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

By

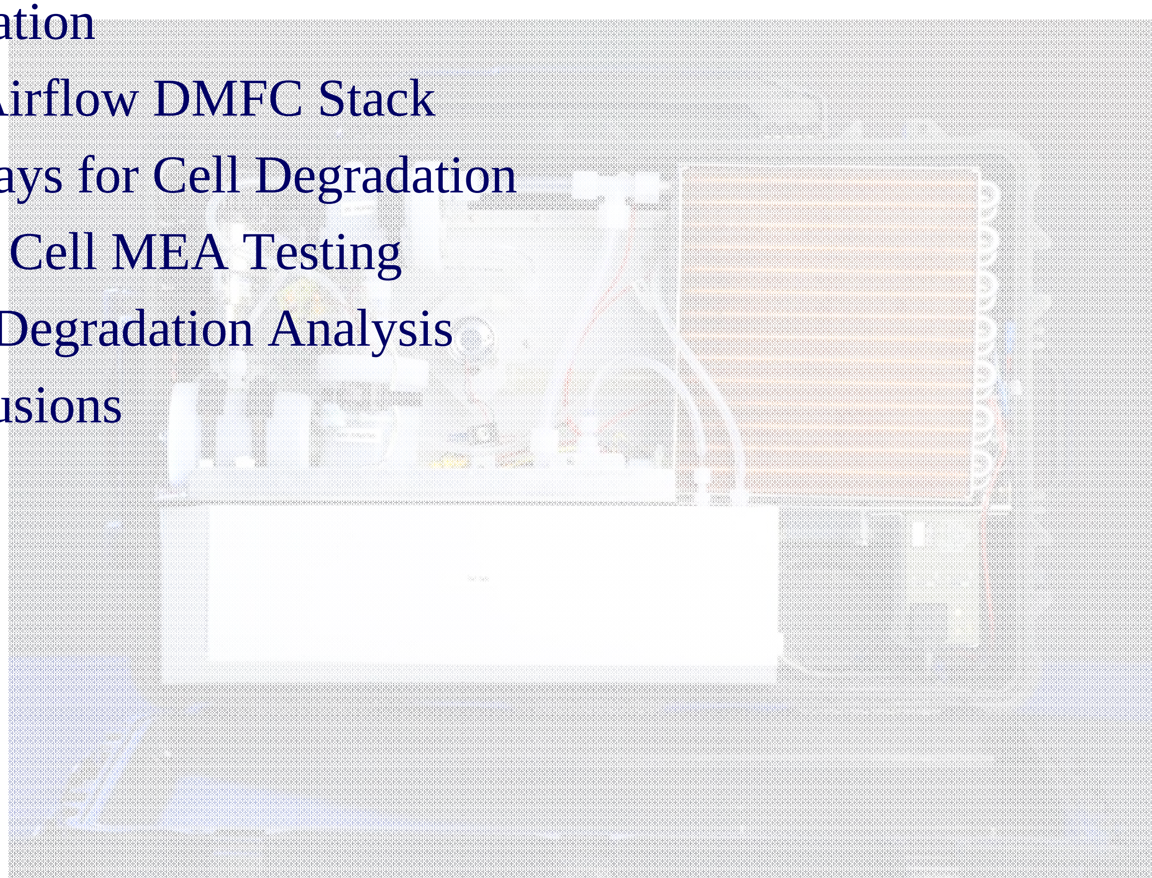
T. I. Valdez[1], S. Firdosy[1], B. E. Koel[2] and S. R. Narayanan[1]

[1]*Jet Propulsion Laboratory, California Institute of Technology*
[2]*University of Southern California*

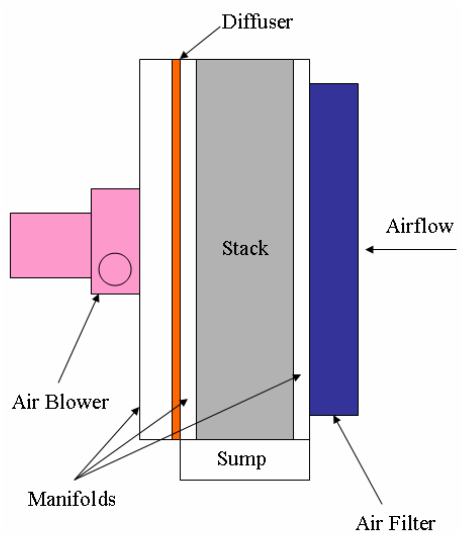
208th Electrochemical Society Meeting
Los Angeles, California

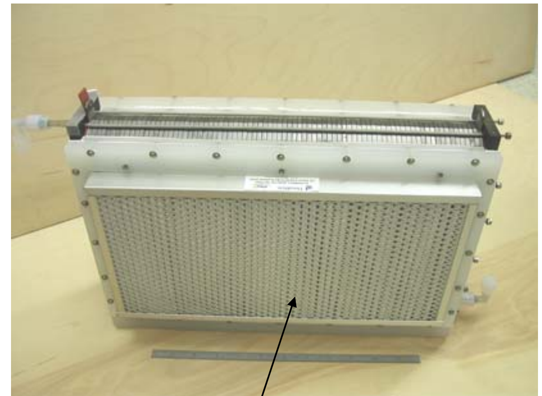
Presentation Outline

- Motivation
- Low Airflow DMFC Stack
- Pathways for Cell Degradation
- Single Cell MEA Testing
- Stack Degradation Analysis
- Conclusions



80-Cell DMFC Low Airflow Stack





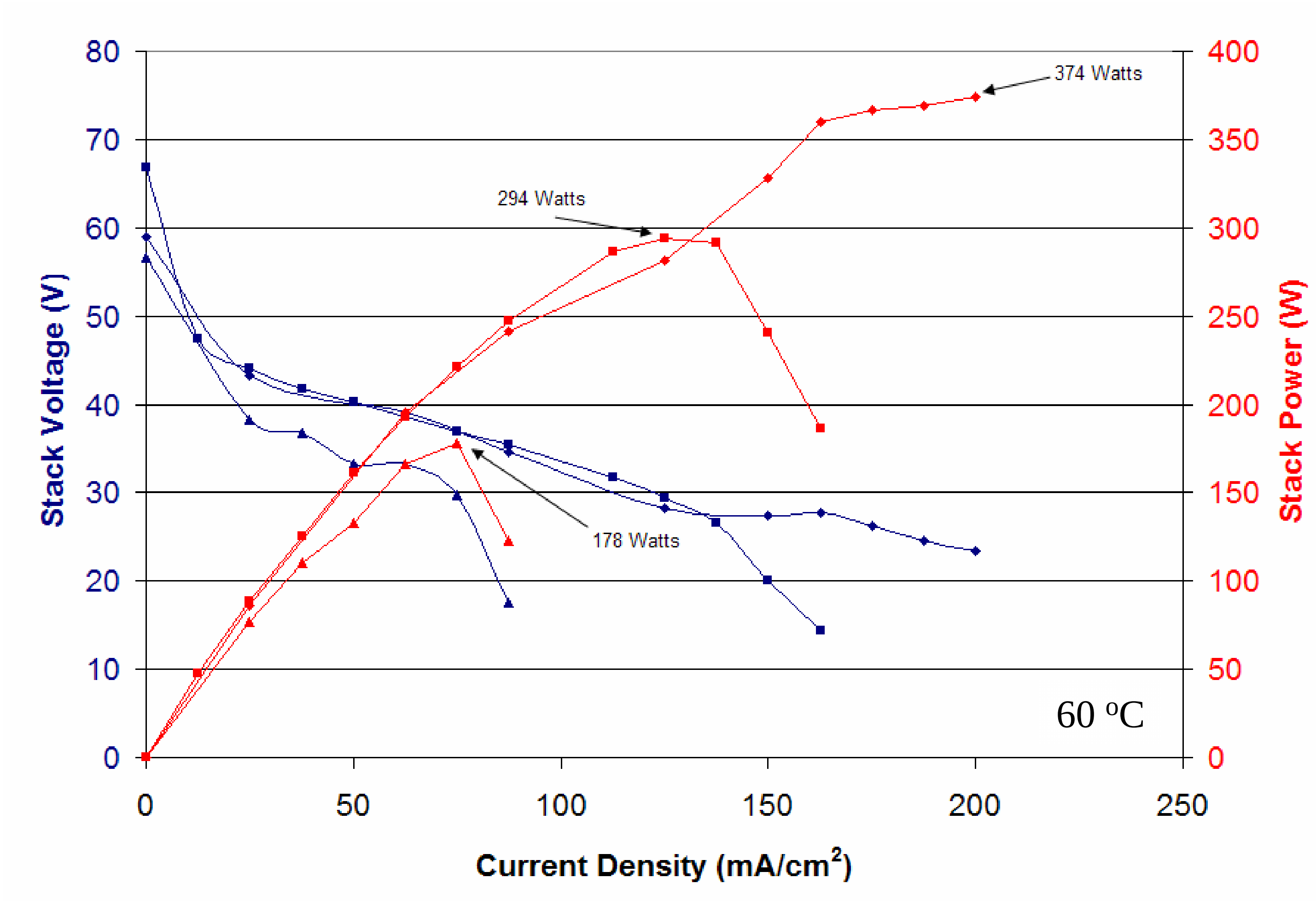
Donaldson Air filter

Advanced Air blower

- Advantages
  - Well suited for low-airflow MEAs (MEA air Stoichiometry 1.6 to 1.8)
  - Low Pressure Drop
  - Gravity Assisted Water Removal
  - Lightweight *(Power Density: 60 W/kg with air handling hardware)*
- MEA Specifications
  - Active Area: 80 cm^2
  - Anode: Pt-Ru (50:50)
  - Cathode: Pt-Black
  - PEM: Nafion 117

Jet Propulsion Laboratory

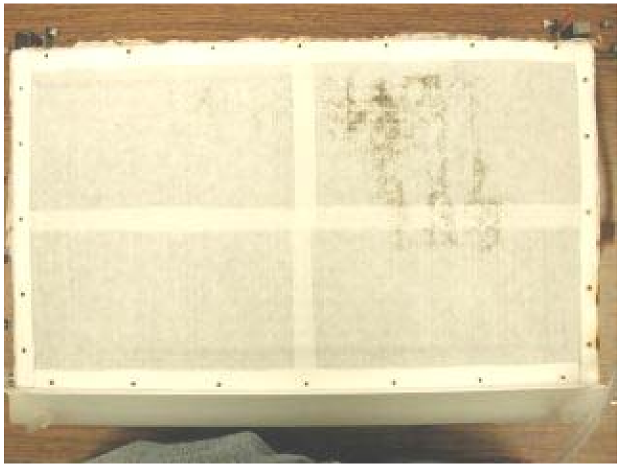
Stack Performance

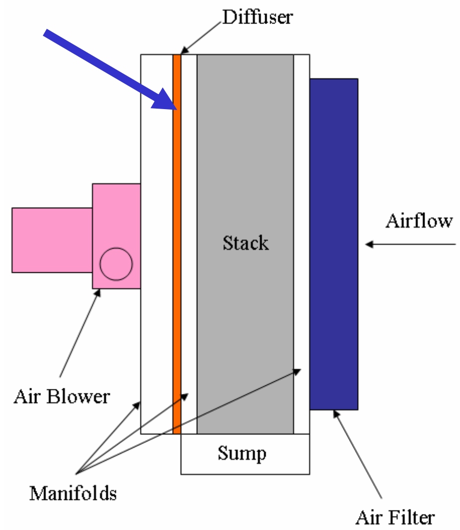


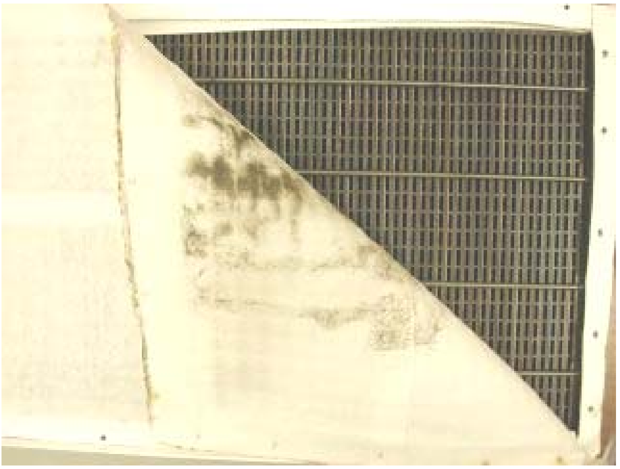
- Initial stack power performance, 374 Watts
- Final stack power performance, 178 Watts

Electrochemical Technologies Group

Stack Observations, Diffuser Cloth



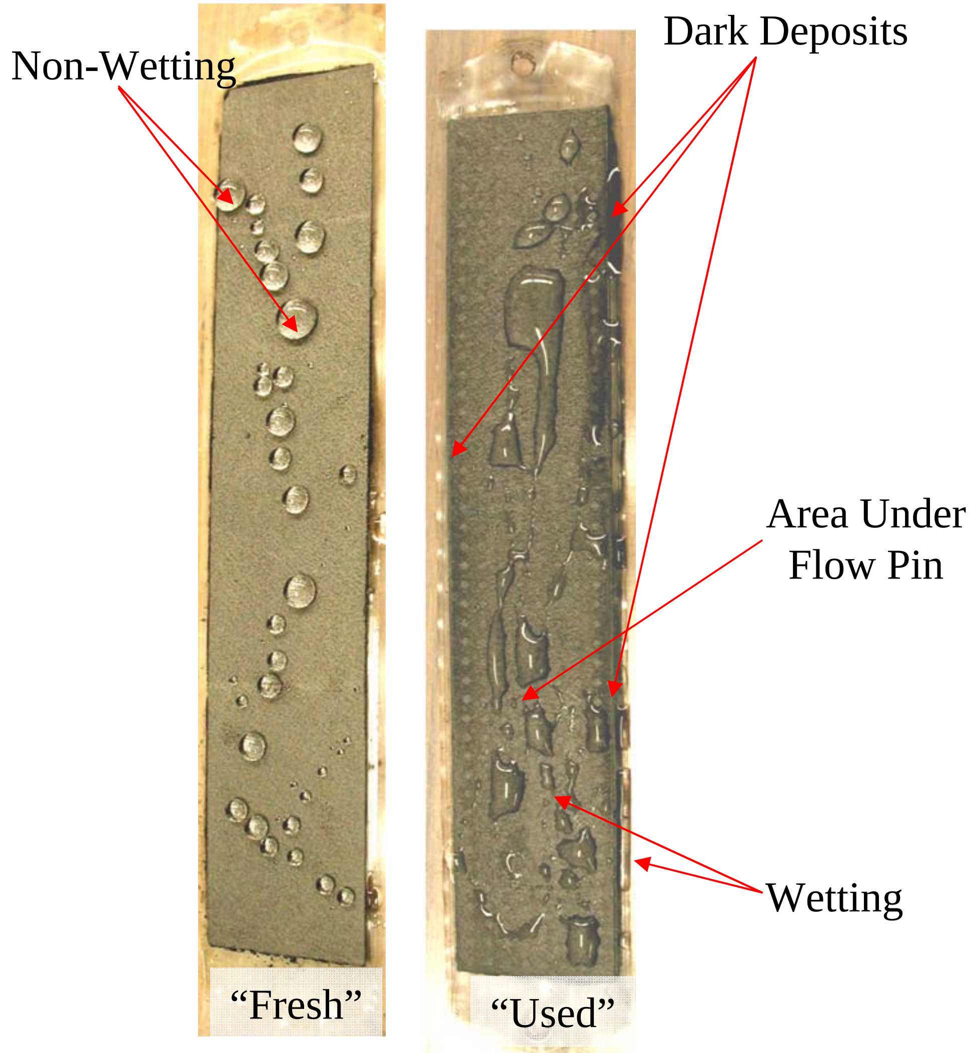




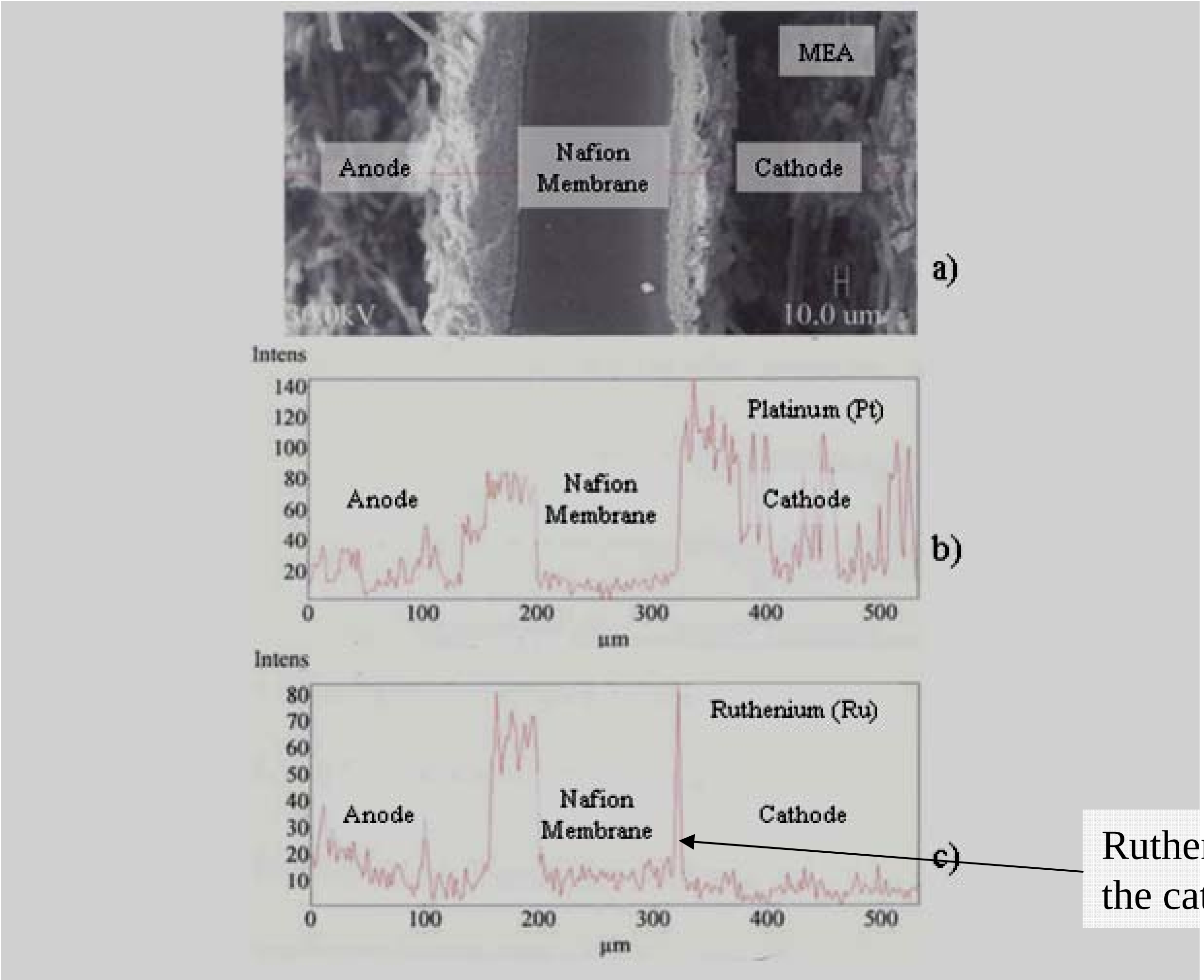
- Diffuser cloth is located at the exit of the stack
- Brownish black precipitate was found on the cloth in contact with the stack
- Precipitate was identified as ruthenium

Stack Observations, MEAs

- 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



Ruthenium found at the cathode

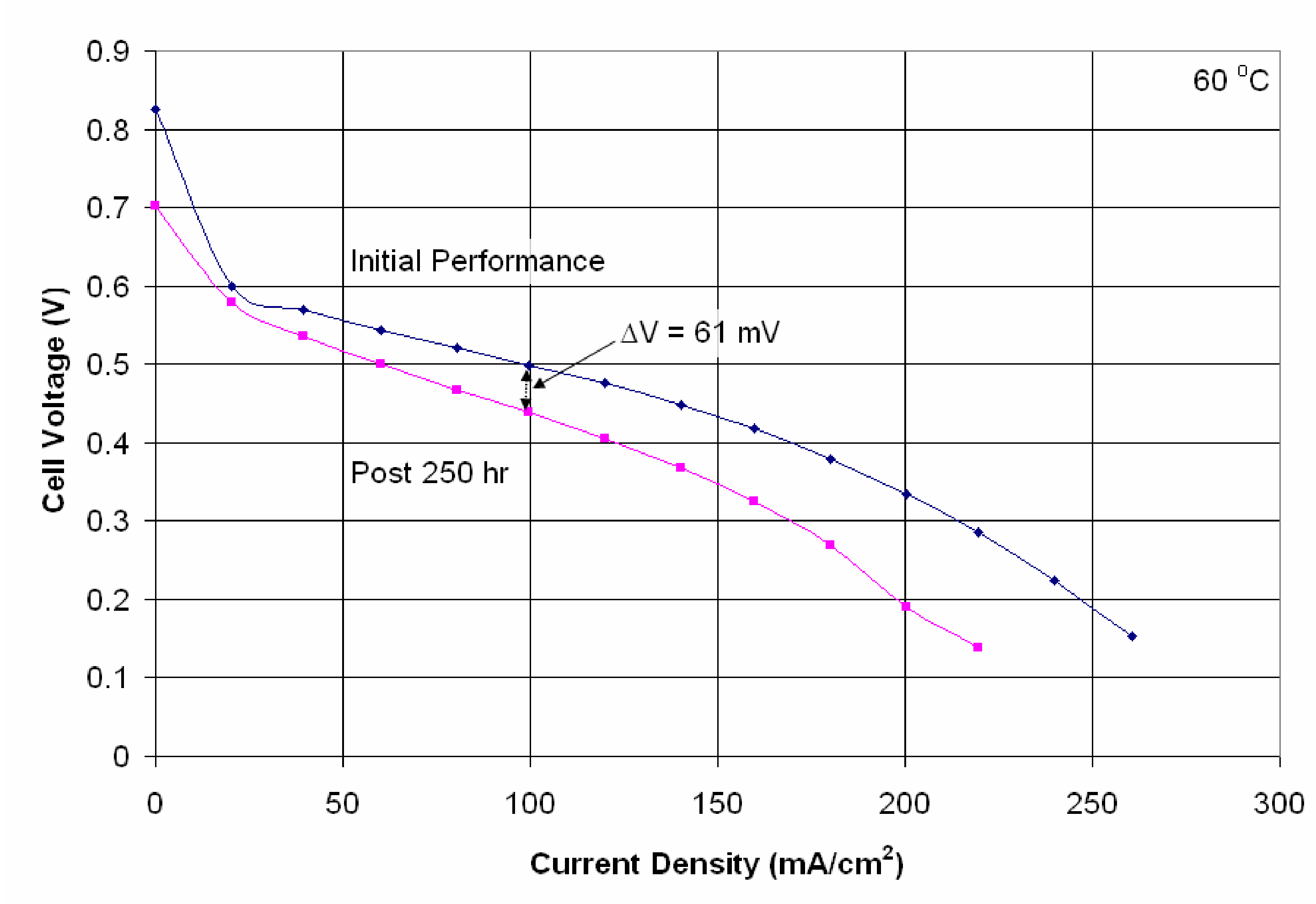
Pathways for Cell Degradation

- Degradation pathways
  - Mechanisms for Ruthenium dissolution:
    - ***Instability of platinum-ruthenium commercial catalyst***
    - Over discharge caused by shunt currents
  - Mechanisms for Loss of hydrophobicity at the cathode:
    - ***Inadequate Teflon content***
    - Deposition of RuO_2 at the cathode
- Experimental
  - MEAs Fabricated for Single-Cell Testing

MEA	Anode Catalyst	Cathode Paper Teflon Content
JPL	JPL	15%
JM	JM	15%
JMR	JM*	15%
JM-STD	JM	5%

  - Electrochemical Techniques
    - Initial IV Characterization
    - 250-hour constant-current test
    - Post IV Characterization
    - Anode Polarization

Cell Duration Testing – Single-Cell MEA Performance Comparison



- MEA performance degradation of 61 mV is observed

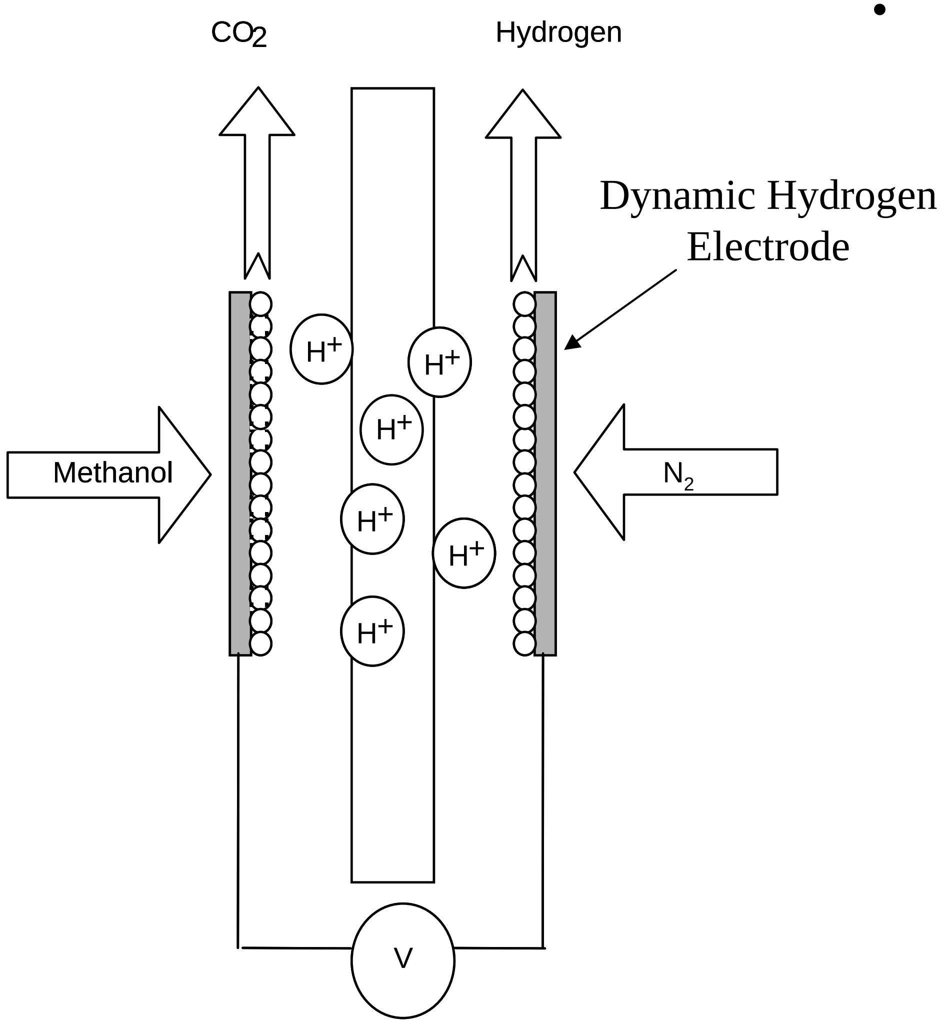
Duration Testing, Single-Cell MEA Analysis - Post 250-hr Testing Performance Summary

*40 ^{o}C

MEA	Formulation	Performance Decline (mV)		Performance Decline (mW/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
JM	Anode: Johnson Matthey Cathode: 15% Teflon	6	67	0.3	6.7
JMR	Anode: Reduced Johnson Matthey Cathode: 15% Teflon	30	107	1.5	10.7
JM-STD	Anode: Johnson Matthey Cathode: 5% Teflon (Standard)	6	96	0.3	9.6

- MEAs fabricated with the commercial Johnson Matthey catalyst exhibited the best performance.
- The test standard, JM-STD, performed the best

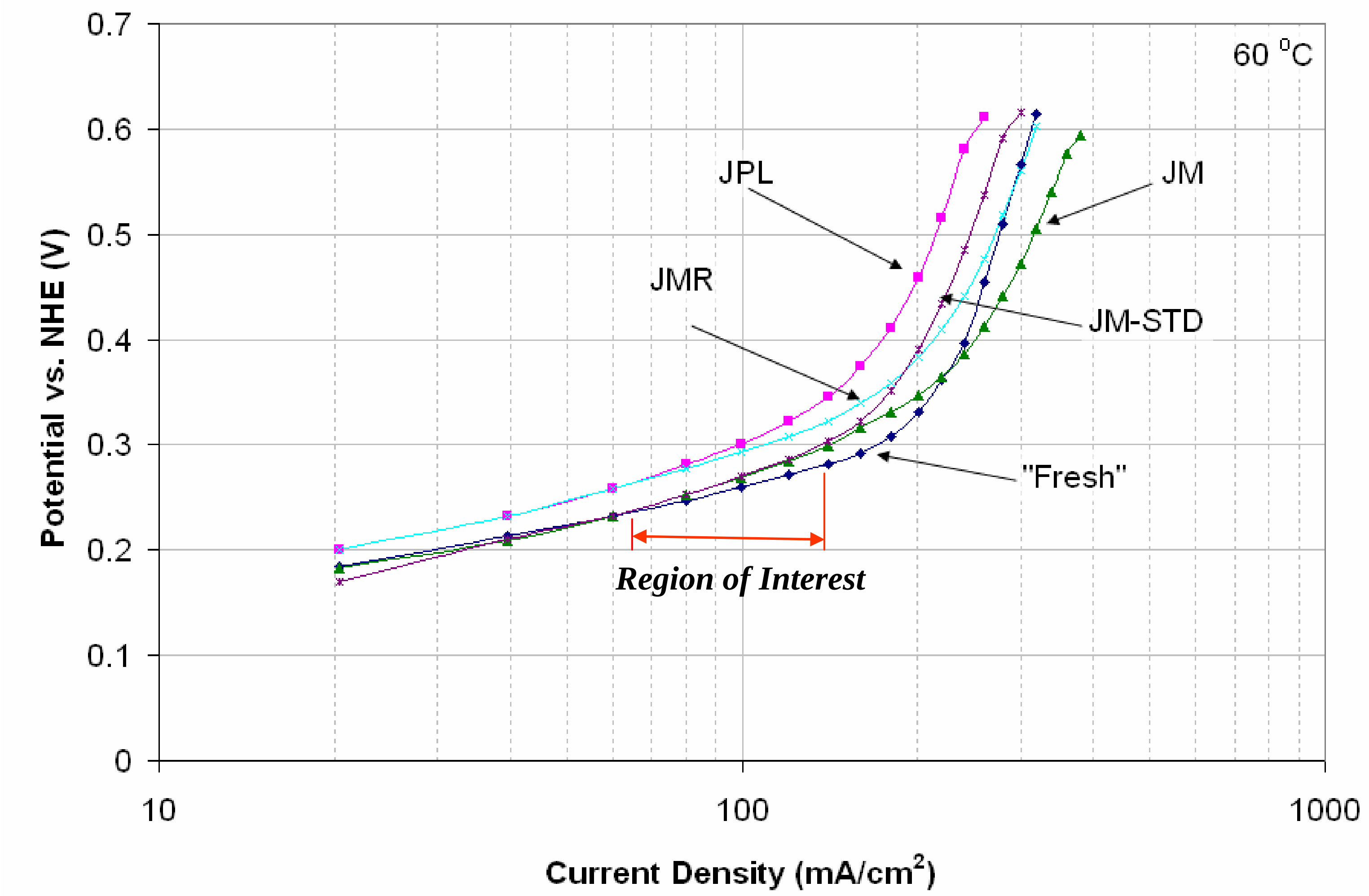
Anode Polarization Subtraction



- Polarization Analysis
  - When the cell is polarized, the resultant curve will be $\mathbf{E_a}$ vs. current density at the chosen operating temperature of the cell.
  - $\mathbf{V_{cell}}$ can be added to $\mathbf{E_a}$ at the same molarity and temperature to get $\mathbf{E_c}$.

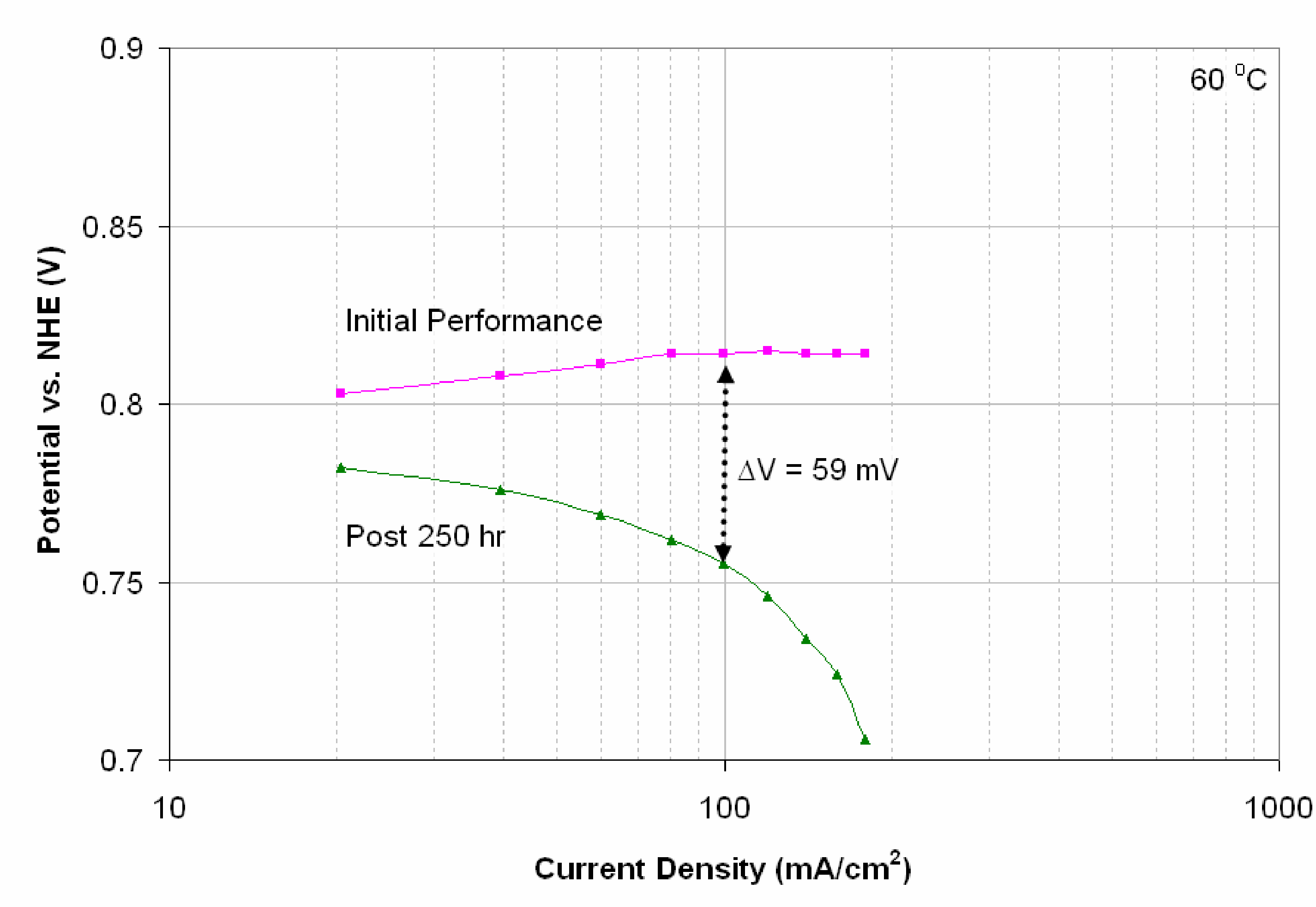
$$E_c = V_{cell} + E_a$$

Duration Testing, Single-Cell MEA Analysis - Anode Performance



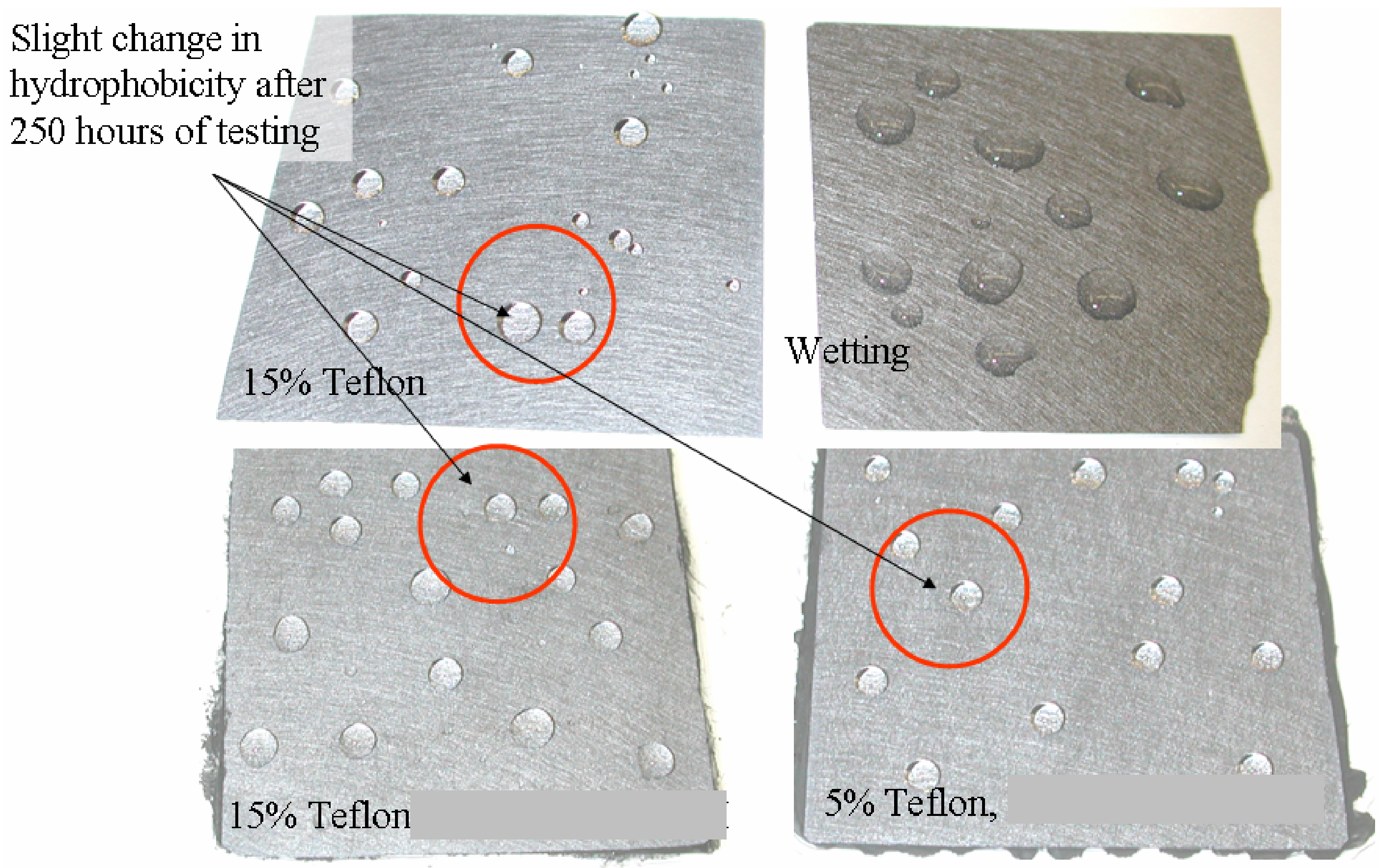
- Anode polarization analysis of the single-cell MEAs reveals minimum changes anode performance

Duration Testing, Single-Cell MEA Analysis - Cathode Performance

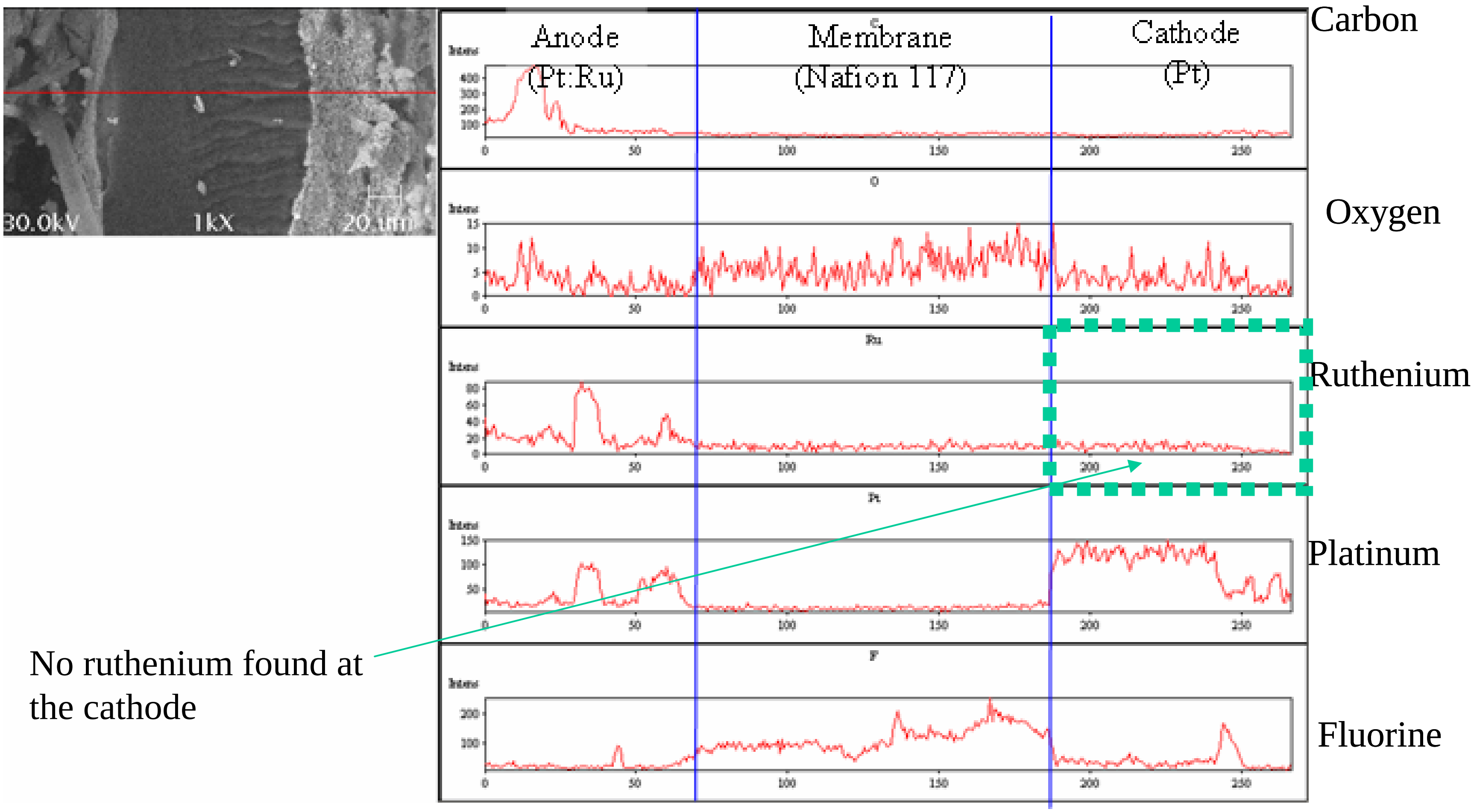


- MEA performance degradation is attributed to losses in cathode performance

Duration Testing, Single-Cell MEA Analysis - Cathode Hydrophobicity Comparisons

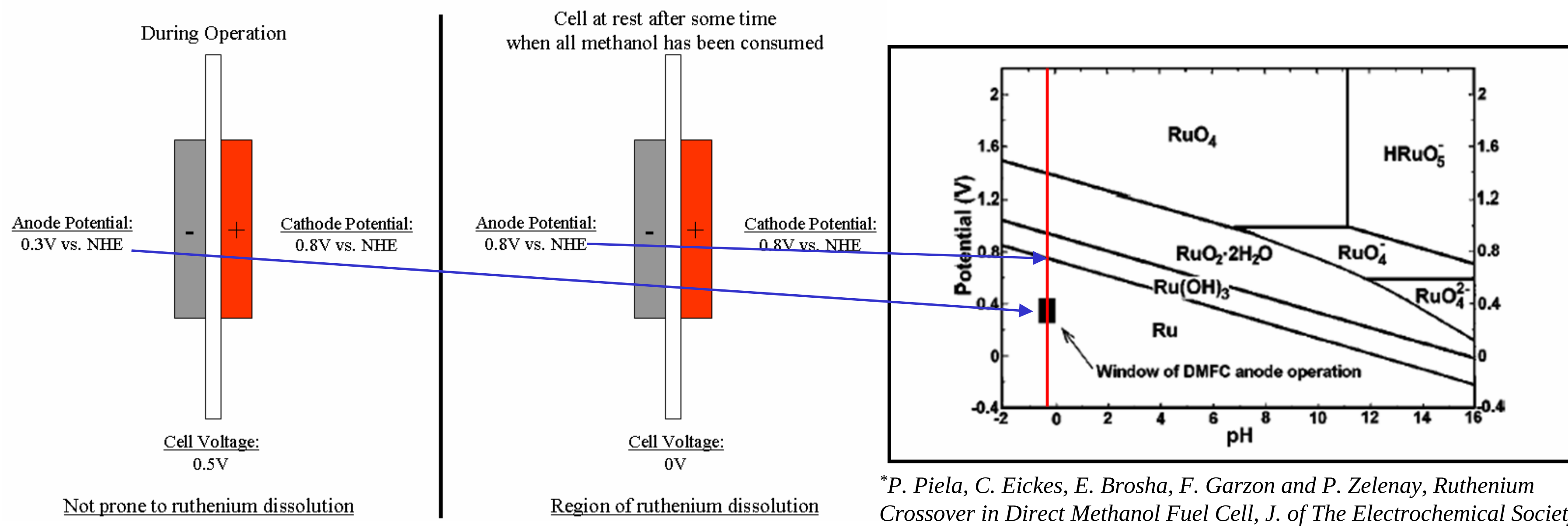


Duration Testing, Single-Cell MEA Analysis - EDAX Analysis



No ruthenium found at the cathode

Stack Degradation Analysis – Over-discharge

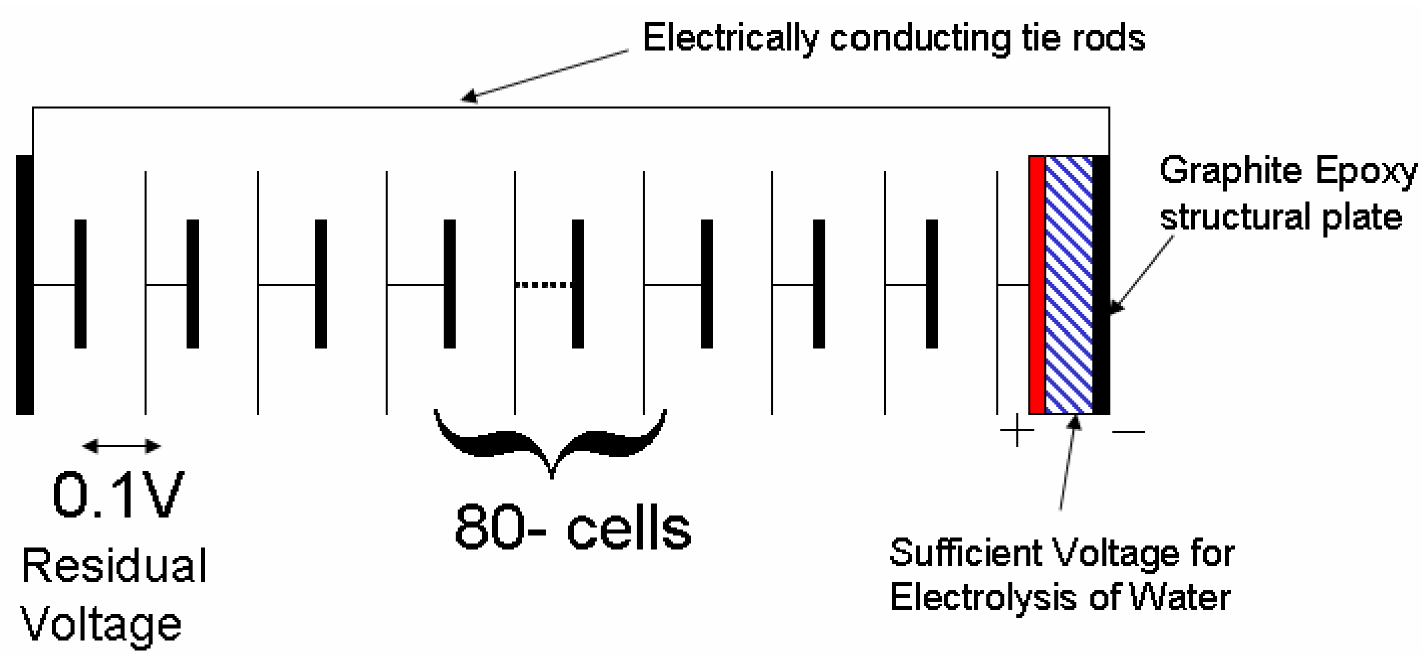


P. Piela, C. Eickes, E. Brosha, F. Garzon and P. Zelenay, Ruthenium Crossover in Direct Methanol Fuel Cell, J. of The Electrochemical Society, 151 (12) A2053-A2059, 2004

1. Reactions without methanol at the anode:
   - Anode: $Ru + 3H_2O \rightarrow Ru(OH)_3 + 3e^- + 3H^+$
   - Cathode: $3/2O_2 + 3H^+ + 3e^- \rightarrow 3H_2O$
2. Ru^{3+} migrates through the Nafion membrane
3. Ruthenium reaction at the Cathode:

$$2Ru(OH)_3 + 1/2O_2 \rightarrow 2RuO_2 + 3H_2O$$

Stack Degradation Analysis - 80-Cell Stack Electrical Schematic



- Open-to-air cathode stack designs allow for an elevated cathode potentials
- Stack shut down will lead to some cells depleting methanol before others
- Cells with methanol will drive cells without methanol negative (Over-discharge)
- The stack potential from residual cell voltages, moisture, conducting tie rods and structural endplates facilitated the flow of shunt currents

Conclusions

- Dissolution of ruthenium was observed in the 80-cell stack
- Duration testing was performed in single cell MEAs to determine the pathway of cell degradation
  - EDAX analysis on each of the single cell MEAs has shown that the Johnson Matthey commercial catalyst is stable in DMFC operation for 250 hours, <u>no ruthenium dissolution was observed</u>
  - Changes in the hydrophobicity of the cathode backing papers was minimum
  - Electrode polarization analysis revealed that the MEA performance loss is attributed to changes in the cathode catalyst layer
- Ruthenium migration does not seem to occur during cell operation but can occur when methanol is absent from the anode compartment, the cathode compartment has access to air, and the cells in the stack are electrically connected to a load (Shunt Currents).
- The open-to-air cathode stack design allowed for:
  - The MEAs to have continual access to oxygen
  - The stack to sustain shunt currents
- Ruthenium dissolution in a DMFC stack can be prevented by
  - Developing an internally manifolded stacks that seal reactant compartments when not in operation
  - Bringing the cell voltages to zero quickly when not in operation
  - Limiting to total number of cells to 25 in an effort to limit 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 Operational Test and Evaluation, Dr. Deryn Chu of the Army Research Laboratory, was managed by Dr. George Shoemaker, Executive Agent for Embedded Instrumentation projects, and Mr. Henry C. Merhoff of the U. S. Army Operational Test Command, Ft. Hood. Dr. Stephen Zakanycz of Institute for Defense Analyses provided both technical and programmatic consulting assistance to this program.