DOE Hydrogen Program

Effects of Fuel and Air Impurities on PEM Fuel Cell Performance

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5/16/2007

FCP#17

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Overview

Timeline

- Project start -FY07
- Status- ongoing

Budget

- Funding in FY06: $800 K
- Funding for FY07: $1200 K
- Non-cost shared

Barriers

- The cost of fuel cells limits their use
  - Fuel and air impurity removal systems add cost
  - Higher Pt loading required to maintain performance in the presence of impurities increases cost
- Durability may decrease in the presence of impurities
- Fuel cell performance is decreased by impurity effects

Partners

- USFCC
- ASME
- ASTM
- SAE
- ISO
- FCTES^{QA}
- OEMs
- Xradia Corp

Objectives

Overall Objective: Contribute to the understanding of the effects of fuel and air impurities on fuel cell performance

Specific Objectives:

- Test fuel cell performance under simulated multi-component hydrogen impurity gas mixtures

- Investigate effects of impurities on catalysts and other FC components

- Understand the effect of catalyst loadings on impurity tolerance

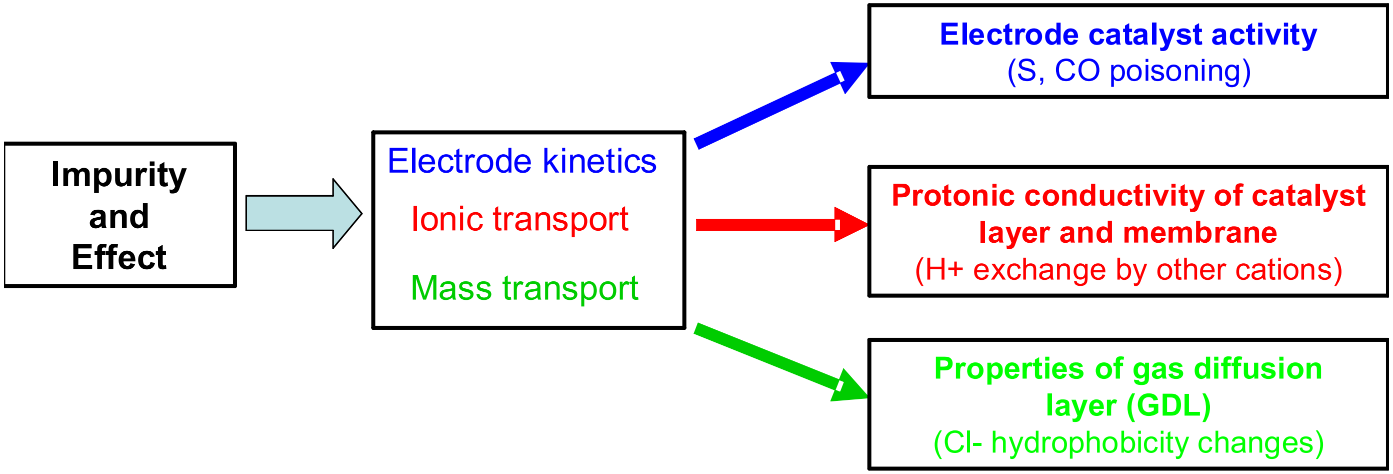
- Investigate the impacts of impurities on catalyst durability

- Develop methods to mitigate negative effects of impurities

- Develop models of fuel cell-impurity interactions

- Collaboration with USFCC, Fuel Cell Tech Team, Industry and other National Laboratories to foster a better understanding of impurity effects

Approach



Impurity and Effect

Electrode kinetics

Ionic transport

Mass transport

Electrode catalyst activity
(S, CO poisoning)

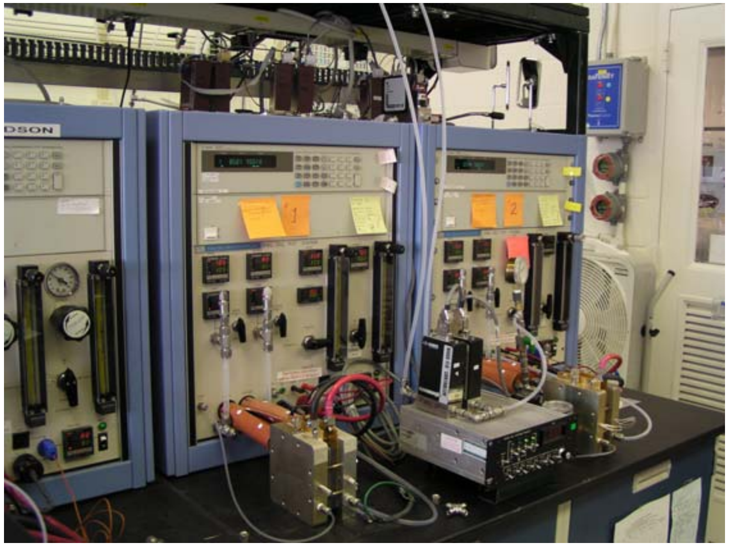
Protonic conductivity of catalyst layer and membrane
(H+ exchange by other cations)

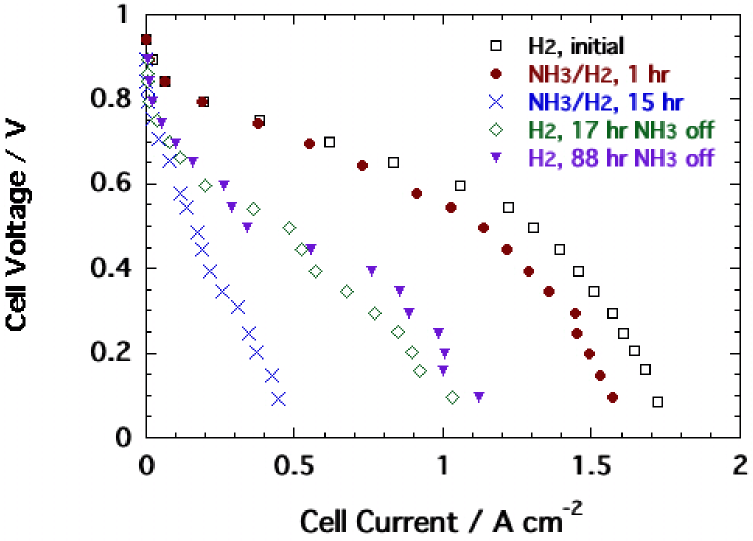
Properties of gas diffusion layer (GDL)
(Cl- hydrophobicity changes)

- Impurities effect fuel cells in many ways:
  - Electrocatalyst poisoning e.g. H_2S, CO and SO_2 adsorption onto Pt catalysts
  - Reduce ionomer conductivity- Na^+, Ca^{++}, NH_3
  - GDLs become hydrophilic and flood at high current densities

Approach

- Fabricate and operate fuel cells under controlled impurity gases
  - Multi-gas mixing manifolds and FC test stations
  - Pre-blend impurity gases
  - Measure performance
  - Steady state and *Drive cycle* conditions
    - Understand degradation mechanisms
    - Study mitigation approaches
- Develop analytical tools for studies
  - Electroanalytical methods
  - *In situ* diagnostics
  - Sub PPM gas analysis
- Analyze and model data



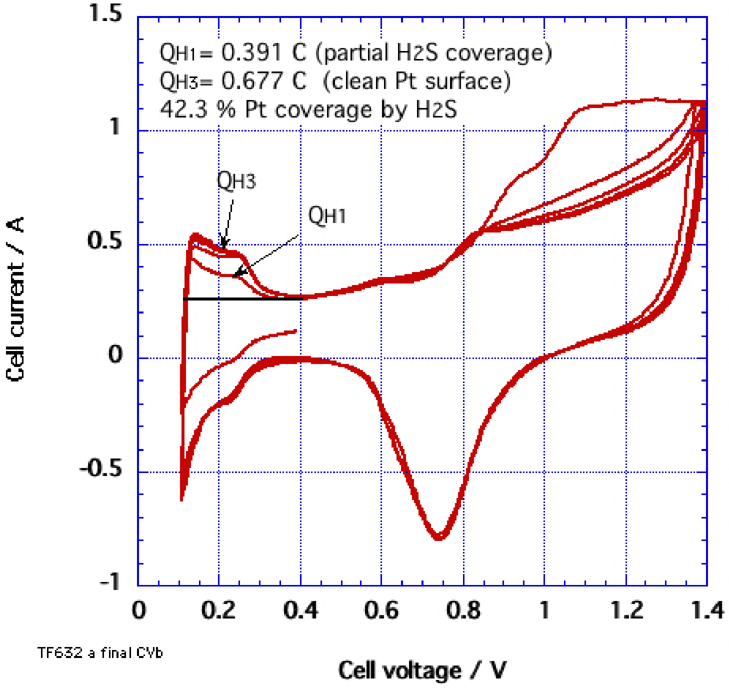


Technical Accomplishments/ Progress/Results

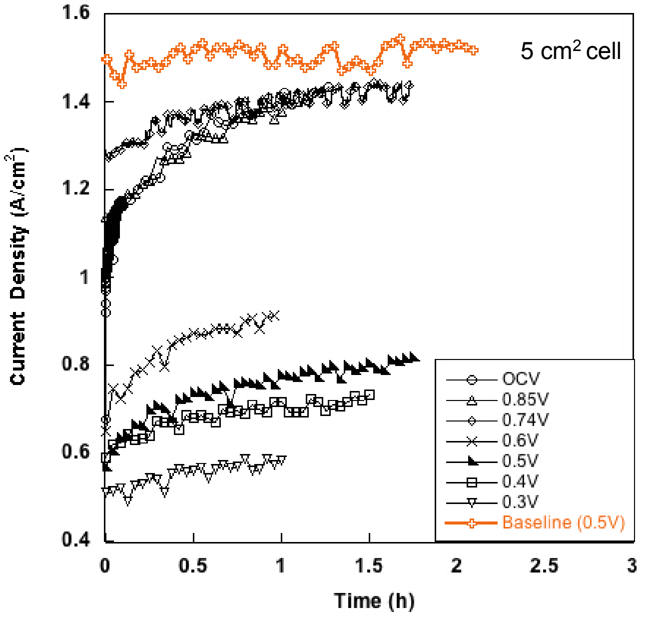
- Hydrogen impurity mixture used to characterize fuel cell performance for different anode loadings
  - 2007 and 2010 anode Pt loadings characterized. Milestone accomplished
  - *Little effect of Pt catalyst loading on impurity performance degradation*
- Experimental evidence for hydrogen sulfide crossover from anode to cathode as a *cathode* poisoning mechanism
- DOE drive cycle durability in the presence of impurities measurements commenced
- New high resolution X-ray CT (Computed Tomography) method develop for studying impurity impacts on durability
- Particulate effects studies commenced
- Sulfur adsorption on Pt electrode modeling commenced
- Cation impurity modeling commenced with Case Western Reserve University
- Wet electrochemical cell experiments validate fuel cell results

H_2S Effects in Fuel Cells

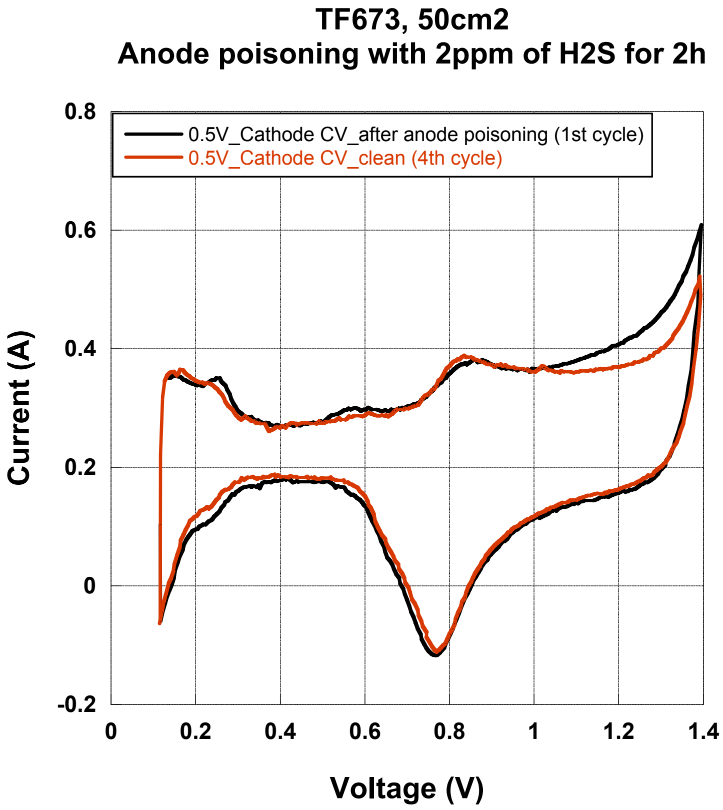
- Past results show relative large performance losses due to ppb quantities of H_2S introduced from hydrogen fuel.
  - Stripping voltammetry indicated partial coverage of the anode~ 40% of the sites for 10 ppb exposure 1000 hrs
  - Not enough sites blocked to account for >10% performance drop
  - Poisoning the cells at low operating voltages resulted in much more performance loss than at high cell voltages
- Is *impurity crossover* to cathode also responsible for performance loss?
  - Cathode electrocatalyst kinetics are much more sensitive to site blocking than anodes due to lower reaction rates.
- Experiments designed to study the possibility of hydrogen sulfide crossover effects

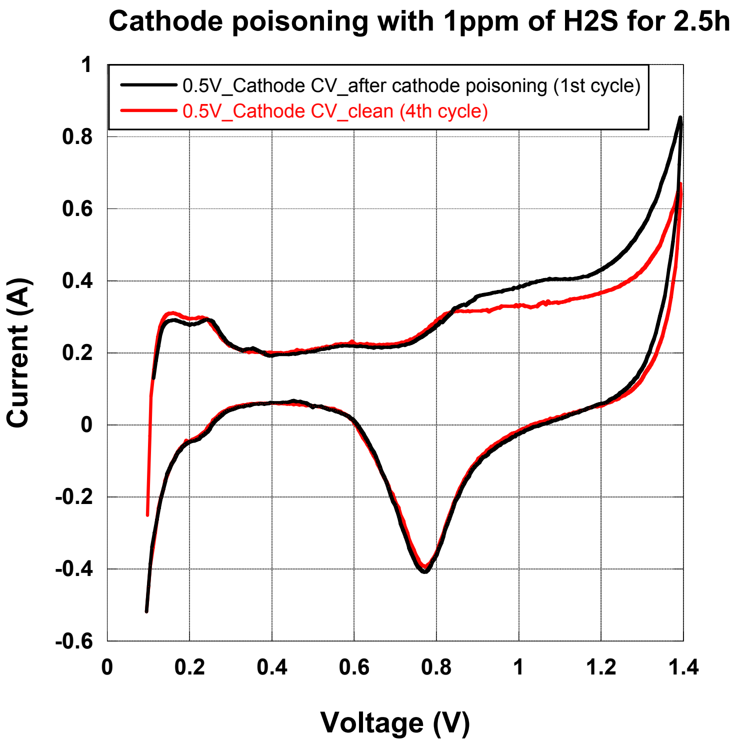


Cell performance recovery (at 0.5 V) after anode exposure to H_2S at different voltages



H_2S Crossover Studies

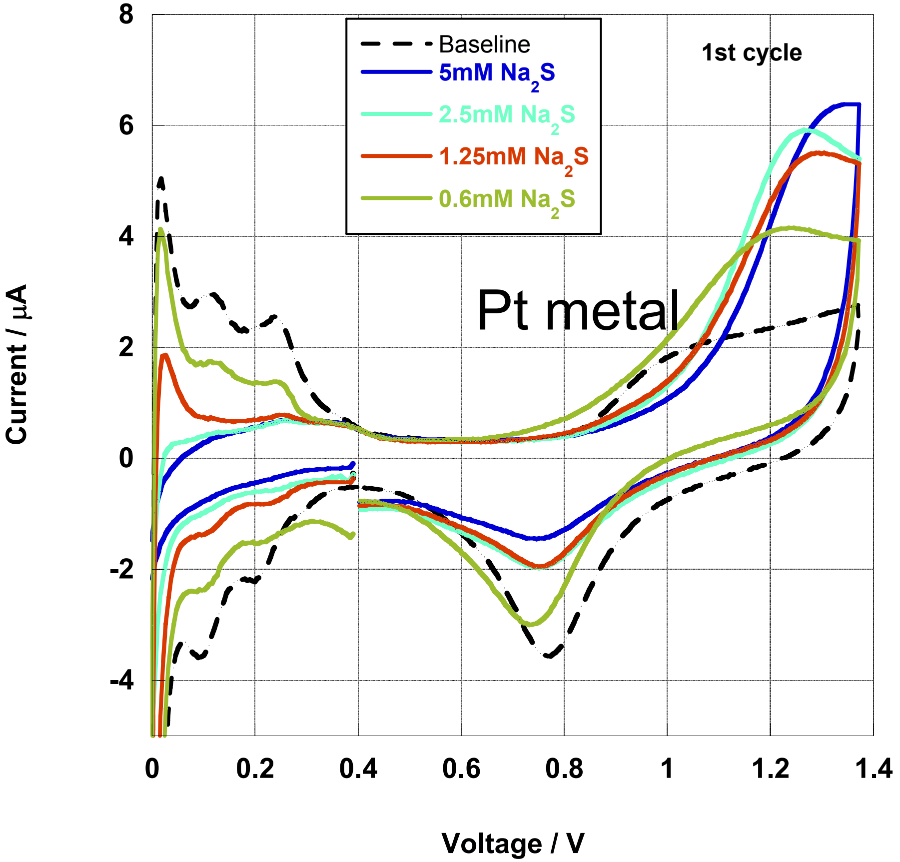


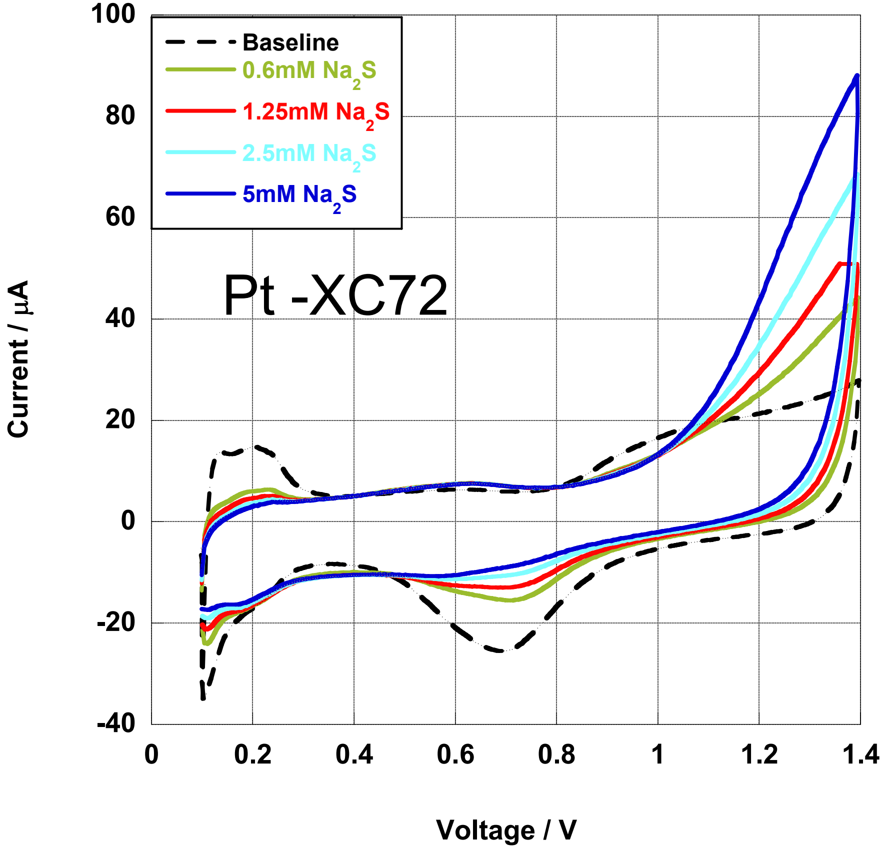


- H_2 /H_2S mixture was passed through the anode. The cathode was purged and then the CV was run
- CV indicates a strong adsorbate
  - Not stripped until high potentials achieved

- Air/ H_2S mixture was passed through the cathode. The cathode was purged and then the CV was run
- CV indicates a similar strong adsorbate

Impurity Effects: Electrochemical Cell Studies





- Pt anodes, Pt metal and Pt 20%- XC 72 were pre-poisoned with sodium sulfide, then placed in sulfuric acid cells
- Severe reduction in hydrogen adsorption sites by S poisoning for both cases
- Note the more pronounced poisoning of the supported fuel cell catalyst than the bulk Pt metal catalyst
  - *Demonstrates the importance of studying the behavior of the actual carbon supported fuel cell catalyst*

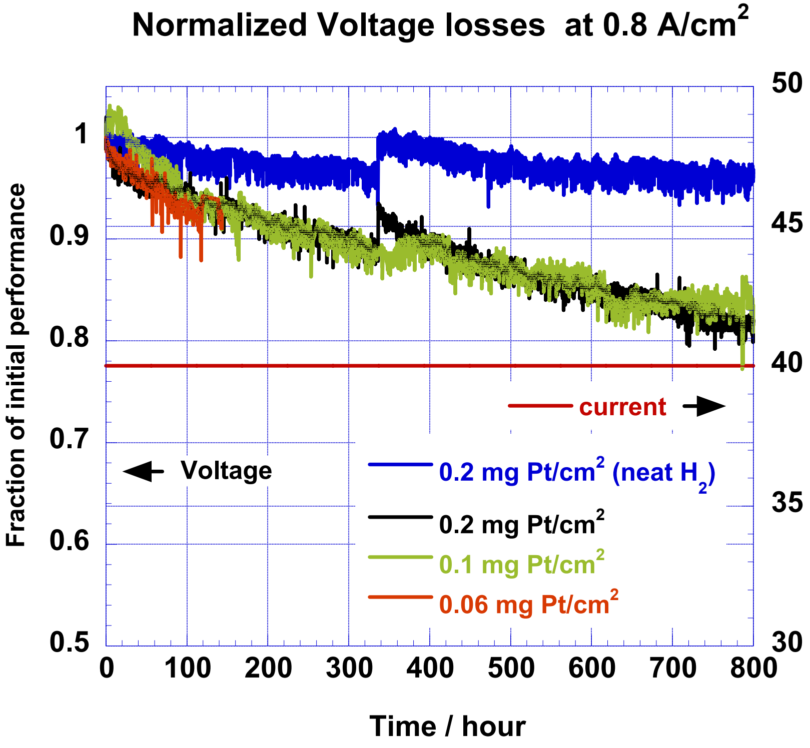
Hydrogen Impurity Mixture

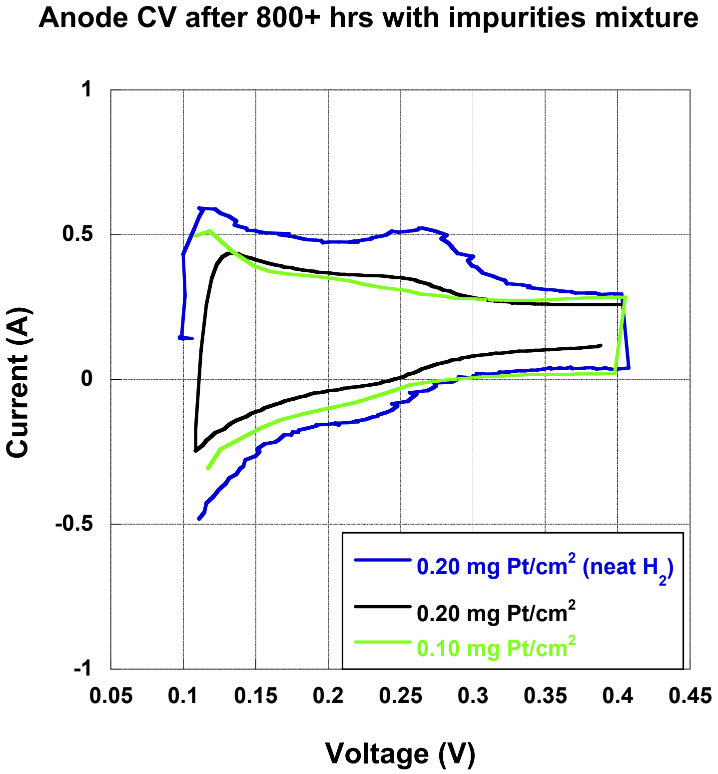
FreedomCAR Fuel Cell Tech Team proposed hydrogen impurity spec.

Component	*Level*	*LANL Test*
Hydrogen	> 99.9	95-99 *
Sulfur (as H_2S)	10 ppb	10 ppb
CO	0.1 ppm	0.1 ppm
CO_2	5 ppm	5 ppm
NH_3	1 ppm	1 ppm
NMHC	100 ppm	50 ppm ethylene
Particulates	Conform to ISO 14687	not included in first test

**** Includes dilution due to inert gas in stock mixtures***

Impurity Effects: Low Pt loadings





- *Similar losses for all Pt loadings*
- Impurities caused 100 mV performance loss after 800 hrs
- H_2S partial poisoning detected at the anode by CV
- Membrane conductivity also affected as indicated by increase of HFR

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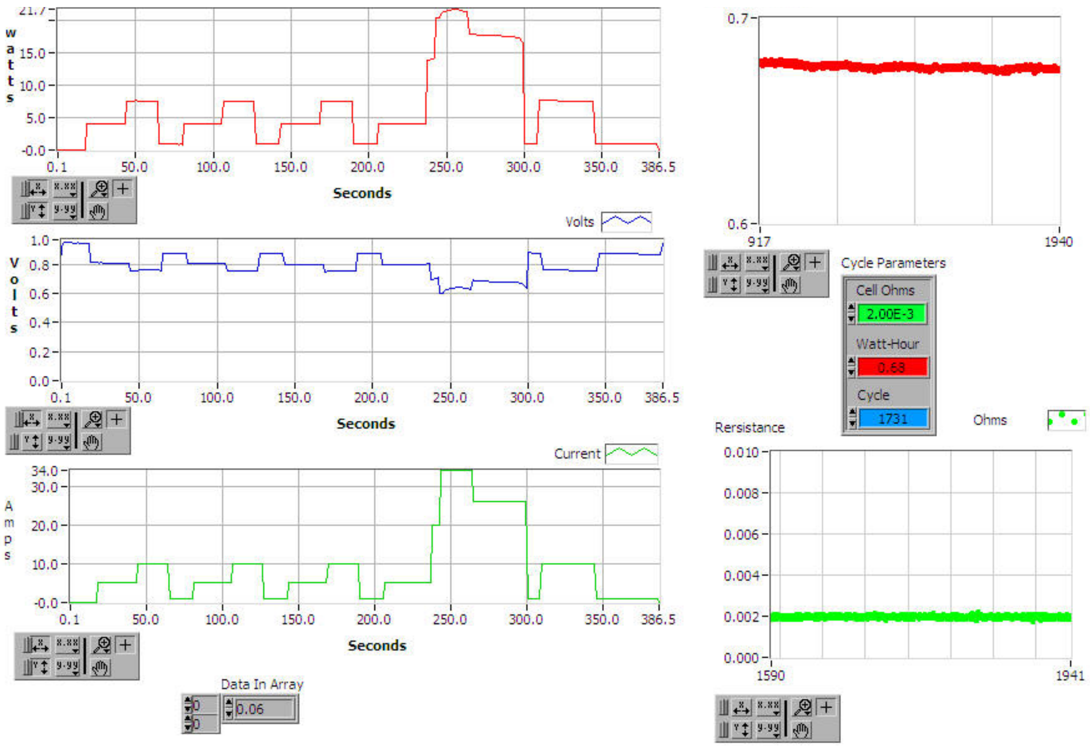
Impurity Impacts On Durability

- Impurities may impact durability of PEMFC fuel cells
- Electrocatalyst growth may be accelerated
- Ionomer lifetimes may decrease
- GDL properties may change faster in the presence of impurities
- DOE drive cycles with and without start and stop used to test durability under non steady-state conditions



Cycle Parameters

Cell Ohms 2.00E-3

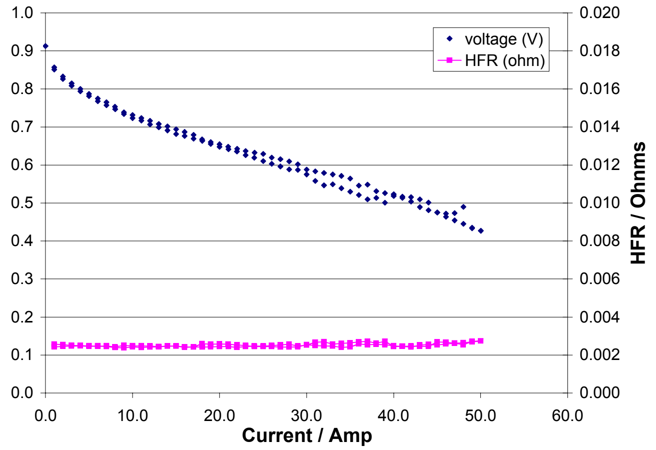
Watt-Hour 0.68

Cycle 1731

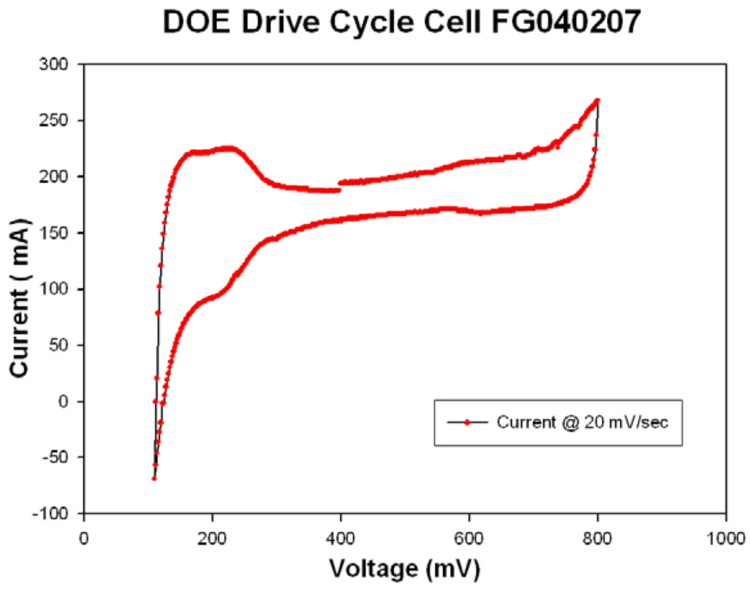
Data In Array 0 0 0.06

Impurity Effects Durability Tests Commenced

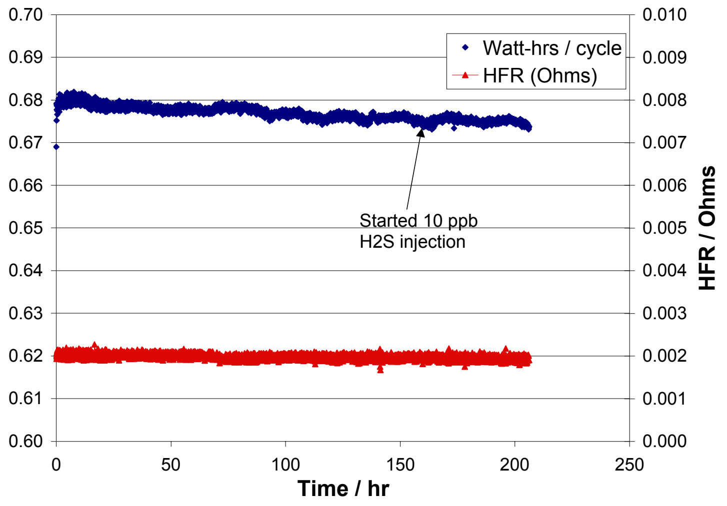
- Drive Cycle testing started
- 10 ppb H_2S used as impurity for first tests
- Baseline degradation rate established



•Initial polarization curve for drive-cycle test

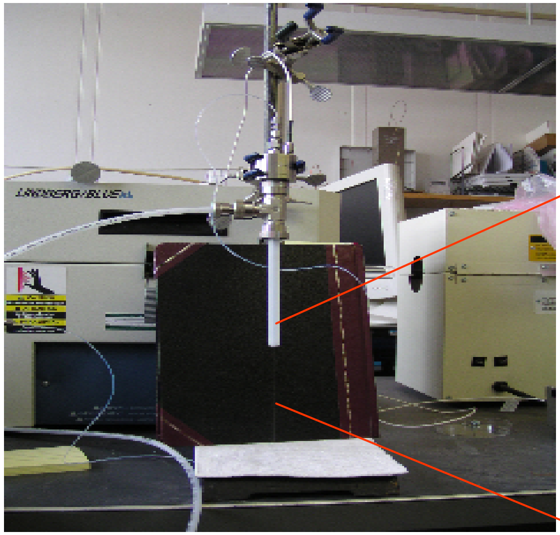


•Initial anode CV for drive-cycle test



•Baseline established and test started

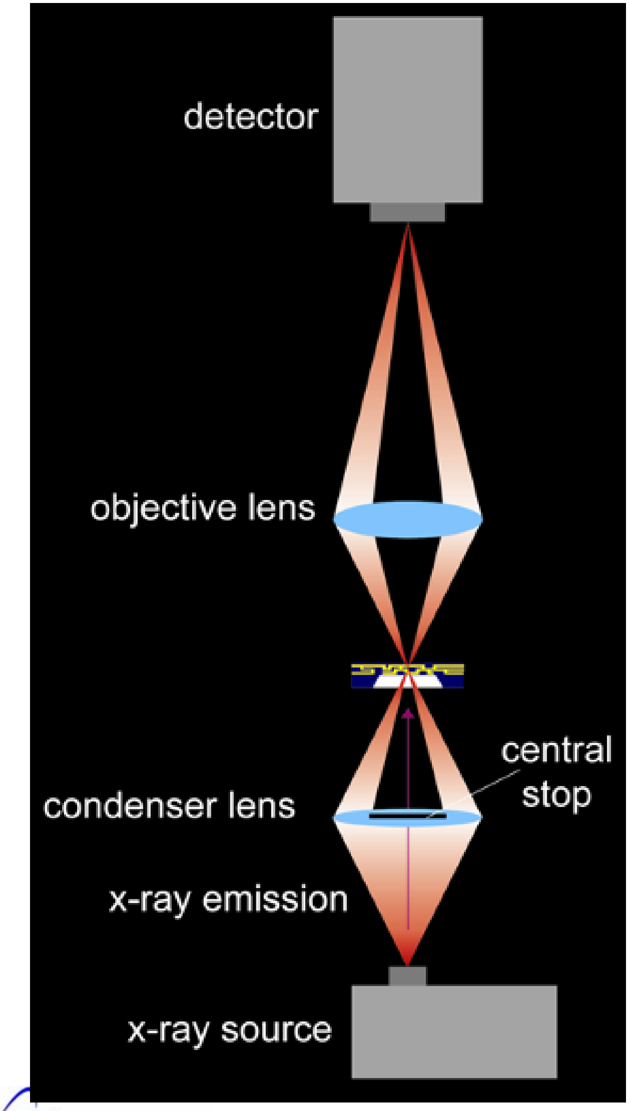
Cathode impurities: Particulates



To date we have:

- -Successfully produced particulates under 10 microns
- -Modified existing fuel cell hardware to inject particulate matter into a pressurized anode feed

XRadia nanoXCT 8-50Z Laboratory System For Imaging FC MEAs

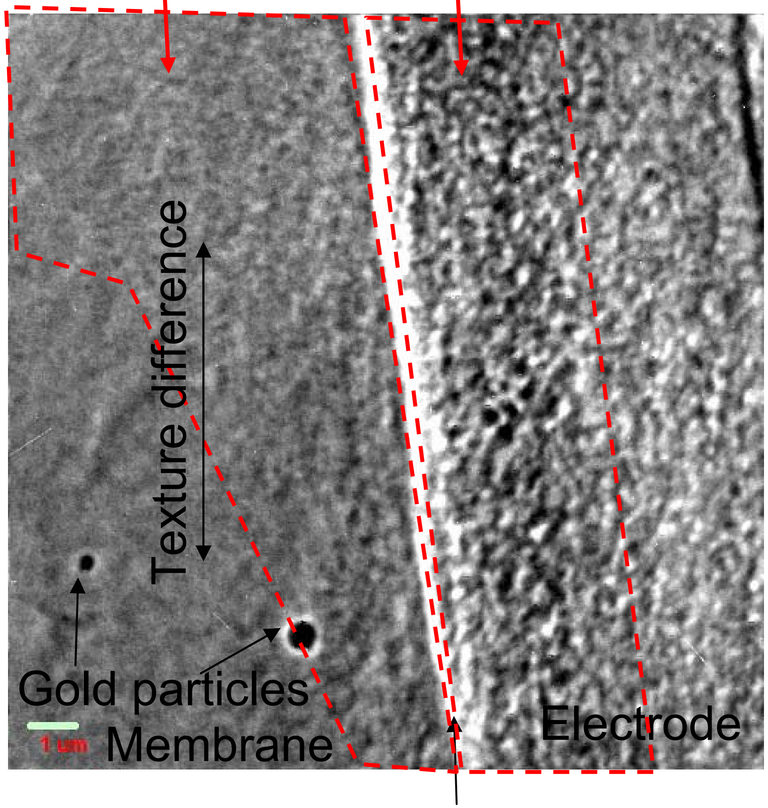


- 8 keV Cu target x-ray source
- 3-D resolution: 50 x 50 x 80 nm
- Automated x-ray tomography
- Negative Zernike phase-contrast for imaging low contrast samples
- Samples run in air

High-resolution X-ray Imaging for Impurity-Durability Studies

High concentration but **fine** Pt particles

This region has high concentration **coarse (large)** Pt particles



Interface

- Xradia Corp-LANL collaboration
  - Minimal sample prep needed for CT scans
- FC membrane went through DOE Drive cycle test until failure
- Large Pt particles (a few hundred of nanometers) were formed in the electrode.
- Smaller Pt particles were found in the membrane near the membrane-electrode interface
- Non-uniform distribution in the membrane
- Their size appeared larger near interface than further into the membrane
- Tool will be used to characterize impurity-durability samples

Impurity Effects Modeling- Electrodes

- Surface/speciation model in development
  - Modification of USGS Parkhurst PHREEQE codes
    - Predominate sulfur species are H_2S, *S-Pt, PtS,* PtS_2 and HSO_4-
- Predicts *decreased* stability of Pt nanoparticles to S chemisorption as compared to bulk Pt
- Predicts Pt sulfur coverage at -0.15 volts with increasing coverage as anode potential is raised for 1 ppb H_2S
- Predicts that the oxidation cleaning mechanism is inhibited by kinetics not thermodynamics

$$S_\theta - Pt + 4H_2O = HSO_4- + Pt + 7H+ + 6e-$$

- Surface speciation model will be coupled to fuel cell electro-kinetics model

Future Work

- Continued contaminant crossover studies:
- Fundamental electrokinetic measurements of poisoned electrodes
- Lower cathode loading impurity studies
- Impurity effects on durability studies
  - humidity dependence
- Refine and validation of electrode impurity modeling efforts
- Salt impurity modeling commencing
- Development of impurity tolerant electrode materials
- Future key milestones
  - Impurity effects on durability studies

Summary

- **Relevance**
  - Trace impurities do impact fuel cell performance and degradation and cost
    - **Approach**
      - Expose fuel cells to common fuel and air impurities and measure the impact on performance and durability

- **Results**
  - Decreasing the fuel cell anode loading is not having a great impact on the performance degradation behavior of PEMFCs.
  - Sulfur species adsorb very strongly on Pt for a wide range of potentials and concentrations
  - Crossover effects of impurities need to be considered. Hydrogen sulfide crossover from anode to cathode may be occurring
  - Oxygen reduction at the cathodes is easily affected by impurities
  - Carbon particulates will negatively impact GDL properties
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