Investigation of Ruthenium Dissolution in Advanced Membrane Electrode Assemblies for Direct Methanol Based Fuel Cell Stacks

By

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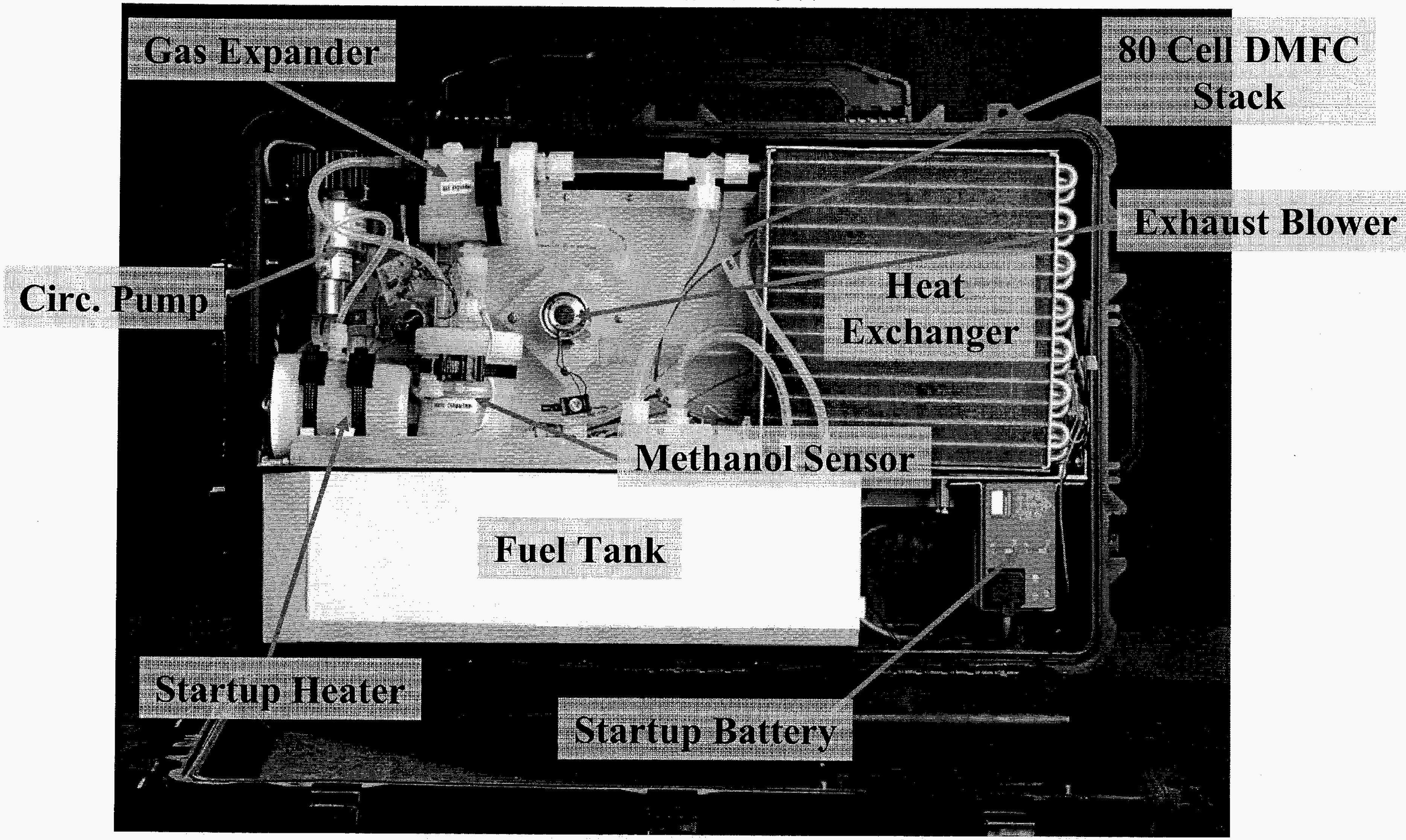
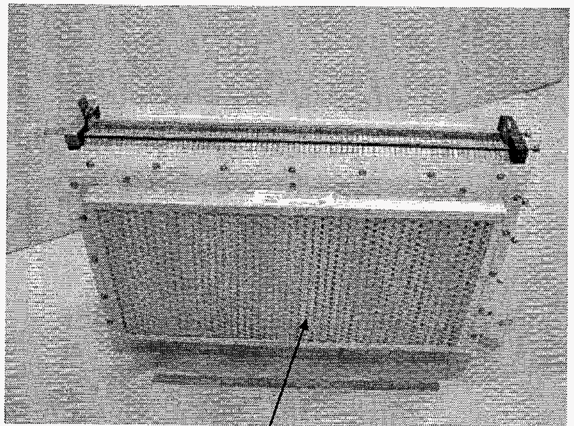
Presentation Outline

- Motivation
  - System Specifications
  - Stack Details
  - Stack Performance Degradation
  - Stack Observations
- Pathways for Cell Degradation
- Cell Duration Testing
- Duration Testing, MEA Analysis
- Stack Degradation Analysis
- Conclusions

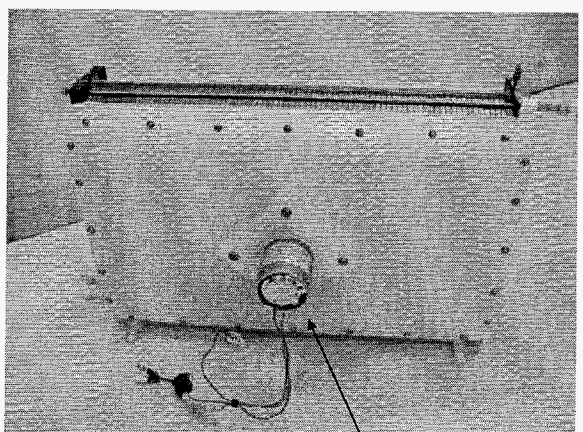
300W Direct Methanol Fuel Cell Power Source, Detailed View



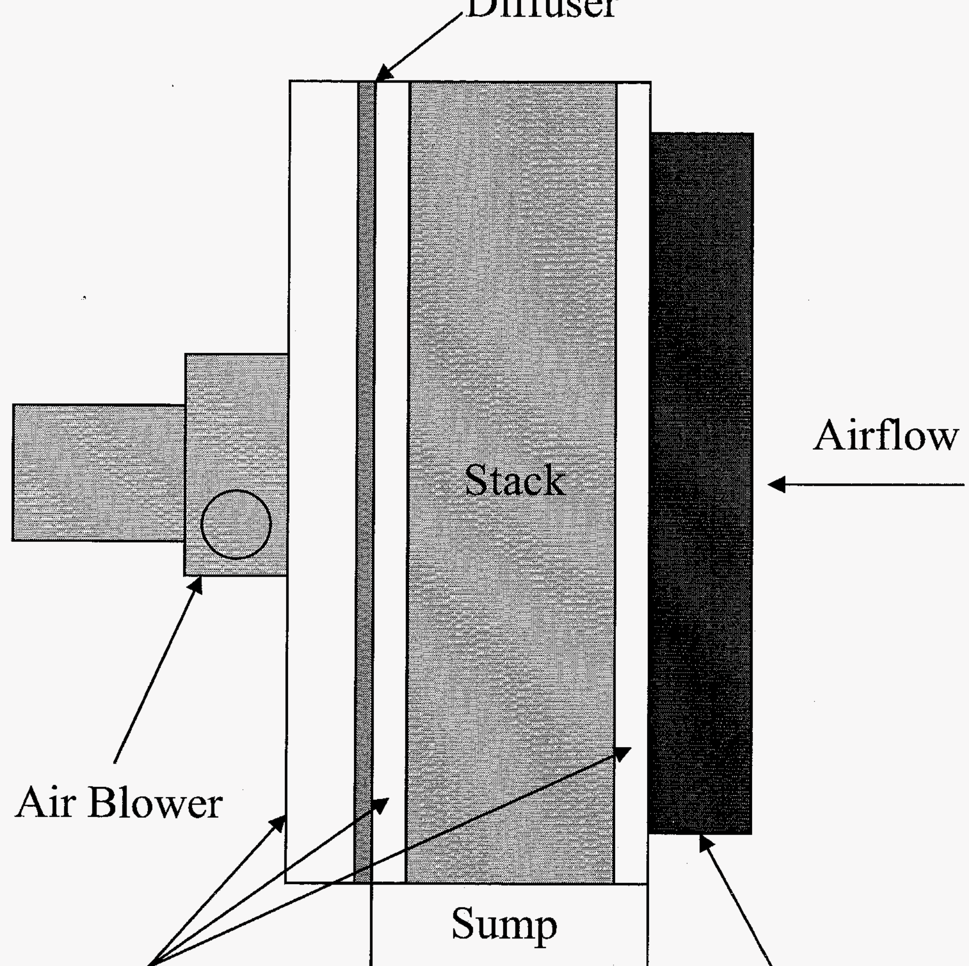
80-Cell DMFC Low Airflow Stack



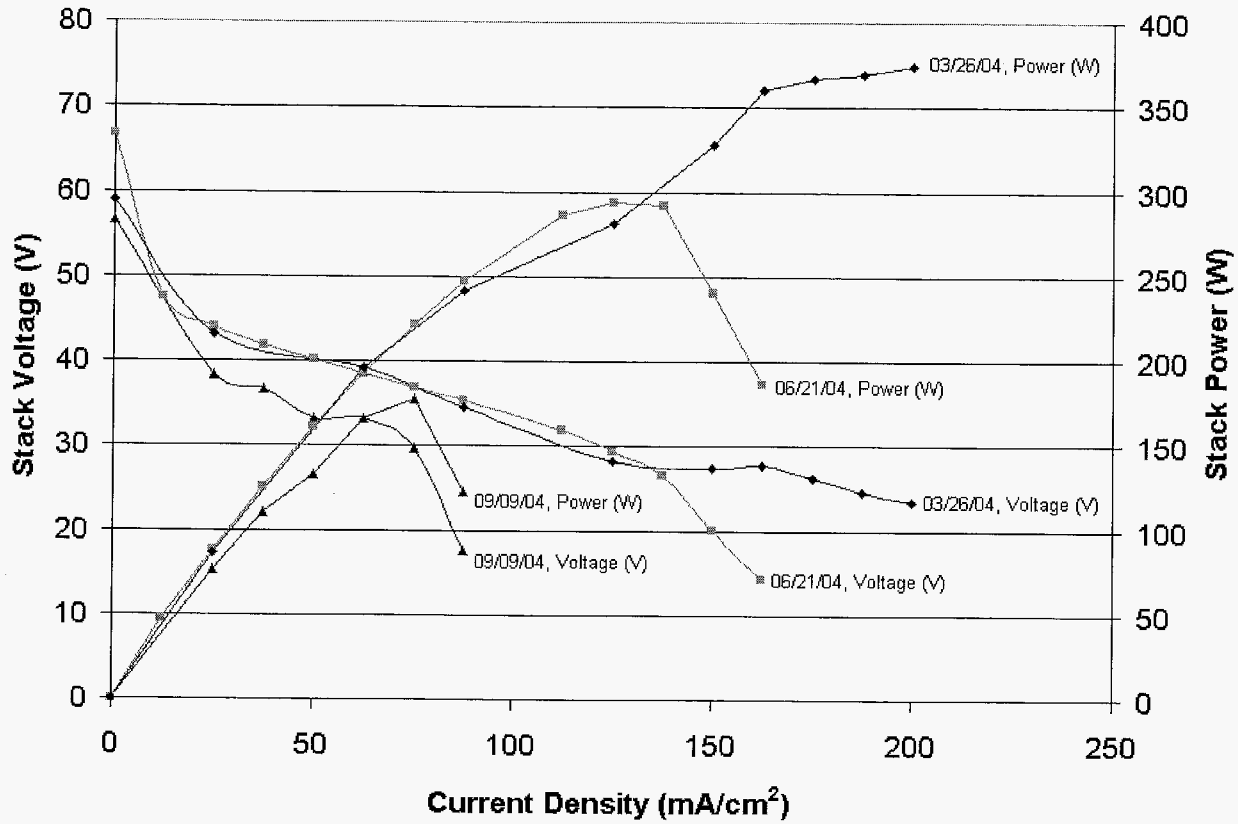
Donaldson Air filter



Advanced Air blower

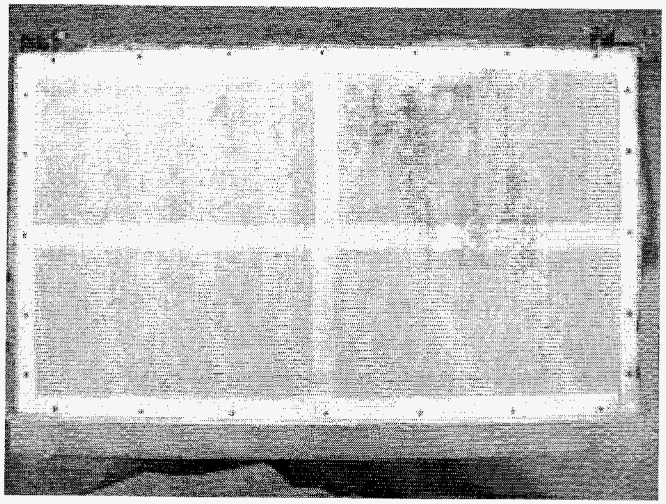


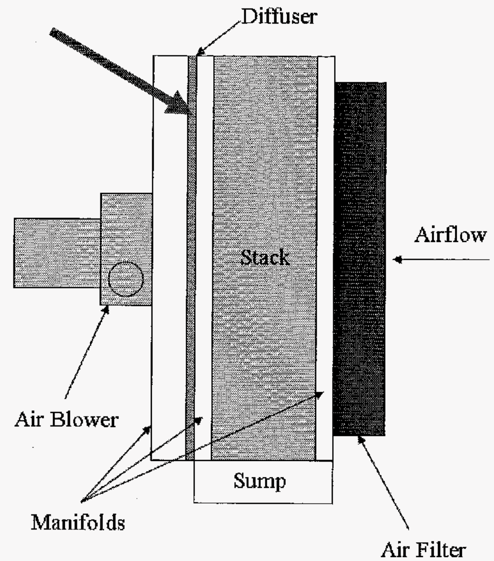
Stack Performance

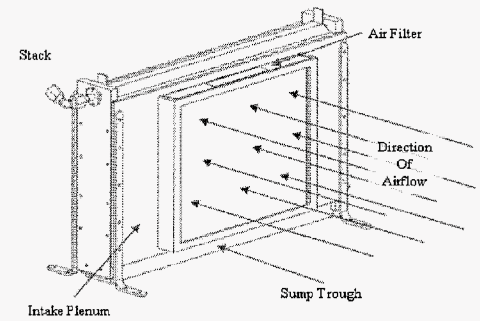


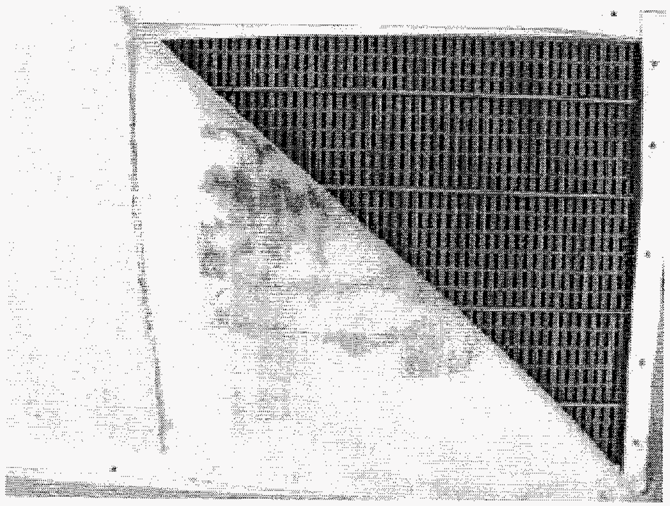
- Initial stack power performance, 374 Watts
- Stack performance continuously declined over a period of less than six months
- Final stack power performance, 177 Watts

Stack Observations, Diffuser Cloth





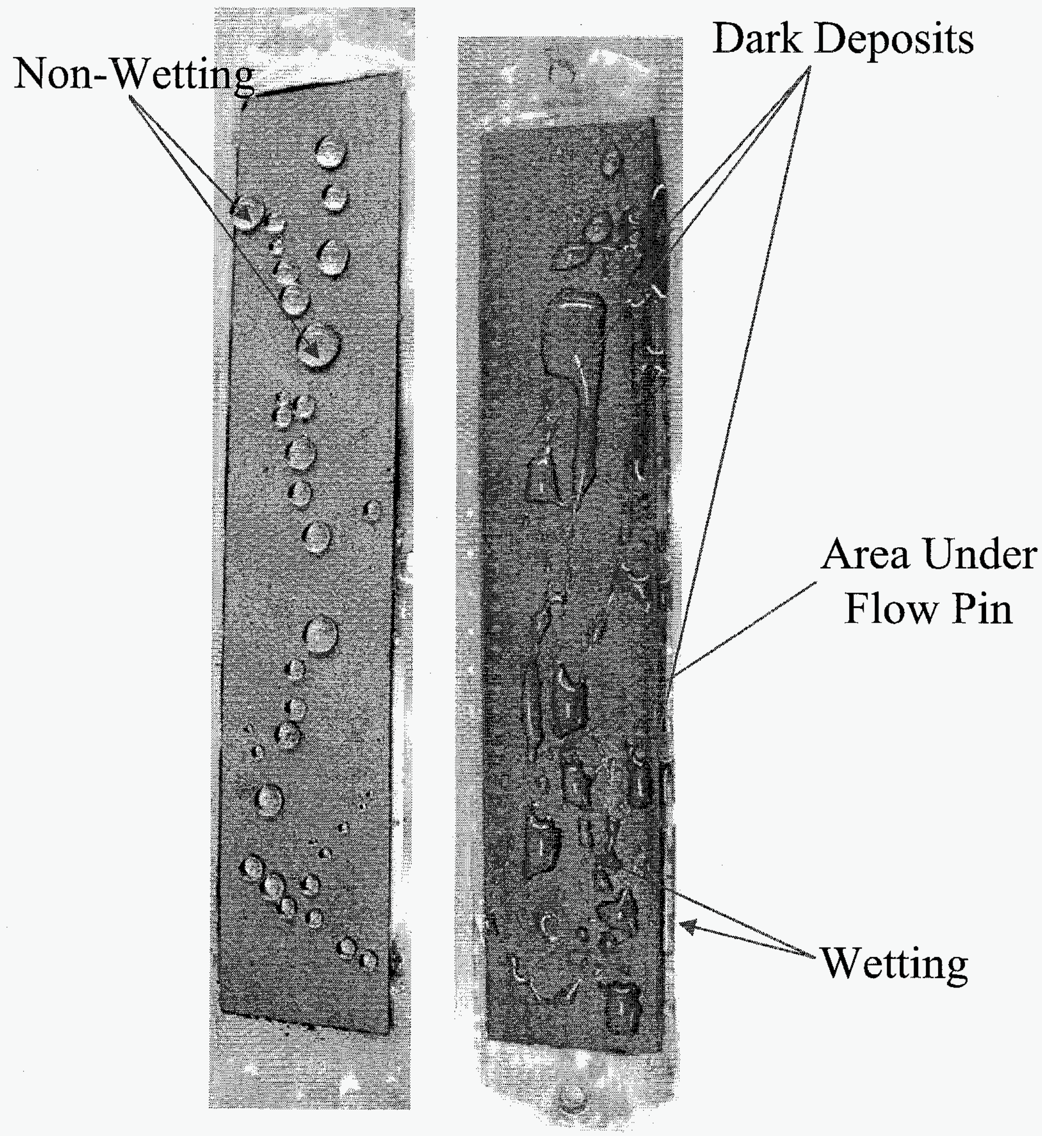




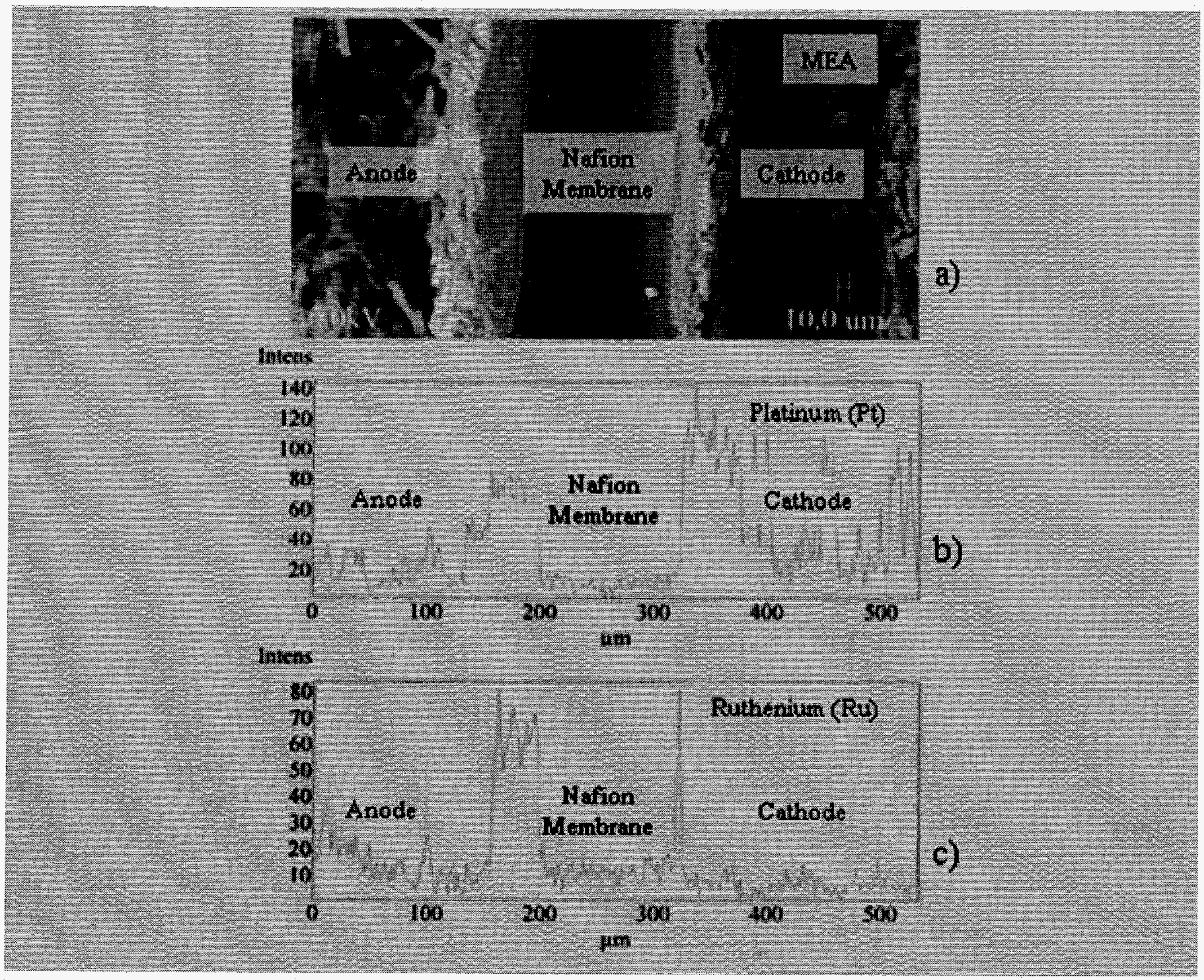
- Diffuser cloth is located at the exit of the stack
- Brownish black precipitate was identified on the cloth in contact with the stack
- Precipitate was identified as ruthenium
- ruthenium found at the cathode is washed out by water and absorbed on to the diffuser

Stack Observations, MEA Observations

- Cathodes of MEAs from the stack exhibited increased wettability compared to a "fresh" MEA.
- Patches of dark gray "deposits" found on various parts of the cathode
- The areas with dark deposits were more wettable than the lighter areas.
- Several representative MEAs showed the same type of cathode changes
- Areas under the flow field pins remained "non-wettable"
- Flow field impressions were light and did not appear to damage the cathode papers

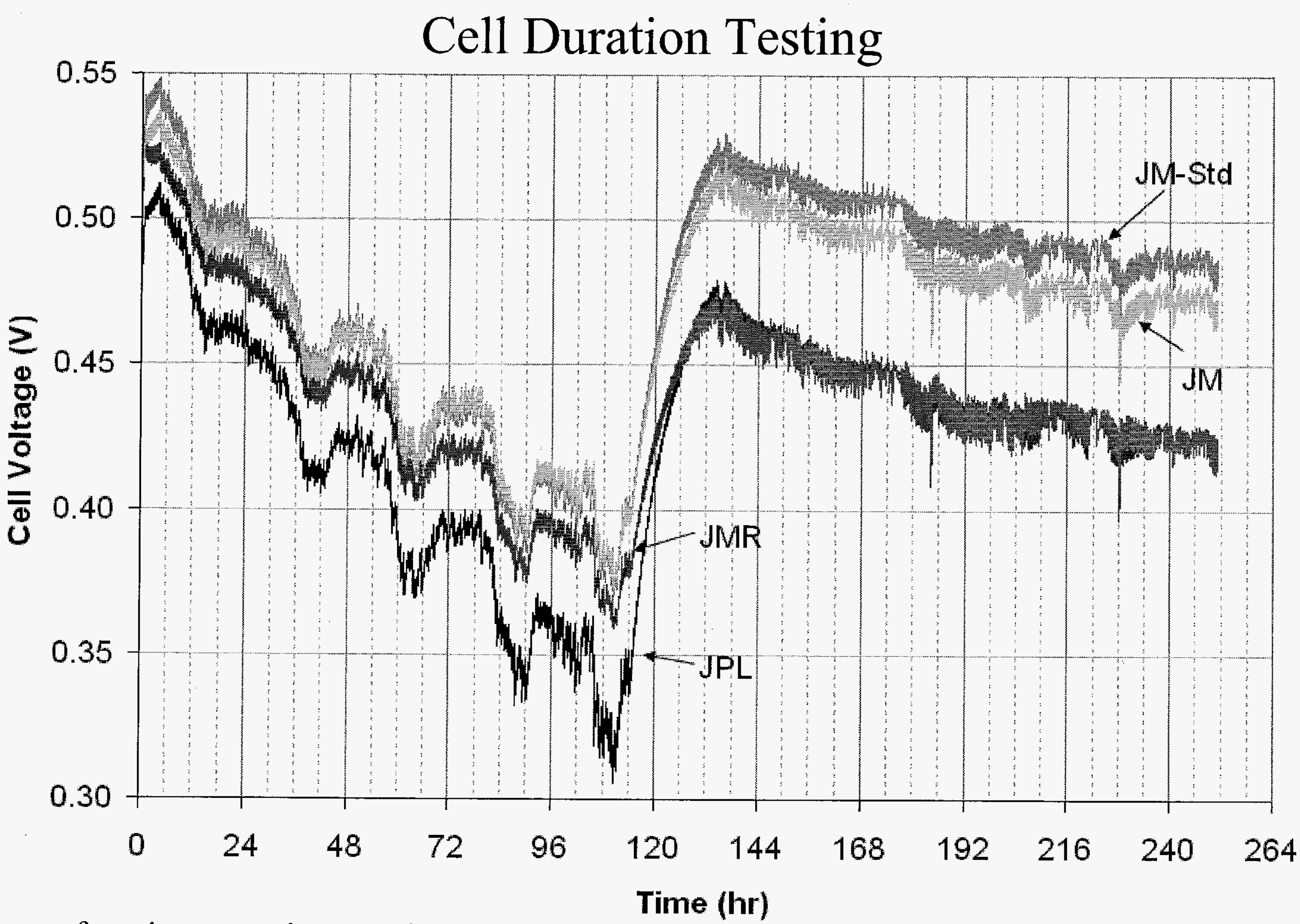


Stack Observations, EDAX Analysis of MEAs



Pathways for Cell Degradation

- Hypothesis For Cell Degradation
  - Stack performance loss is caused by the ruthenium dissolution from the anode catalyst, the deposition of ruthenium at the cathode, and the loss of hydrophobicity at the cathode
  - Degradation pathways
    - Mechanisms for Ruthenium dissolution:
      - Over discharge caused by shunt currents
      - *Instability of platinum-ruthenium commercial catalyst*
    - Mechanisms for Loss of hydrophobicity at the cathode:
      - *Inadequate Teflon content*
      - Deposition of RuO_2 at the cathode
- Experimental
  - Two degradation pathways were investigated, the **stability of platinum-ruthenium commercial catalyst** and the **cathode backing Teflon content**
  - MEAs Fabricated
    - JPL, Anode: JPL-prepared Pt-Ru, Pt Cathode, 15% Teflon backing
    - JM, Anode: Johnson Matthey Pt-Ru, Pt Cathode, 15% Teflon backing
    - JMR, Anode: Reduced Johnson Matthey Pt-Ru, Pt Cathode, 15% Teflon backing
    - JM-STD, Anode: Johnson Matthey Pt-Ru, Pt Cathode 5% Teflon backing (Standard or control MEA)



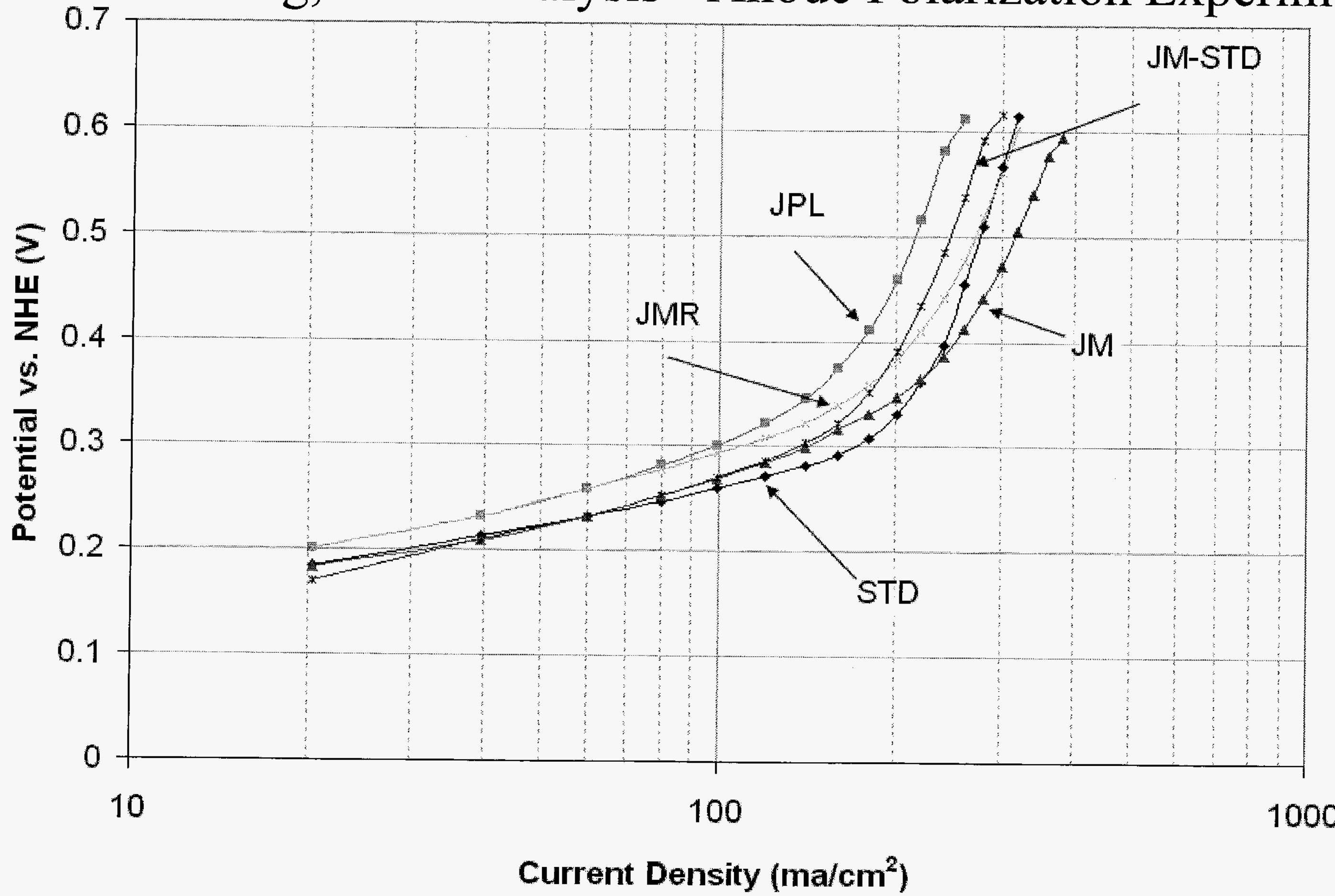
- 250 hours of continuous testing complete
- The decrease in cell performance in the initial hundred hours of testing is a result of sensor calibration
- The slopes of the voltage curves after 134 hours are also controlled by methanol concentration control
- In general, the JM-Standard MEA performed the best

Duration Testing, MEA Analysis - Post 250-hr Testing Performance Summary

MEA	Formulation	Performance Decline (mV)		Performance Decline (mW/cm^2)		Rate of Decay (V/hr)	
		50 mA/cm^2	100 mA/cm^2	50 mA/cm^2	100 mA/cm^2	50 mA/cm^2	100 mA/cm^2
JPL	Anode: JPL Cathode: 15% Teflon	48	150	2.4	15	0.00019	0.0006
JM	Anode: Johnson Matthey Cathode: 15% Teflon	6	67	0.3	6.7	0.00002	0.00027
JMR	Anode: Reduced Johnson Matthey Cathode: 15% Teflon	30	107	1.5	10.7	0.00012	0.00043
JM-STD	Anode: Johnson Matthey Cathode: 5% Teflon (Standard)	6	96	0.3	9.6	0.00002	0.00038

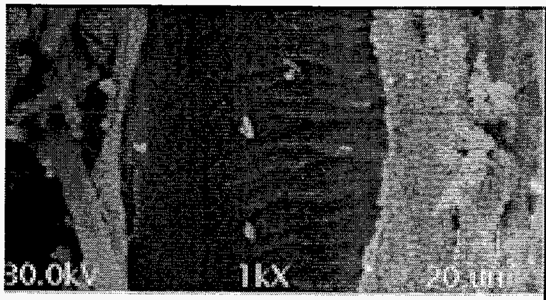
- MEA "JPL" logged 20 more hours of testing than any other MEA
- MEAs fabricated with the commercial Johnson Matthey catalyst showed the least performance decline
- The MEA fabricated with Johnson Matthey anode catalyst and 15% Teflon content cathode paper, showed slightly lower performance decline at high current densities than the MEA fabricated with Johnson Matthey anode catalyst and 5% Teflon content cathode paper
- The MEA fabricated with the reduced Johnson Matthey anode catalyst performed similar to the MEA fabricated with the JPL catalyst
- The test standard performed the best during the durability experiments
- The rate of voltage decay for all MEAs tested is similar to values observed in the past

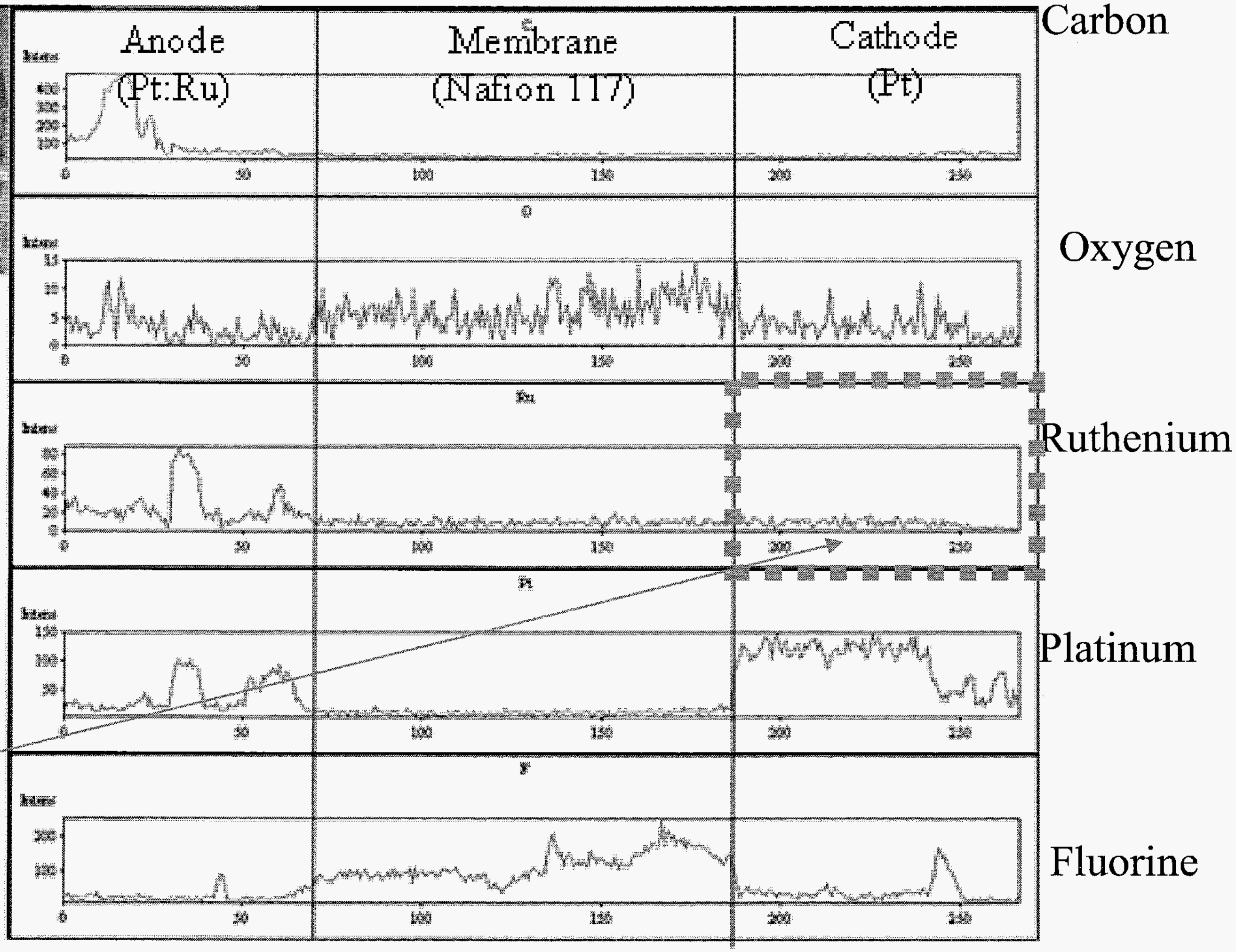
Duration Testing, MEA Analysis - Anode Polarization Experiments



- Anode polarization analysis of the cell post duration experiments reveal no changes anode performance

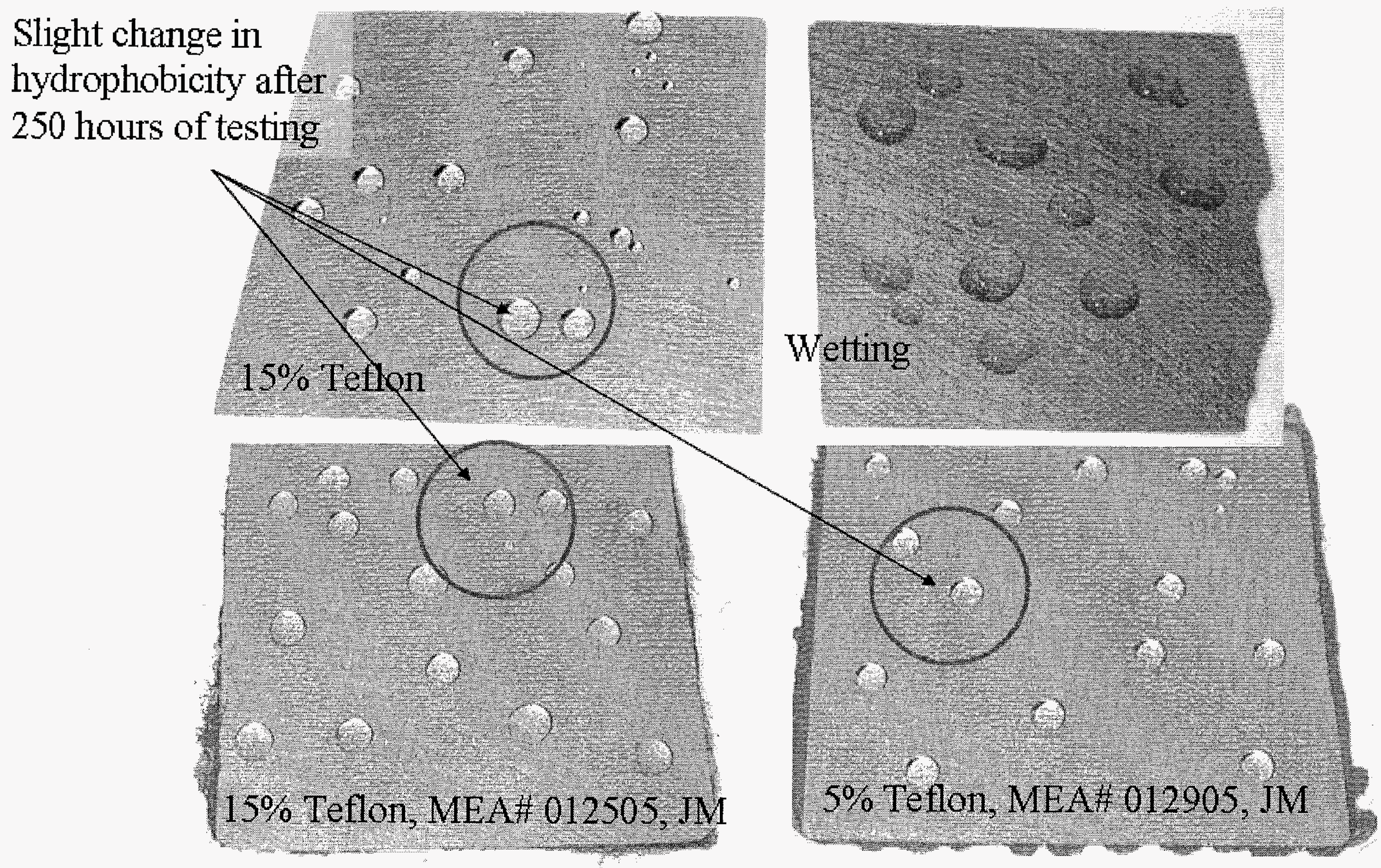
Duration Testing, MEA Analysis - EDAX Analysis



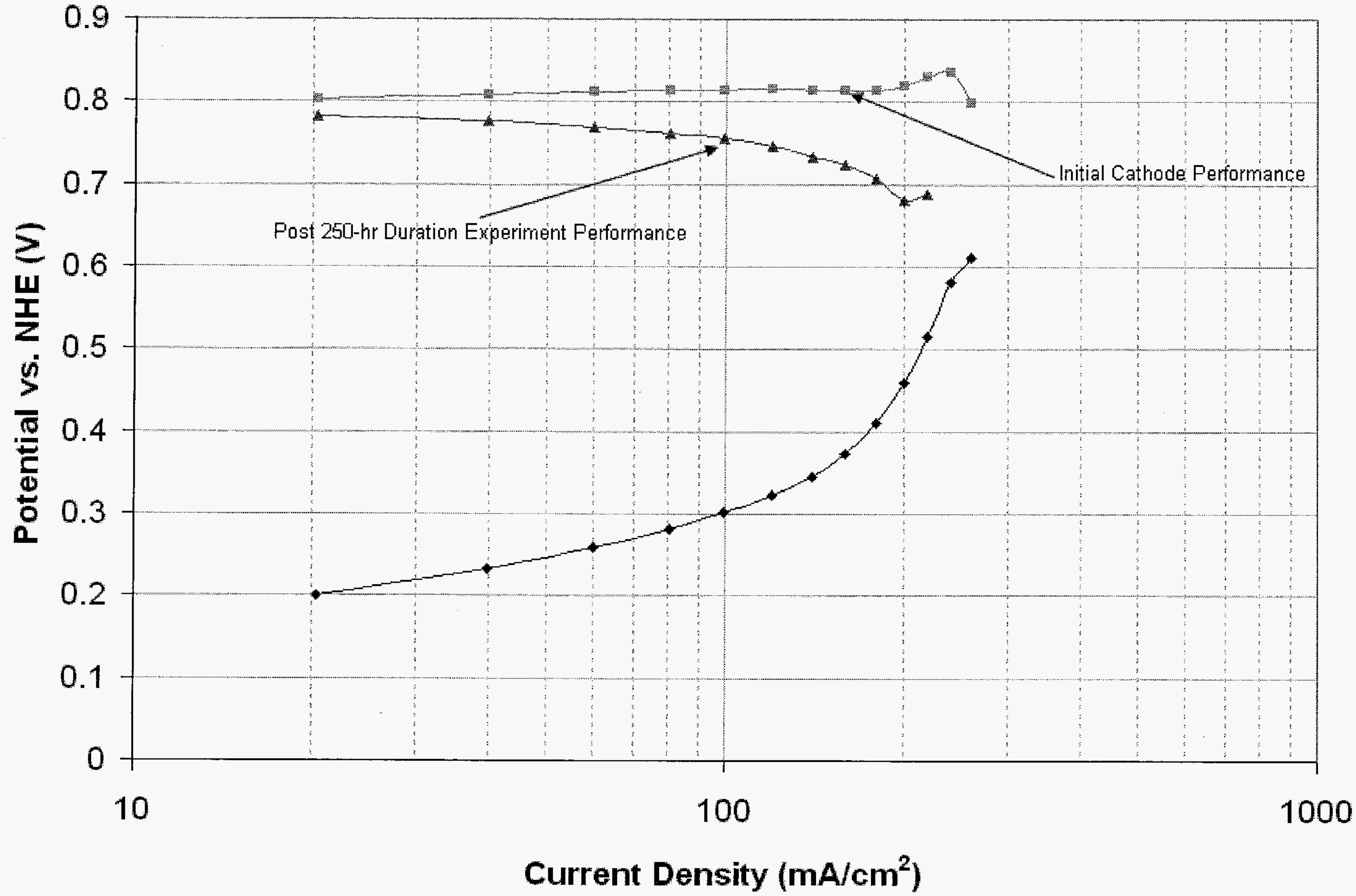


No ruthenium found on the cathode

Duration Testing, MEA Analysis - Cathode Hydrophobicity Comparisons

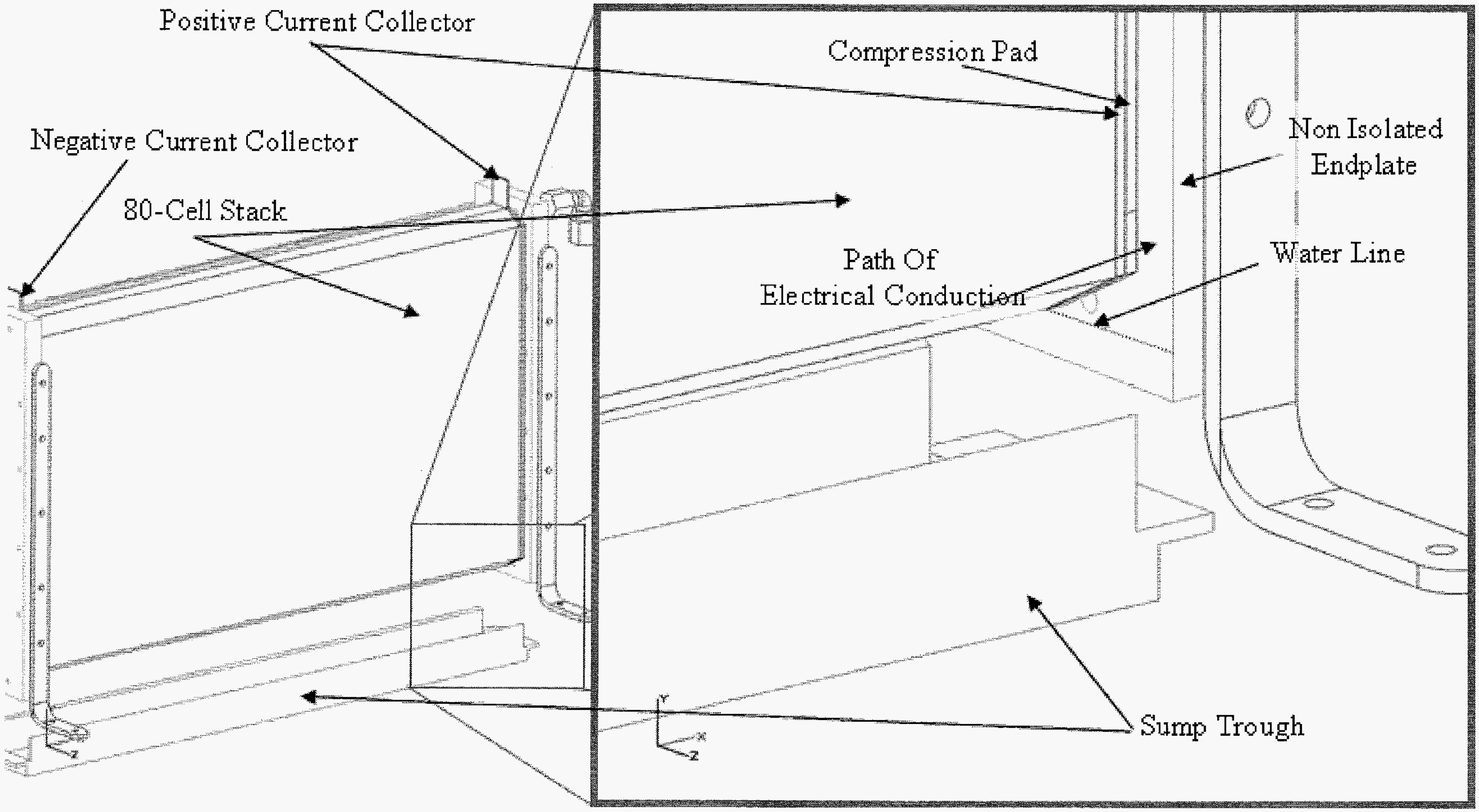


Duration Testing, MEA Analysis - Anode and Cathode Performance

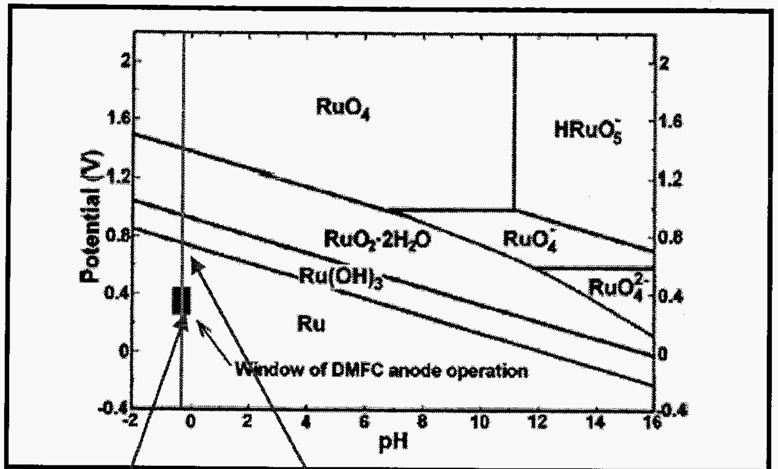


- MEA performance degradation is attributed to losses in cathode performance

80-cell stack current collection hardware



Stack Degradation Analysis – Over-discharge



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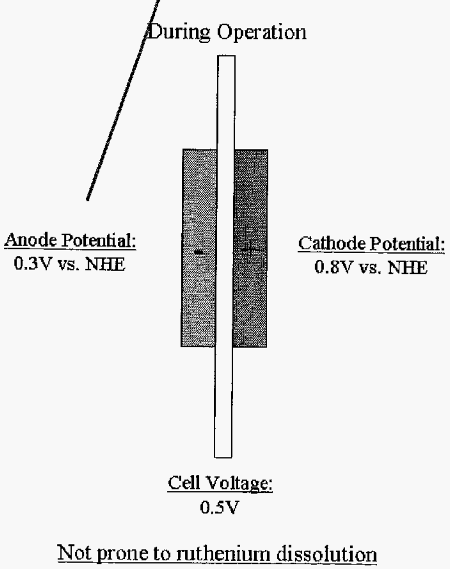
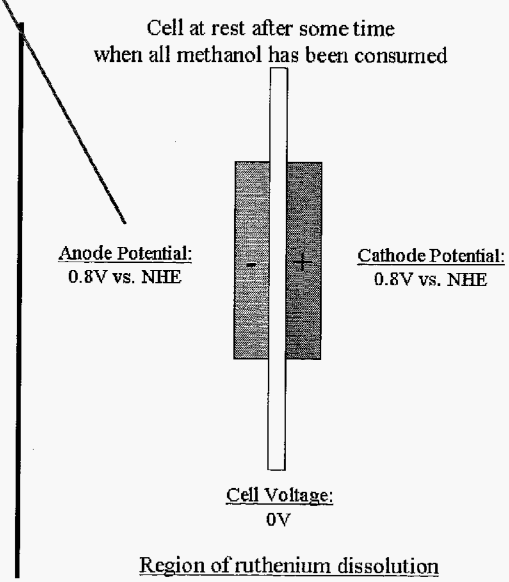
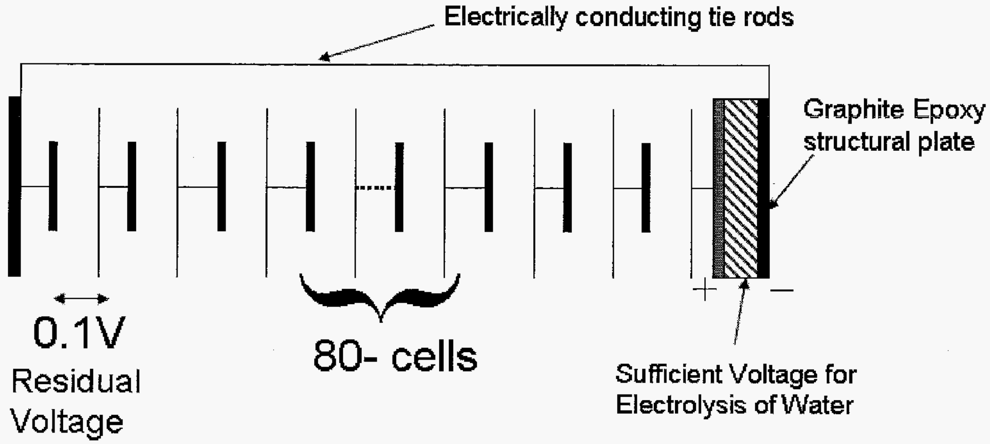






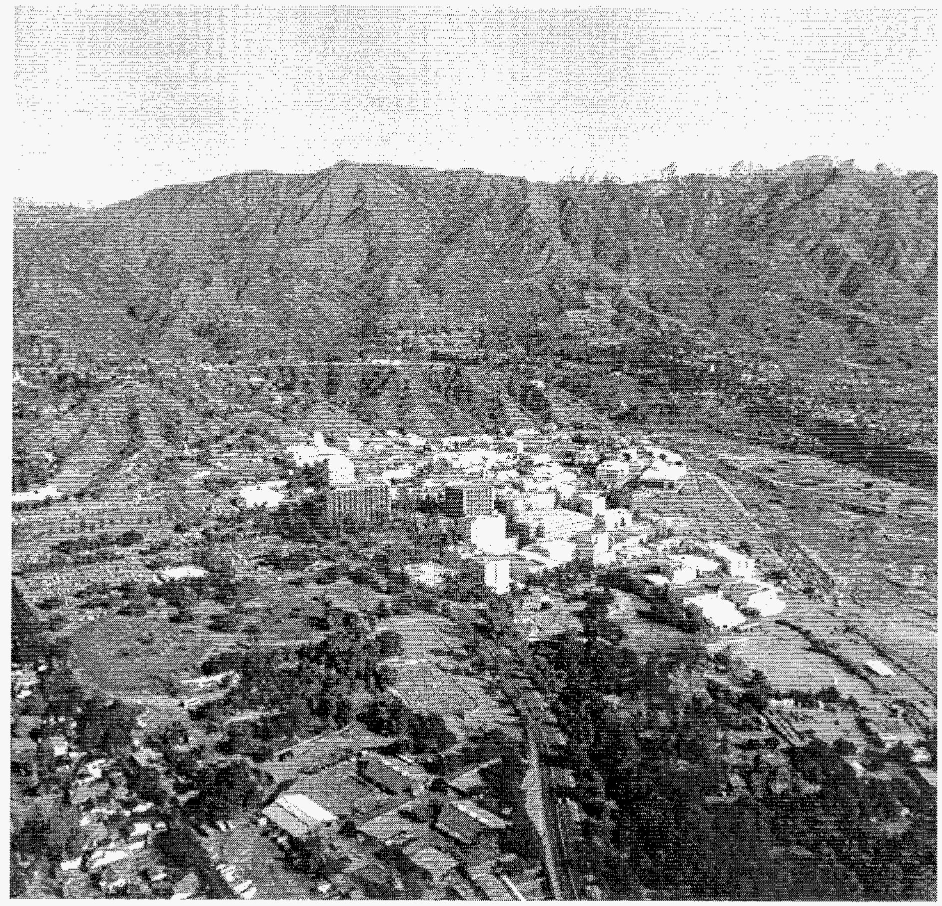
1. Reactions without methanol at the anode:
   - Anode: $2Ru \rightarrow 2Ru^{3+} + 6e^-$
   - Cathode: $3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$
2. Ru^{3+} migrates through the Nafion membrane
3. Cathode: $2Ru^{3+} + 3H_2O + 1/2\ O_2 \rightarrow 2RuO_2$ (black) $+ 6H^+$

Conclusions

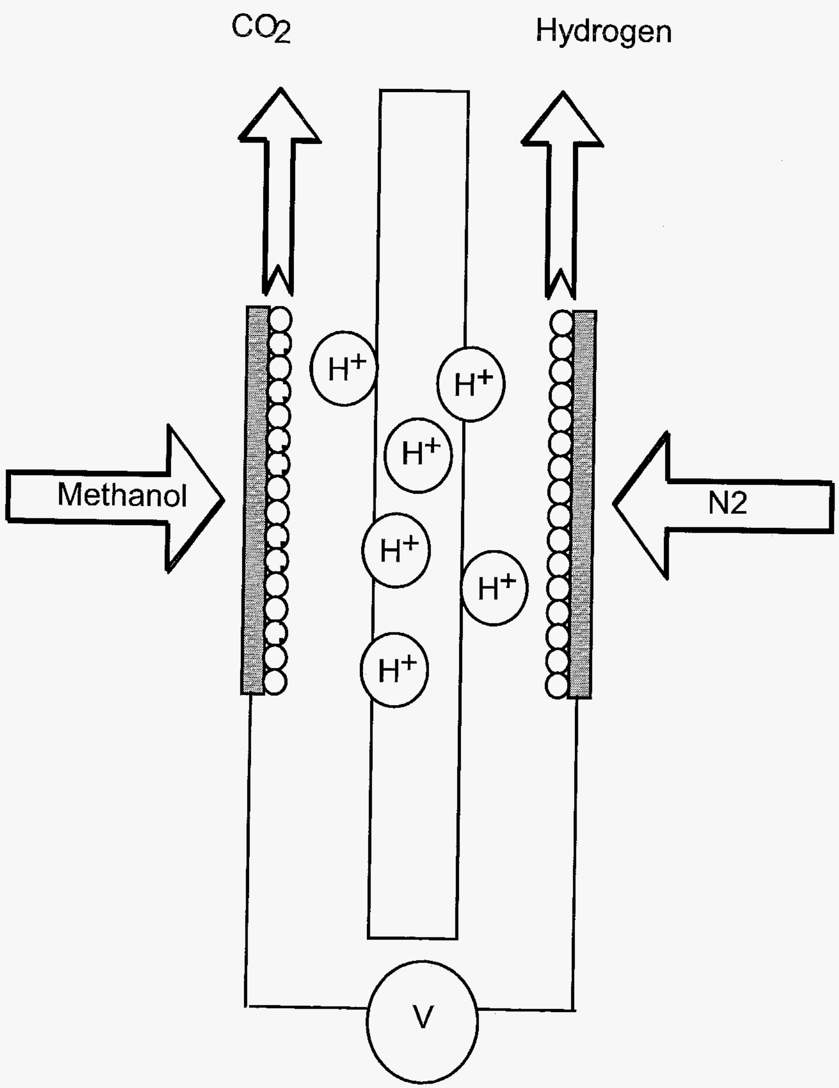
- Dissolution of ruthenium was observed in the 300-Watt system stack
- Duration testing was performed in cells to determine the pathway of cell degradation, no ruthenium dissolution was observed for cells after 250 hours of operation
- EDAX analysis on each of the MEAs has shown that the Johnson Matthey commercial catalyst is stable in DMFC operation for 250 hours
- Ruthenium migration does not seem to occur during cell operation
- Dissolution of ruthenium occurs when methanol is absent from the anode compartment, the cathode compartment has access to air, and the stack is electrically connected to a load (Shunt Currents).
- Stack design allowed for conditions in which the anode could experience elevated potentials for long durations and allow for ruthenium dissolution
- The open-to-air cathode and water collecting trough of this stack design allowed for:
  - The MEAs access to oxygen
  - The system to sustain shunt currents
  - Water accumulated at the manifolds that blocked uniform airflow to portions of the stack and may have contributed to shunt currents
- To prevent ruthenium dissolution, a stack should be designed that can address fuel cell reaction product water removal, allow for uniform airflow to each cell, and limit shunt currents
- Ruthenium dissolution can be prevented by
  - Developing an internally manifolded DMFC stack
  - Insulate the structural endplates from the stack
  - Limit to total number of cells to 25 to limit the shunt currents

Acknowledgements

The work presented here was carried out at the Jet Propulsion Laboratory, California Institute of Technology for the National Aeronautics and Space Administration. This research was sponsored by Ms. Lisa Davis from the Office of the Director, Operational Test and Evaluation, was managed by Dr. George Shoemaker, Executive Agent for Embedded Instrumentation projects, and Mr. Henry C. Merhoff of the US Army Operational Test Command, Ft. Hood. Dr. Stephen Zakanycz of Institute for Defense Analyses provided both technical and programmatic consulting assistance to this program.



Anode Polarization Subtraction



- Test Set-up
  - Nitrogen is introduced into the cathode compartment of the fuel cell. The cathode of the fuel cell now becomes a dynamic hydrogen electrode.
  - When the cell is polarized, the resultant curve will be $\mathbf{E_a}$ vs. current density at the chosen operating temperature of the cell.
- Polarization Analysis
  - $\mathbf{E_{cell}}$, at any air flow rate, can be added to $\mathbf{E_a}$ at the same molarity and temperature to get Ec corresponding to the flow rate.

    $$\mathbf{E_c = E_{cell} + E_a}$$
  - When Ea and Ec are plotted together as a function of current density, the kinetics of the reaction can be seen.