyst-coated glassy carbon rotating-disk electrode, 0.5 M HClO_4 , 60°C , 1600 rpm, 5 mV/s, curves not corrected for double layer charging
- In agreement with published data on Pt/C
(T.J. Schmidt et al., J. Electroanal. Chem., 508 (2001) 41-47.)

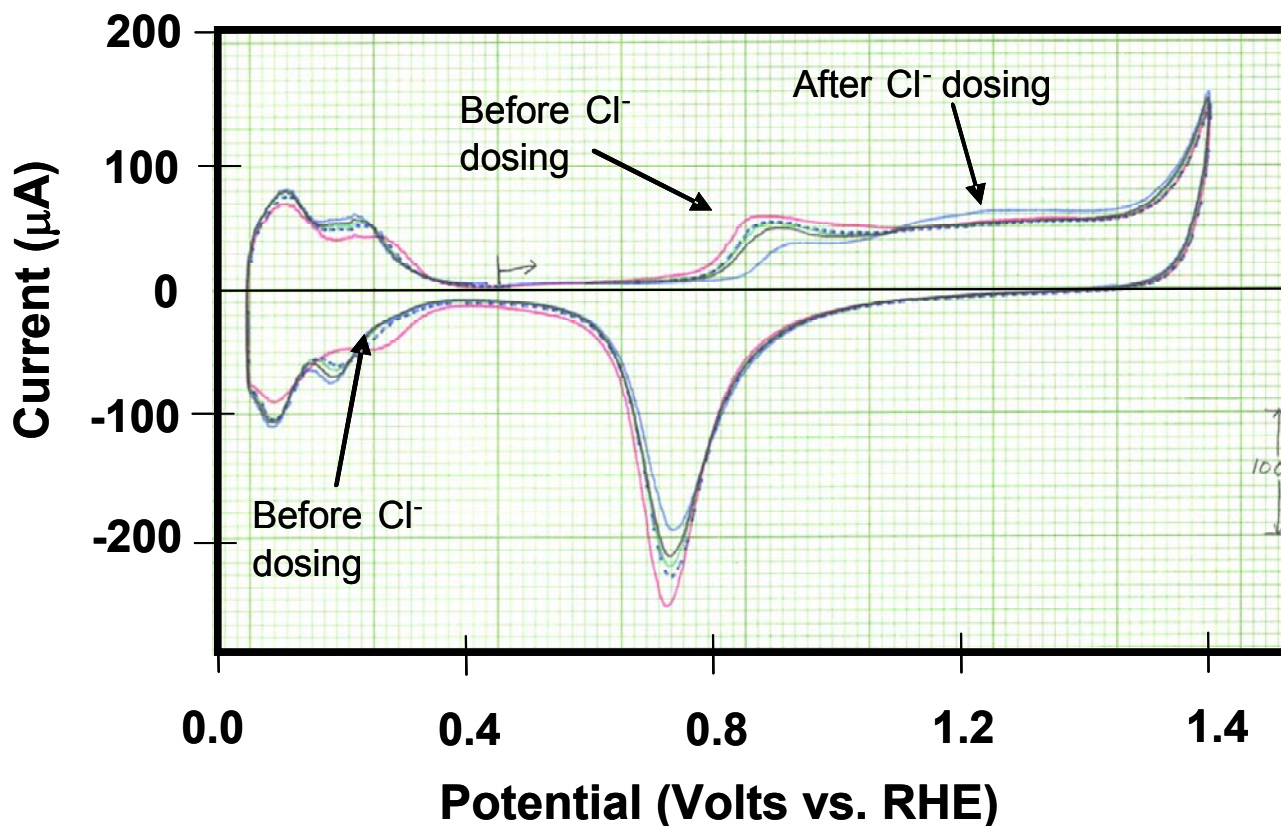
Chloride blocks the adsorption of hydrogen and the formation of oxide on Pt_3Co

■ 60°C, 50 mV/s, 900 rpm, 0.5 M $HClO_4$, steady-state voltammograms



Multiple potential cycles are necessary to remove adsorbed chloride from Pt

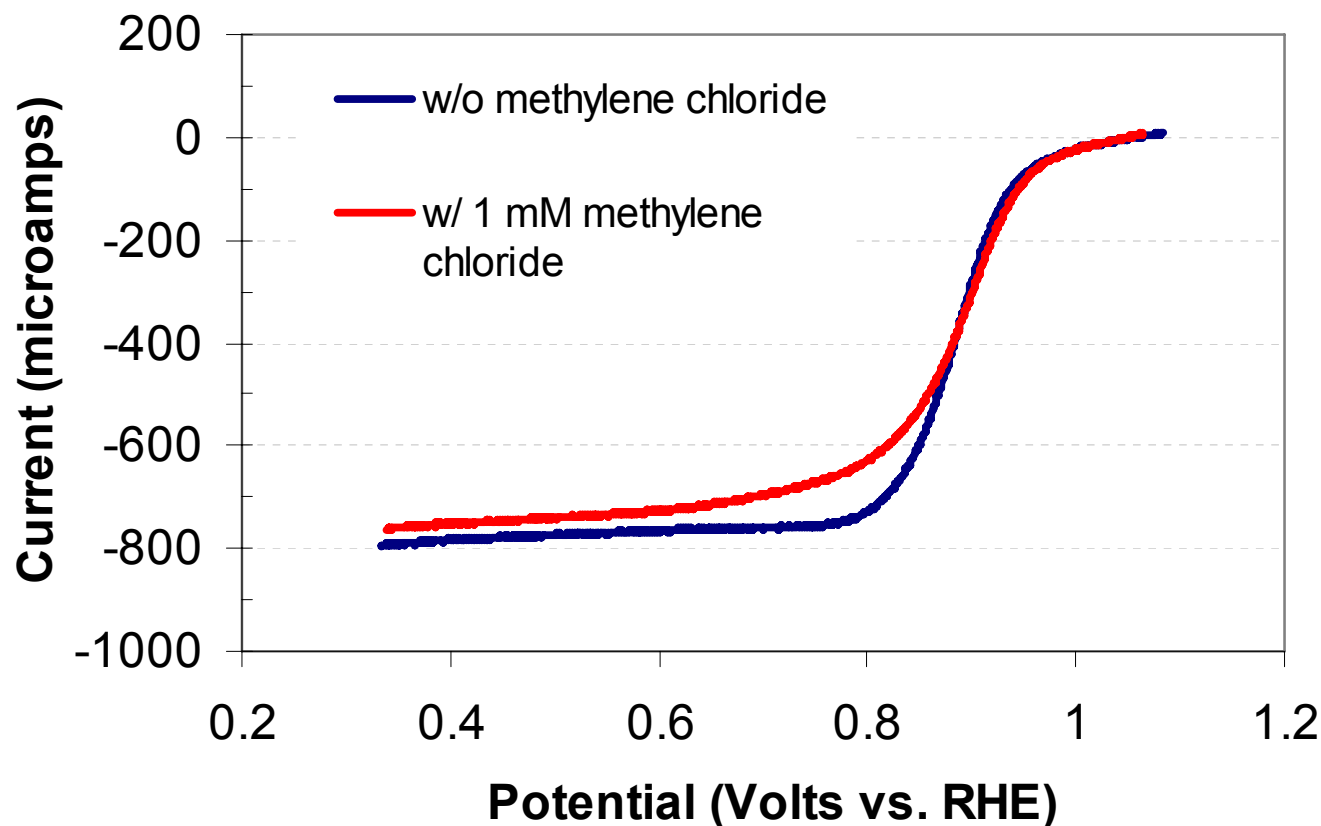
- Cyclic voltammogram of Pt wire does not return to pre-chloride trace after four potential cycles between 0.05 and 1.4 V



- Chloride dosed from 1 mM HCl onto polycrystalline Pt wire at 0.46 V, scans taken in clean 1 M HClO_4 at 50 mV/s, stagnant solution

Methylene chloride impurity has minimal effect on ORR on Pt_3Co/C

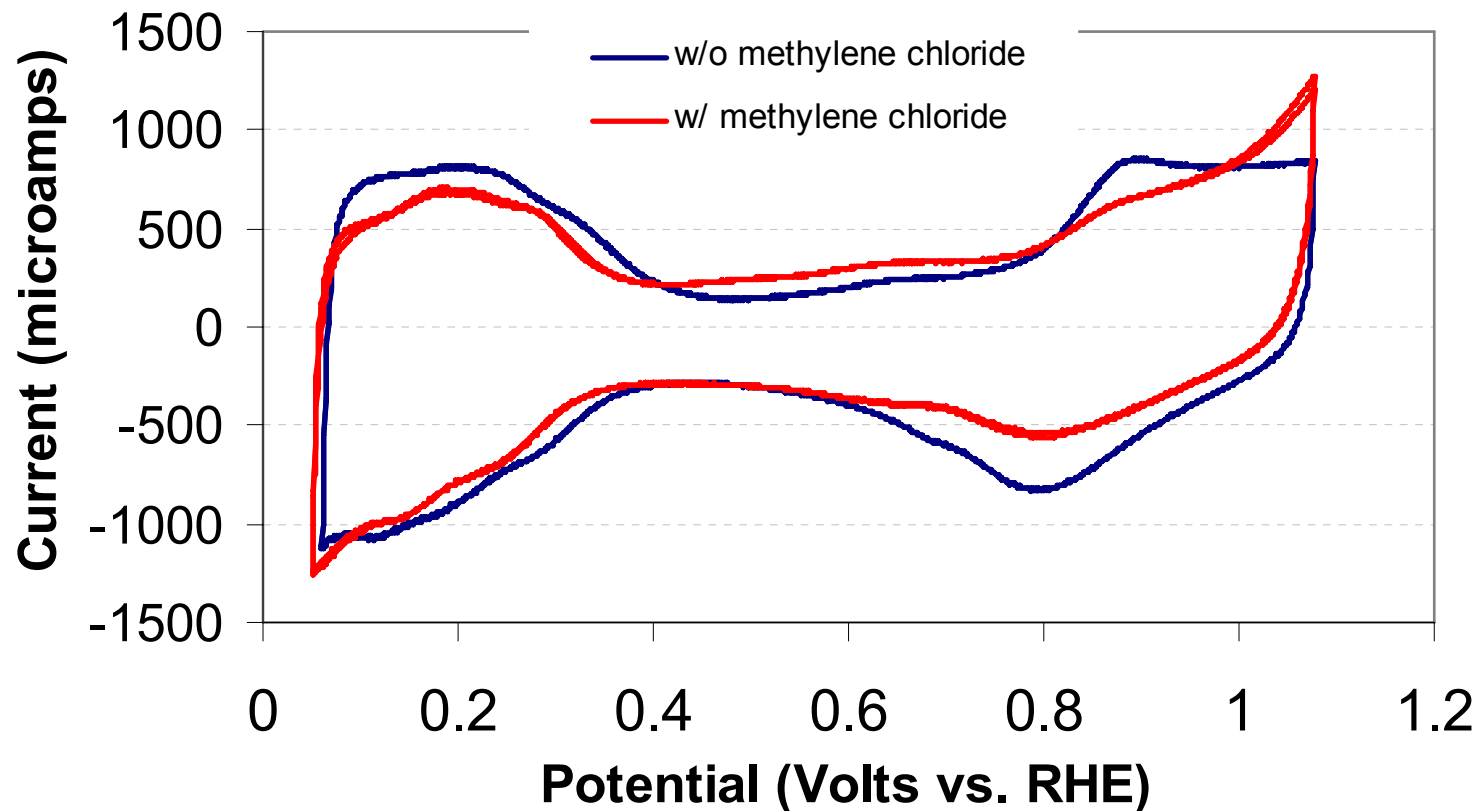
- Kinetic current of ORR at 0.9 V is unaffected by 1 mM methylene chloride



- Catalyst-coated glassy carbon rotating-disk electrode, 0.5 M $HClO_4$, 60°C, 1600 rpm, 5 mV/s, traces not corrected for double layer charging

Methylene chloride slightly inhibits oxide formation on Pt_3Co/C

■ 50 mV/s, 900 rpm, deaerated 0.5 M $HClO_4$, steady-state voltammograms



Future Work

■ Remainder of FY'06:

- Effect of temperature and concentration of chloride, chloride-containing organic, C₇ aliphatic, C₇ aromatic on
 - *Oxygen reduction reaction kinetics and selectivity*
 - *Hydrogen oxidation reaction kinetics*
 - *Electrode layer conductivity*
 - *Membrane conductivity*
- Incorporate effect of chloride into Argonne's stack performance model

Summary

- The potential for oxygen reduction on $\text{Pt}_3\text{Co}/\text{C}$ is shifted by >100 mV in the presence of 1 mM chloride, at 60°C
- Multiple oxidation-reduction cycles are necessary to remove adsorbed chloride from platinum
- Kinetic current at 0.9 V of oxygen reduction on $\text{Pt}_3\text{Co}/\text{C}$ is unaffected by 1 mM methylene chloride, at 60°C
- A stack performance model is being developed and validated with measured stack performance data