# Technical Assistance to Developers

*T. Rockward, F. Garzon, R. Mukundan, D. Spernjak, and R. L. Borup*
*Los Alamos National Laboratory, Los Alamos, NM 87545*

*May 15, 2012*

Project ID: FC052

# Overview

- **Timeline**
  - Start: 10/03
  - End: ongoing
  - % complete: N/A
- **Budget**
  - FY11 funding: $570K
  - Proposed FY12 funding: $450K
  - DOE share: 100%
  - Cost share: N/A
- **Barriers**
  - Sharing technical assistance to developers
  - A. Durability
  - B. Cost
  - C. Electrode performance
- **Partners/Collaborators**
  - See list for FY12

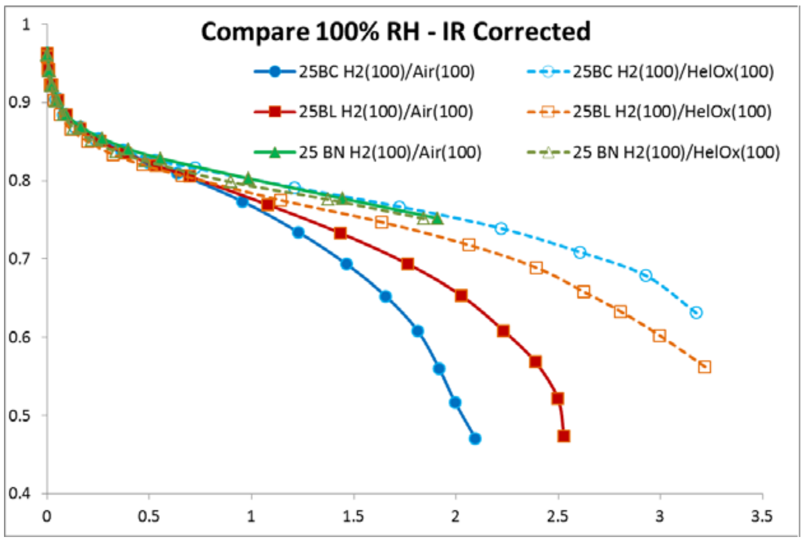
# Approach for Technical Assistance

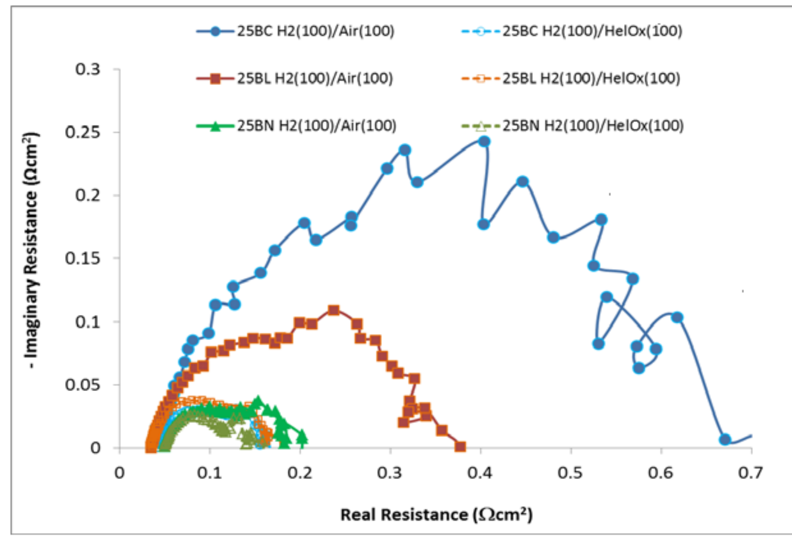
This task supports Los Alamos technical assistance to fuel-cell component and system developers as directed by the DOE. This task includes testing of materials and participation in the further development and validation of single cell test protocols. This task also covers technical assistance to Working Group 12, the U.S. Council for Automotive Research (USCAR) and the USCAR/DOE *Driving Research and Innovation for Vehicle efficiency and Energy sustainability* (U.S. DRIVE) Fuel Cell Technology Team. This assistance includes making technical experts available to DOE and the Fuel Cell Tech Team as questions arise, focused single cell testing to support the development of targets and test protocols, and regular participation in working group and review meetings.
**Assistance available by Request and DOE Approval.**
**LANL capabilities handout available.**

# Evaluation of Novel MPL Materials

## Cathode GDL Study: Vary MPLs; same carbon-fiber substrate

50 $cm^2$ cell, quad serpentine
Cathode loading: (0.4 $mg/cm^2$)
Anode loading: (0.2 $mg/cm^2$)
80°C, 100% RH, $H_2$/Air:1.2/2 stoich and 28.4 psi backpressure




**Summary:**

25BC = standard MPL (carbon+PTFE+binder)

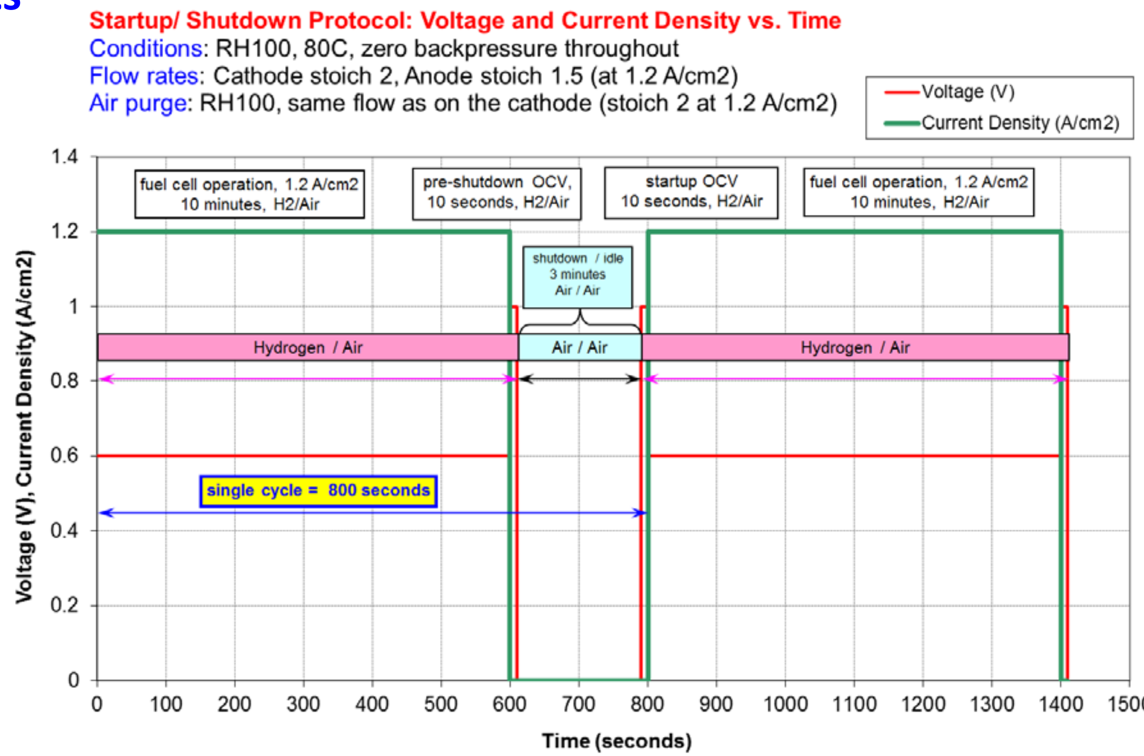
25BL = standard MPL with hydrophilic treatment: Mass-transport improvement; Durability issues

25BN = standard MPL with C-nanotubes: **Mass-transport improvement; Improved durability**

# Development of Startup/ Shutdown Protocol

In Collaboration with Ballard Power, Greg James

## Accomplishments



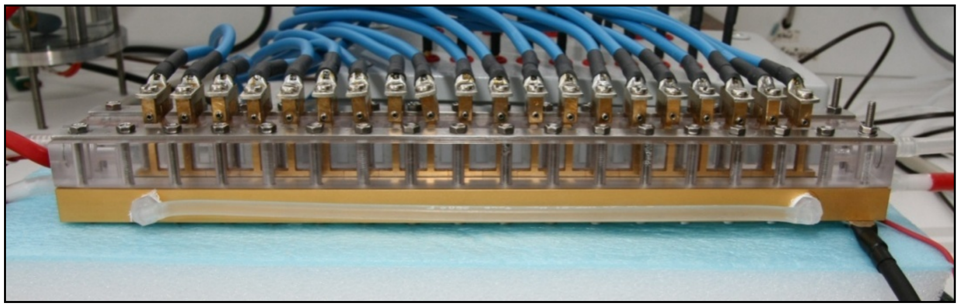

| Step Name | Duration (seconds) | Total time (seconds) | Voltage (V) | Load | Cathode gas | Cathode flow rate | Anode gas | Anode flow rate | RH | Cell T (deg C) | Current Density (A/cm²) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 0 | 0 | Off | | | | | 100 | 80 | 0 |
| FC operation | 600 | 600 | 0.6 | On | Air | stoich 2 (at 1 A/cm2) | Hydrogen | stoich 1.2 | 100 | 80 | 1.2 |
| Pre-shutdown | 10 | 610 | 1 | Off | Air | 0 | Hydrogen | stoich 1.2 | 100 | 80 | 0 |
| Shutdown/ Idle | 180 | 790 | 0 | Off | Air | stoich 2 (at 1 A/cm2) | Air | stoich 2 (at 1 A/cm2) | 100 | 80 | 0 |
| Startup | 10 | 800 | 1 | Off | Air | stoich 2 (at 1 A/cm2) | Hydrogen | stoich 1.2 | 100 | 80 | 0 |
| FC operation | 600 | 1400 | 0.6 | On | Air | stoich 2 (at 1 A/cm2) | Hydrogen | stoich 1.2 | 100 | 80 | 1.2 |
| Pre-shutdown | 10 | 1410 | 1 | Off | Air | stoich 2 (at 1 A/cm2) | Hydrogen | stoich 1.2 | 100 | 80 | 0 |

**Accomplishments**

# Nancy-Université: Start-up/Shut-down Segmented Cell Measurements

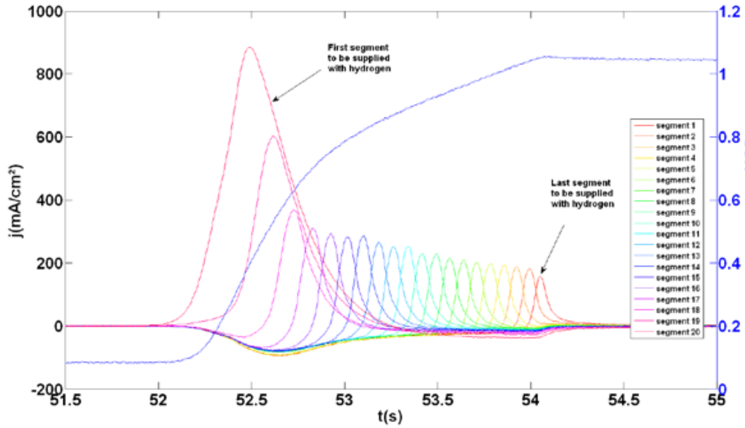
**LEMTA, Nancy University – CNRS – Vandoeuvre lès Nancy, France**

**A. Lamibrac, G. Maranzana, O. Lottin, J. Dillet, J. Mainka, A. Thomas, S. Didierjean, A. Chenu and C. Moyne**



- Provided Start-up/Shutdown protocol
- Materials for evaluation
- Techniques to measure carbon corrosion in situ

  and compare with measured internal currents




NDIR to measure $CO_2$ in the exhaust.

Residence times: Air < 0.05 s ; $H_2$ < 0.2 s (1 cm x 30 cm cell with 5 straight parallel channels) 100 cycles ~ 22.2 hours

**Summary:**

**Reverse currents observed in Air/Air region of cell during start up**
**Internal currents ~ 100 to 1000 times greater than the corrosion measured via NDIR**
**ECSA loss in various segments correlates with internal current**

# Novel Plate Hydrophobic Treatment Proposed to Promote Water Removal

Flow Channel Wettability Impact on PEM Fuel Cell Performance

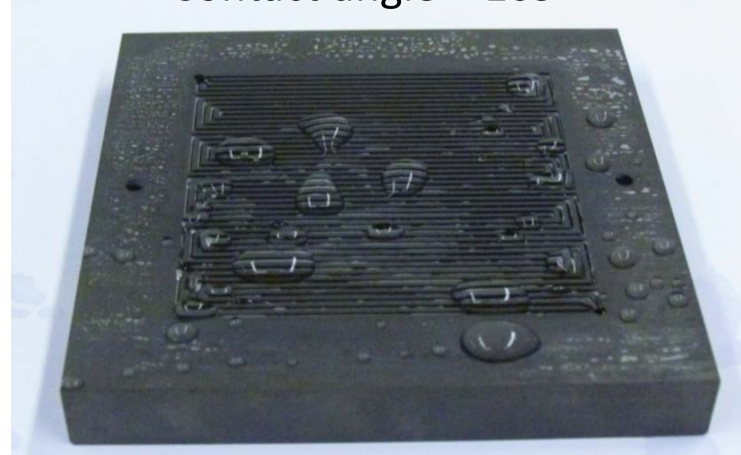
**Vary cathode plate only: plain graphite vs. hydrophobic-treated**

**Plain bipolar plate (graphite).**

Contact angle = 77°

**Treated bipolar plate.**

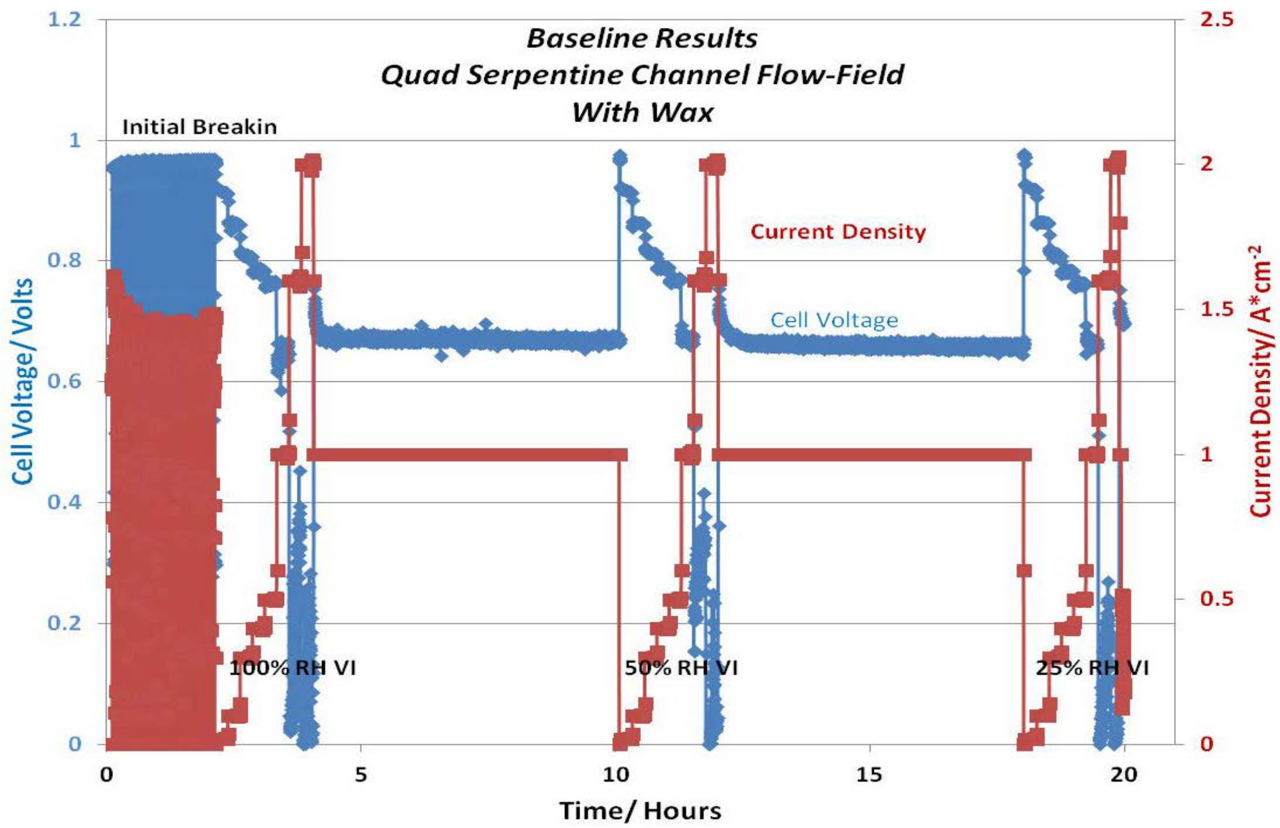
Contact angle = 109°



Hydrophobic treatment was removed from the lands by sanding to minimize contact resistance.

Accomplishments

# Novel Plate Hydrophobic Treatment Test Protocol




Vary the cathode plate only; everything else identical.

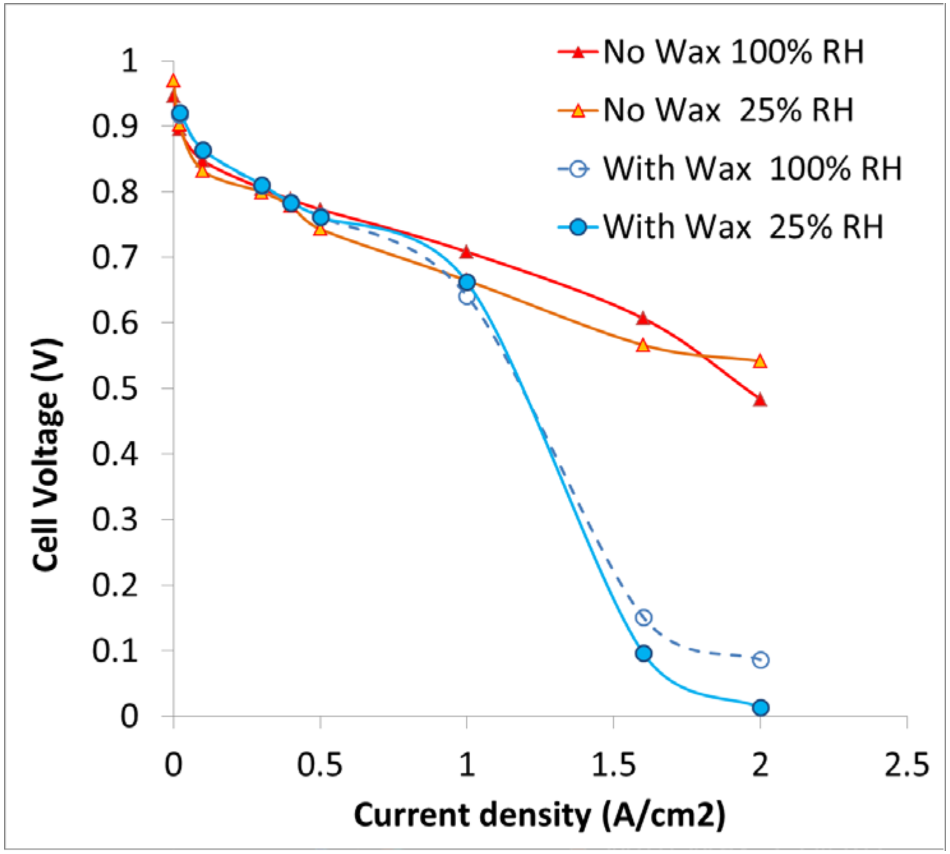
**GDL:** SGL24BC; **MEA:** Gore 0.1/0.4 mg/cm$^2$ Pt, 510 catalyst layer, 710.18 membrane

**Identical protocol: 100, 50, and 25% inlet RH.** Break-in (voltage cycling for 2 hrs), VIR and impedances (0, 0.02, 0.1, 0.2, 0.3, 0.4, 0.5, 1, 1.6, and 2 A/cm$^2$); with 6 hrs steady-state between RH changes.

**Accomplishments**

# Novel Plate Hydrophobic Treatment Polarization Curves

Comparison of plain vs. hydrophobic treated bipolar plates at 100 and 25% RH




**Summary:**

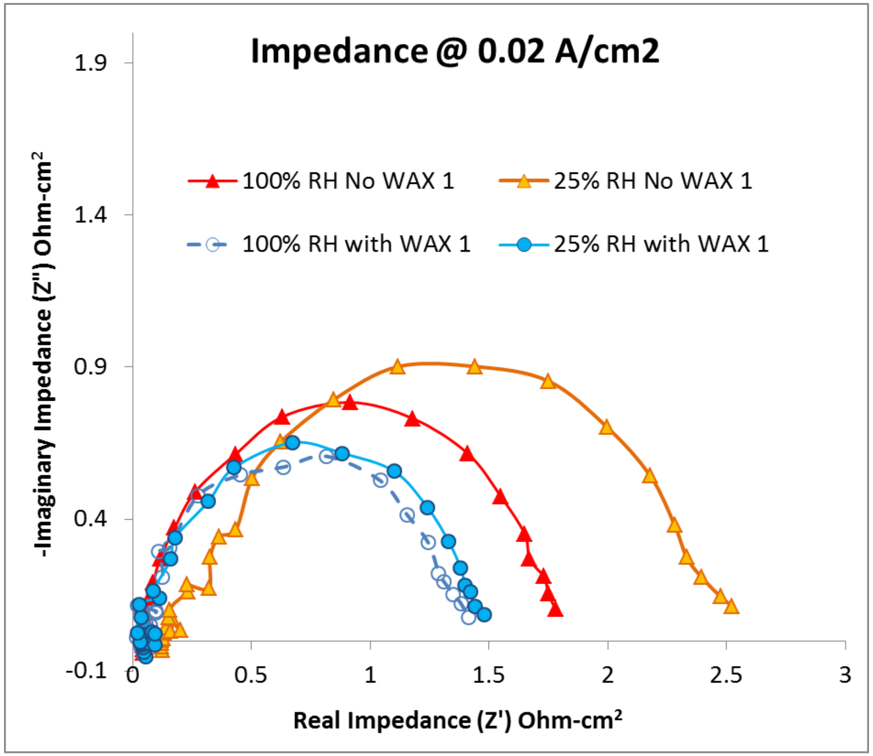
At low currents: hydrophobic plate performs slightly better.

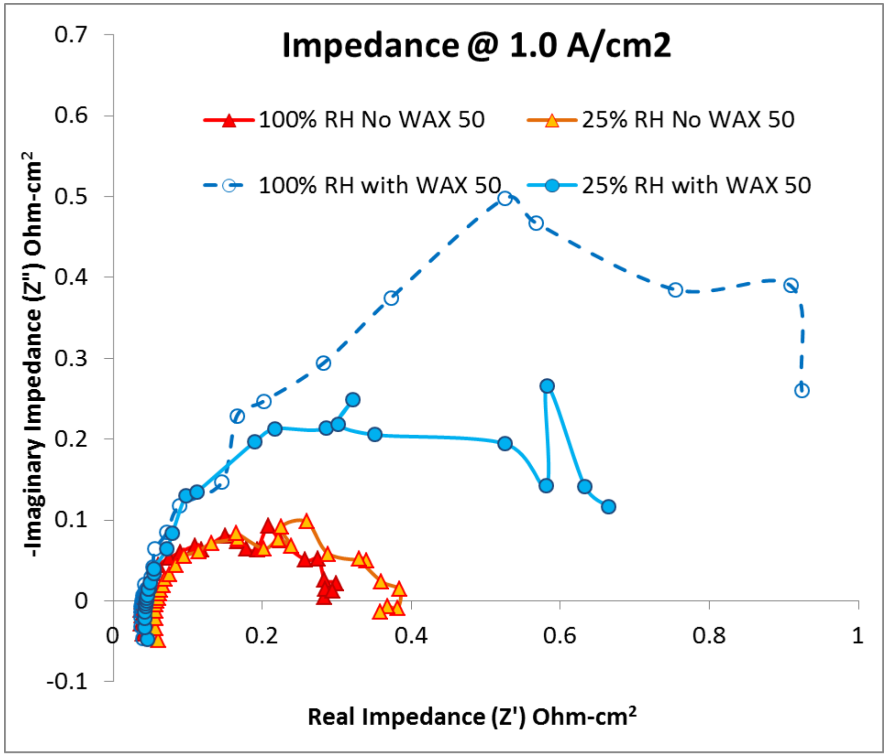
At higher currents: extensive flooding with hydrophobic plate .

To further investigate this phenomenon, impedance spectra in the different regions of the VI were run.

**Accomplishments**

# Novel Plate Hydrophobic Treatment Impedance Spectra



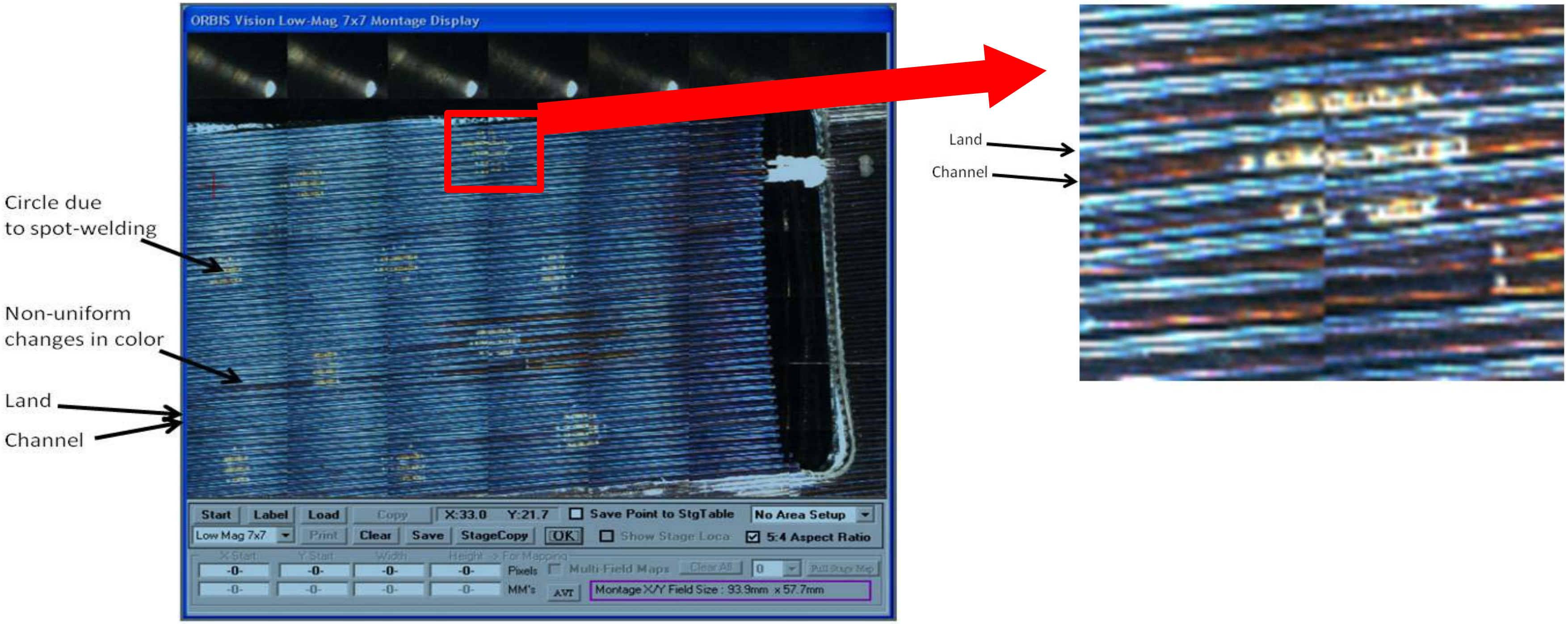




**Summary:**

**At low current densities (0.02 A/cm²) :**
The hydrophobic plate keeps the cathode catalyst layer and MEA more hydrated. This results in improvement in HFR and decreased catalyst sheet resistance. Product water keeps the catalyst layer hydrated especially at drier inlet RH operation.

**At higher current densities (1 A/cm²) :**
The use of a hydrophobic flow field is really detrimental since it leads to increased mass transport resistance due to less efficient water removal from the cathode catalyst layer and GDL.

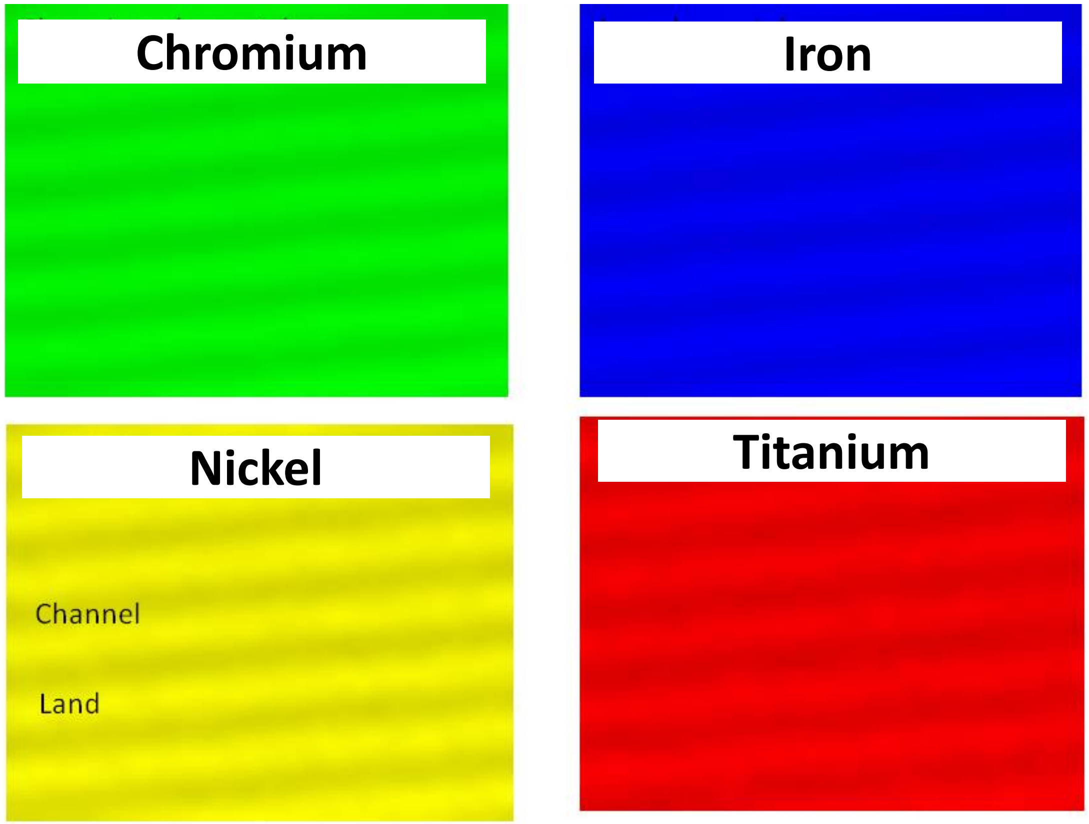
# Imaging of Tested Metal Bi-Polar Plate




- Testing created two areas of discoloration
- Bright circles due to spot-welding
- Darker discoloration in channels sporadically

# Elemental Mapping of Bipolar Plates

## no significant change in composition



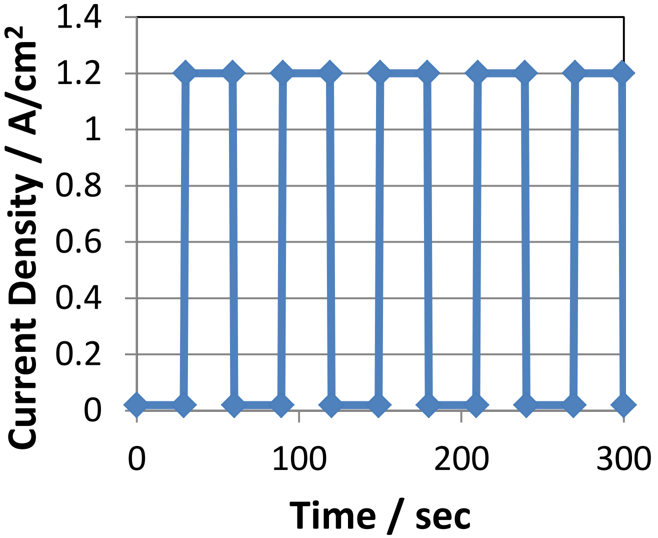

- Chemical analysis suggests little to no corrosion.
- Color changes limited to channels, and do not correspond to loss of metals
- Color differences most likely due to differences in Titanium oxidation state and thickness

Accomplishments

# LANL Fuel Cell Testing of Metal Plates: Drive Cycle Protocol*

## (~ Worst Case Scenario)

- Cell Temperature: 80°C
- **Potential Cycling: 30K cycles total ~500h Operation**
- **Cell current cycled from 1A to 60A for 30 seconds at each point.**
- Anode/Cathode Humid: 83°C dew pt, 85°C inlet
- MEA: Gore 584 / 0.1/0.4 Pt $mg/cm^2$
- GDL: SGL 24BC
- Back pressure: ambient
- $H_2$/Air Flows: 669/1773 sccm

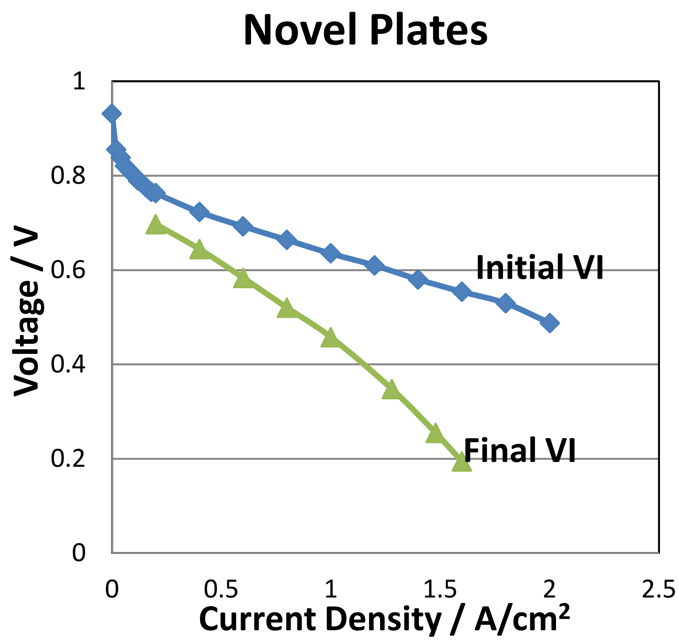


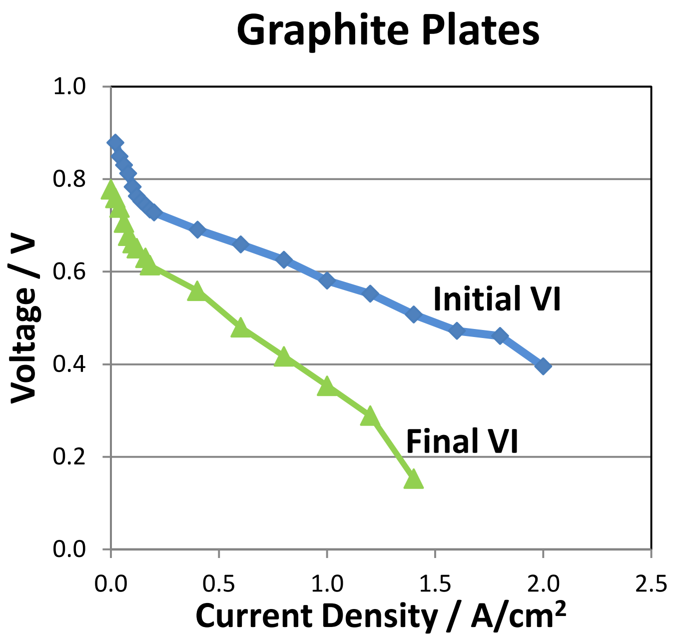

*Cell Component Accelerated Stress Test and Polarization

Curve Protocols for PEM Fuel Cells, Revised December 16, 2012

Accomplishments

# Beginning of Tests Comparison: Initial Performance Similar

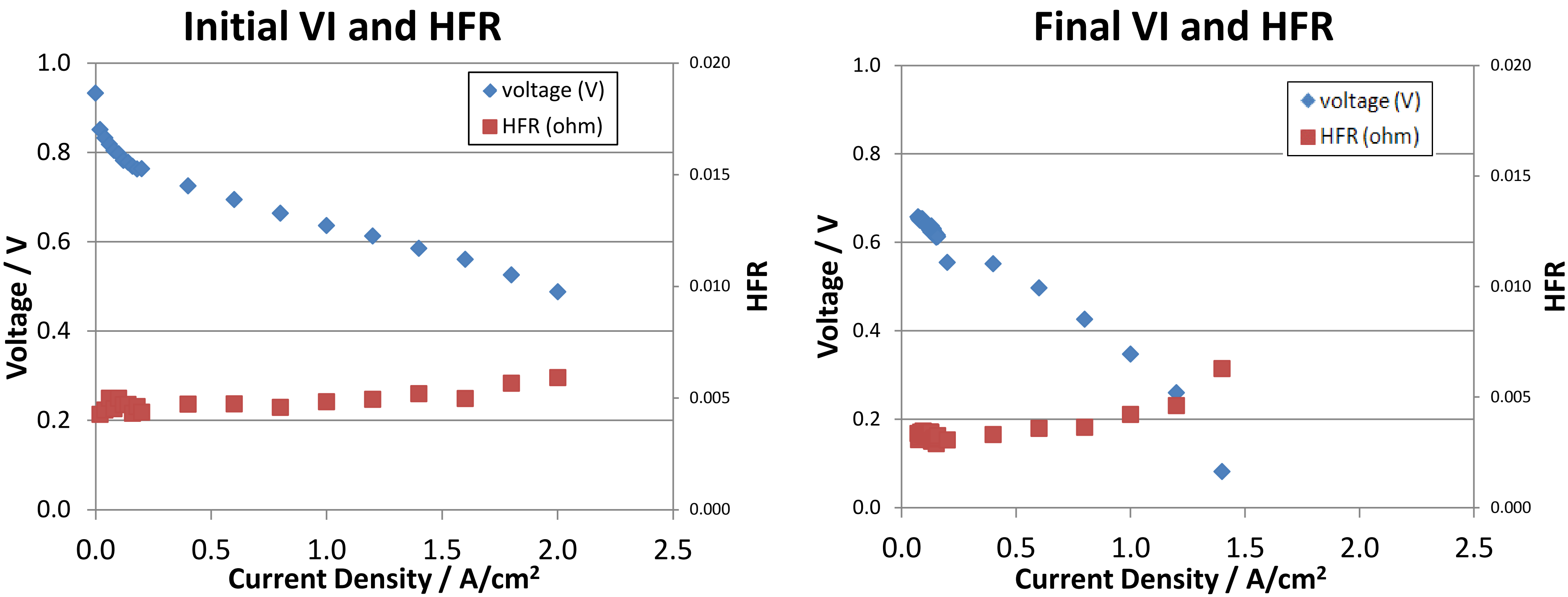



- Initial VI performance slightly higher with metal plate / probably due to MEA/cell assembly variability
- Degradation with metal plate similar to that with graphite plates
- Performance decay due to catalyst ECSA loss and increased $H_2$ cross-over lowering OCV
- Consistent with MEA performance degradation during drive cycle operation

# Comparison of Ohmic Resistance During Testing of Novel Plates

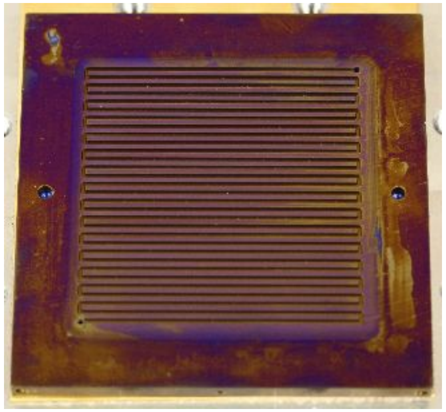
**Accomplishments**




- Large performance decay due to catalyst layer degradation
  - Performance decay not due to increasing membrane resistance
- HFR decreases during testing
  - Low current HFR 4.26E-03 Ohm → 3.39E-03 Ohm
  - Average VIR HFR 4.81E-03 Ohm → 3.68E-03 Ohm

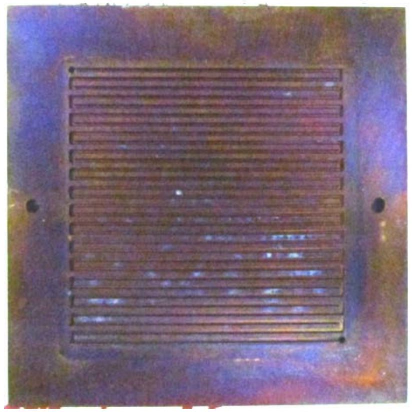
# Image of Novel Metal Hardware

**Before Testing**



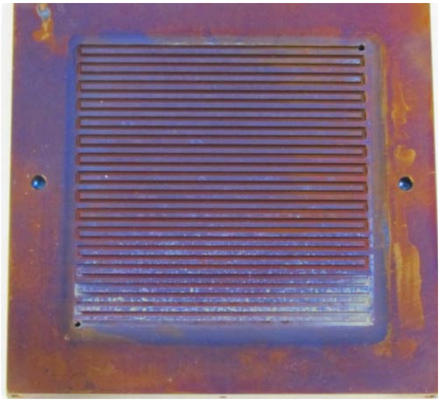
As-received

**After Testing Cathode Plate)**



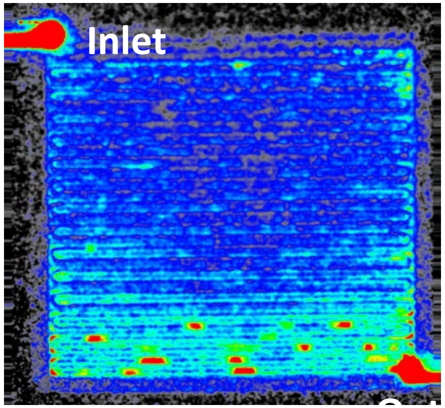
Note: overall color difference due to lighting of picture, not change in plate color

**After Testing (Anode Plate)**



Area with XRF Elemental Mapping

**Neutron Imaging: $H_2O$ in Metal Hardware**



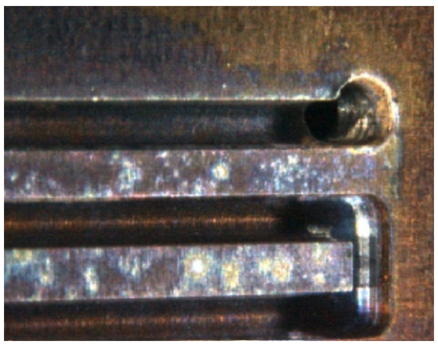

Liquid water content: similar operating conditions to anode plate area with discoloration, results from another LANL project

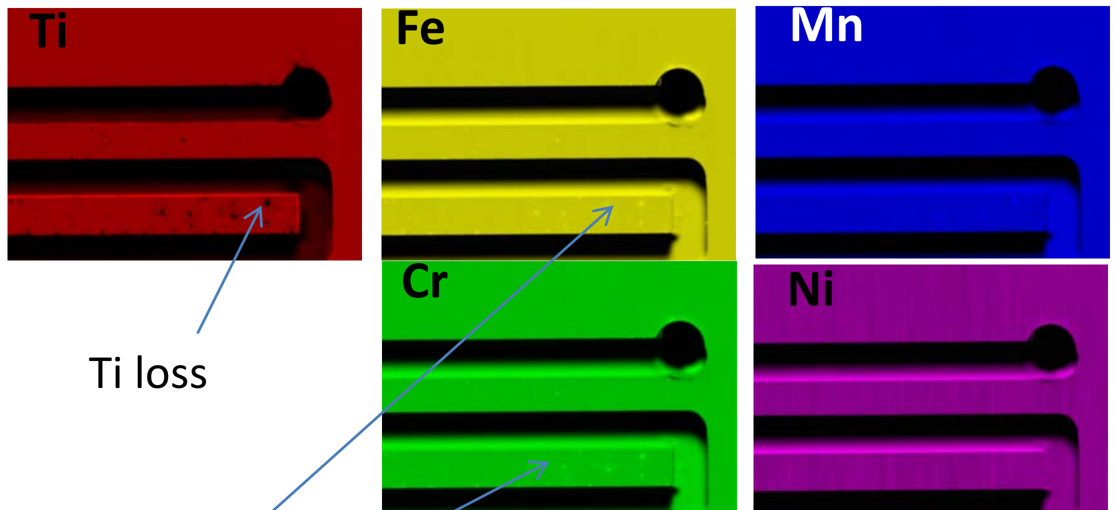
- Changes visible after testing and disassembly
- Anode Plate: bottom (outlet) shows significant coloration changes
- Cathode Plate: sporadic discoloration on lands

Accomplishments

# XRF Mapping: after tests(Anode Plate)

Optical Image



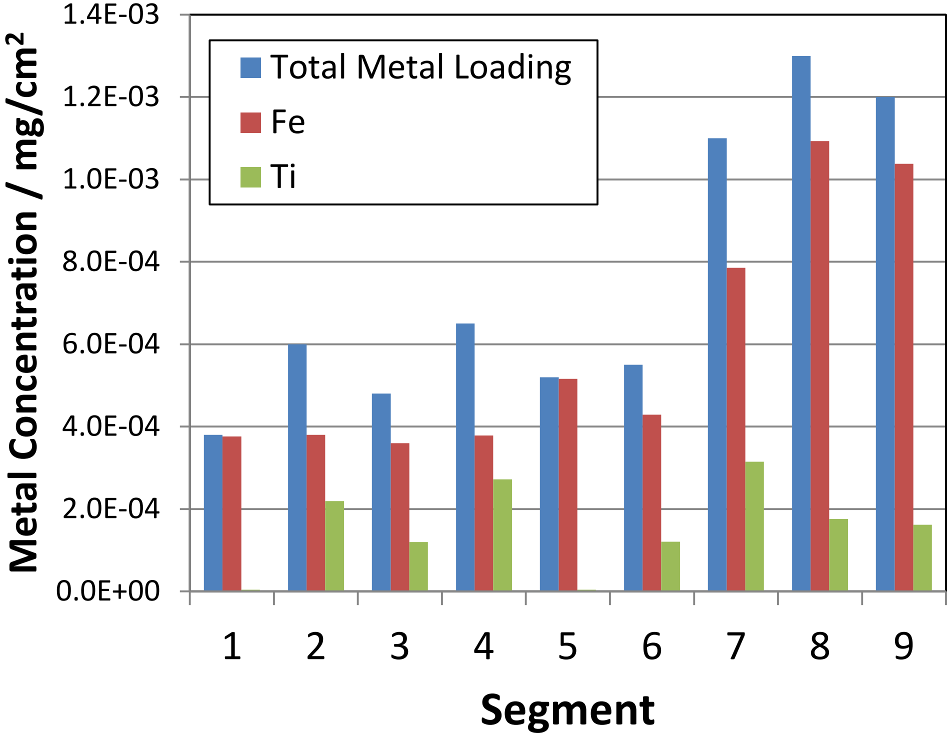



Ti loss

Higher concentration of Fe/Cr due to loss of Ti in outer layer

# Quantifying the Elemental Contamination of MEA using XRF

**Accomplishments**




**Higher concentrations of Metal contaminants observed at outlet where corrosion was evident**

# Bipolar plate testing summary

New Plates Provided to LANL:

Initial Performance of Metal Plates equivalent to graphite plates

'Near-Worst-Case' operation included liquid $H_2O$

Analyses of bi-polar plates (post test):

- Indicates corrosion present on anode plate, typically where large amounts of liquid water is present
- Minimal corrosion present on cathode plate (but not zero)

Analysis of MEAs show:

- Small metal contamination of GDL/MEA
  - Possible ~ 5% - ~ 14% cation blocking of proton
- Higher where liquid water was present

Increase of contact resistance

- Higher on cathode plate

Recommendation: further evaluation for transportation applications requires testing at expected OEM low operating RHs (~ 30% RH)

# 2012 Collaborators and Activities

- **NIST**
  - Bipolar Plates; probing the impact of flow field inaccuracies on FC performance
  - Developing new design for 1 micron imaging fuel cell hardware
- **DOE Fuel Cell Technologies Transport Modeling Working Group**
  - R. Mukundan serving as the co-chair
- **DOE Fuel Cell Technologies Durability Working Group**
  - R. Borup serving as the co-chair
- **Michigan Tech. and California State U.**
  - Investigate the impact of hydrophobic flow plates on fuel cell performance

- **SGL Technologies**
  - Novel MPL/GDL Materials
- **Fuel Cell Technologies**
- **Ballard**
  - Develop standard start-up/shut-down protocol
- **Fuel Cell Tech Team**
  - Active participation, R. Borup Member
- **Nancy-Université:**
  - Spatially resolved measurements during Start-up/Shut-down cycling
  - Materials characterization.

# DOE Working Groups

1. **Durability Working Group meetings:**

   Oct. 13, 2011, Boston, MA

   May 14, 2012, Arlington, VA

   R. Borup presented and led discussion on AST development

   Worked with Ballard to develop shut-down/start-up protocol

2. **Transport Modeling Working Group - 2nd Meeting**

   Aug. 18, 19, 2011, Berkeley

   R. Mukundan led discussion on durability concerns, modeling and helped prioritize the MWGs research areas

3. **Transport Modeling Working Group - 3rd Meeting**

   Jan. 27, 2012, Berkeley

   R. Borup presented PEM Fuel Cell Degradation

   R. Mukundan presented on knowledge gained from fuel cell and imaging experiments

4. **Fuel Cell Tech Team** – R. Borup Member

# Acknowledgements

LANL acknowledges The US DOE Office of Fuel Cell Technologies and Technology Development Manager **Nancy Garland** for their support.