

Fuel Cell Development at the Jet Propulsion Laboratory

By

Thomas I. Valdez

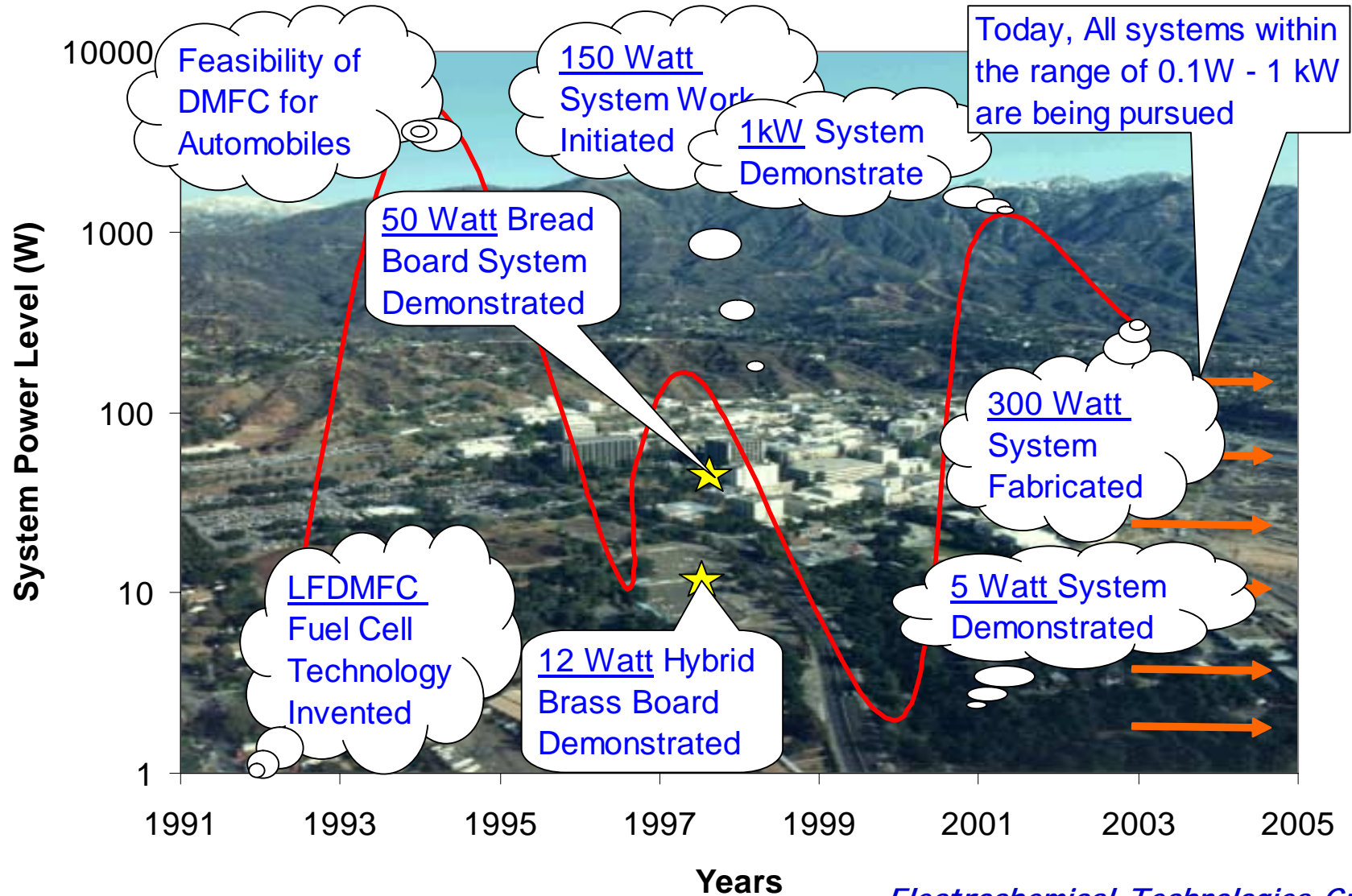
Jet Propulsion Laboratory, California Institute of Technology

MEA Fabrication Workshop, University of Illinois,
Urbana-Champaign
June 26th, 2005

Presentation Outline

- Fuel Cell Research at the Jet Propulsion Laboratory
 - Systems Development
 - Fuel Cell Group Members
- JPL's Role and Responsibilities for the NASA ECP Program
 - Task Overview
 - Program Schedule
- DMFC MEA Testing Techniques
 - Test Stand Setup
 - Cell Voltage-Current Characterization
 - Anode Polarization
 - Methanol Crossover
- DMFC MEA Fabrication Studies
- Methanol-Hydrogen Peroxide Studies
- DMFC System Design
- ECP Program Status
 - Accomplishments
 - Program Schedule Detail
 - Future Work

DMFC System Development Progress at JPL





Fuel Cell Team

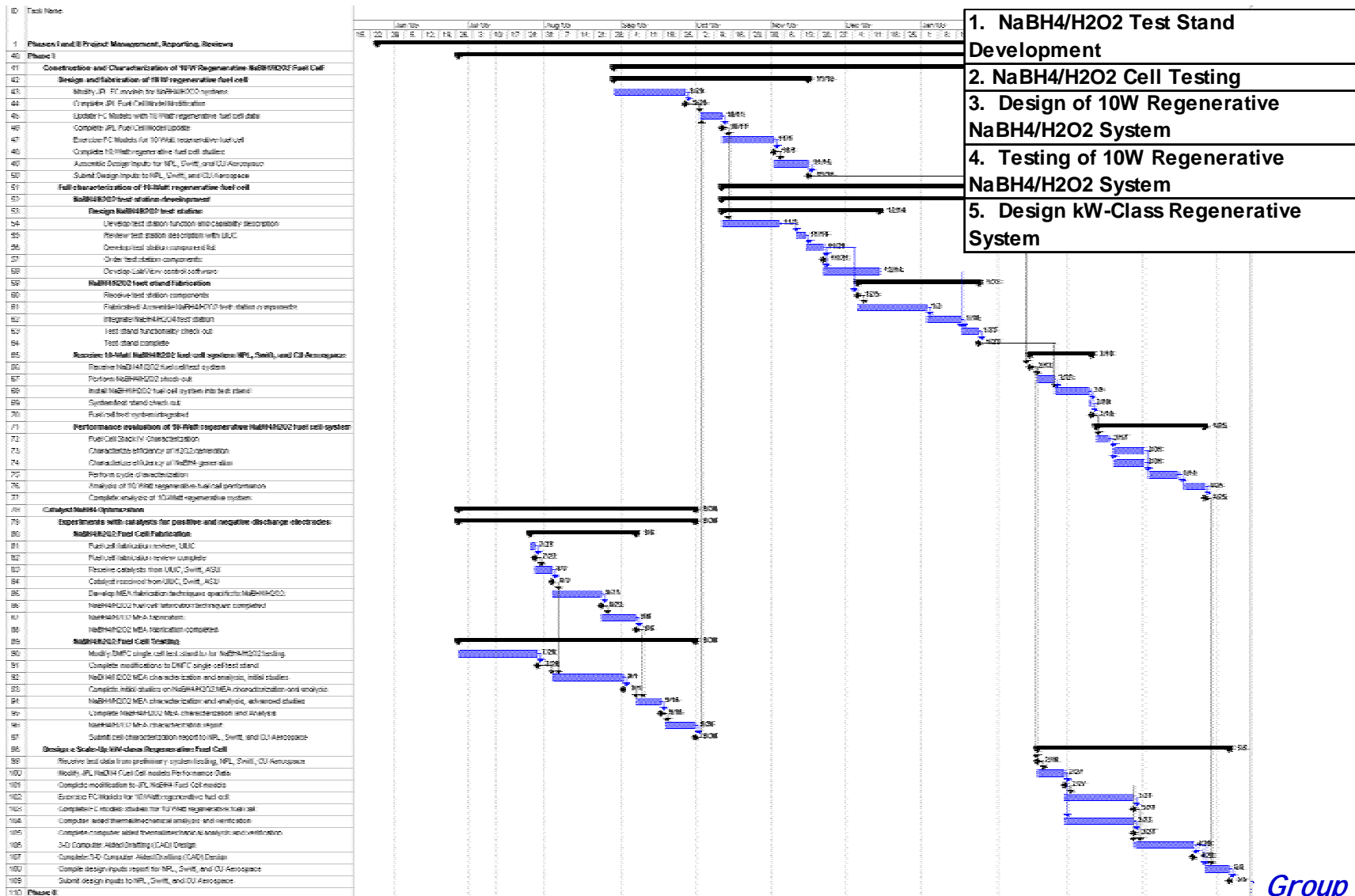
- Program Manager
 - R. Surampudi (Power Systems Manager)
- Technical Team
 - S. R. Narayanan (DMFC Team Leader, Electrochemical Technologies Group Supervisor)
 - T. I. Valdez (Principal Investigator)
 - J. F. Whitacre (Advanced Catalyst Development)
 - A. Kindler (System Design/ Component Selection)
 - S. Firdosy (Laboratory Support)
 - D. Suazo (Laboratory Support)
 - F. Clara (Lab Materials Processing)
 - E. Yen (Materials Support)
 - A. Abatahi (Electronics Development)
 - M. Young (Mechanical Support)
 - P. Shakottai (Thermal and Fluids Modeling)

JPL Task Overview

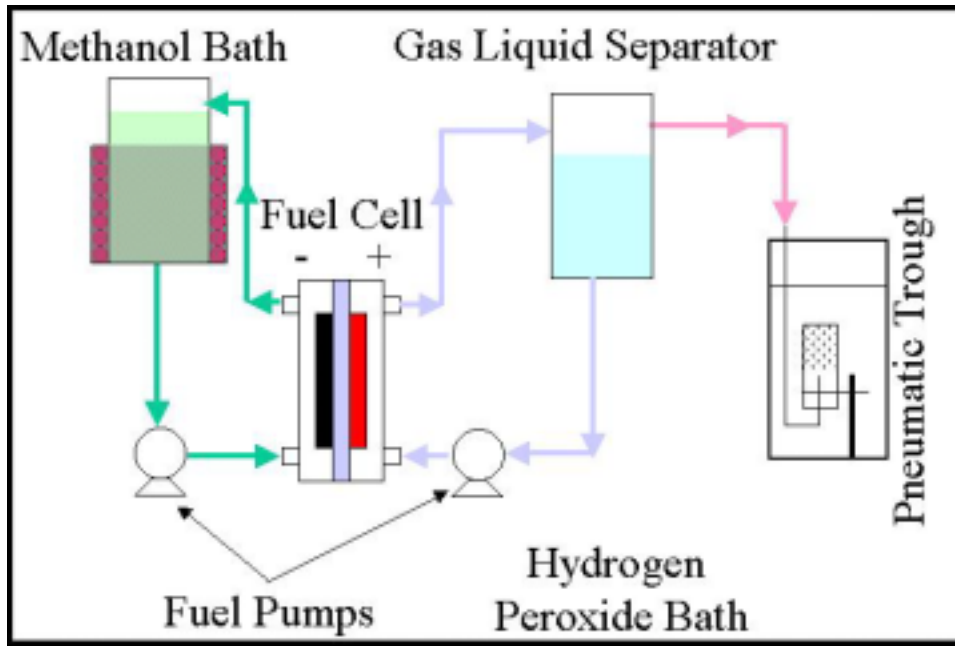
- Technical Objectives of Phase-I
 - Characterize state-of-art NaBH₄/H₂O₂ fuel cells
 - Evaluate new materials supplied by partners for improving reactant regeneration in NaBH₄/H₂O₂ regenerative fuel cells
 - Test a NaBH₄/H₂O₂ regeneration fuel cell based system fabricated by the industry team members
 - Support the development of a preliminary system design for kW-class regenerative NaBH₄/H₂O₂ fuel cell based power source
- Technical Objectives of Phase-II
 - Characterize the performance of a kW-class NaBH₄/H₂O₂ regeneration fuel cell system fabricated by the industry team members



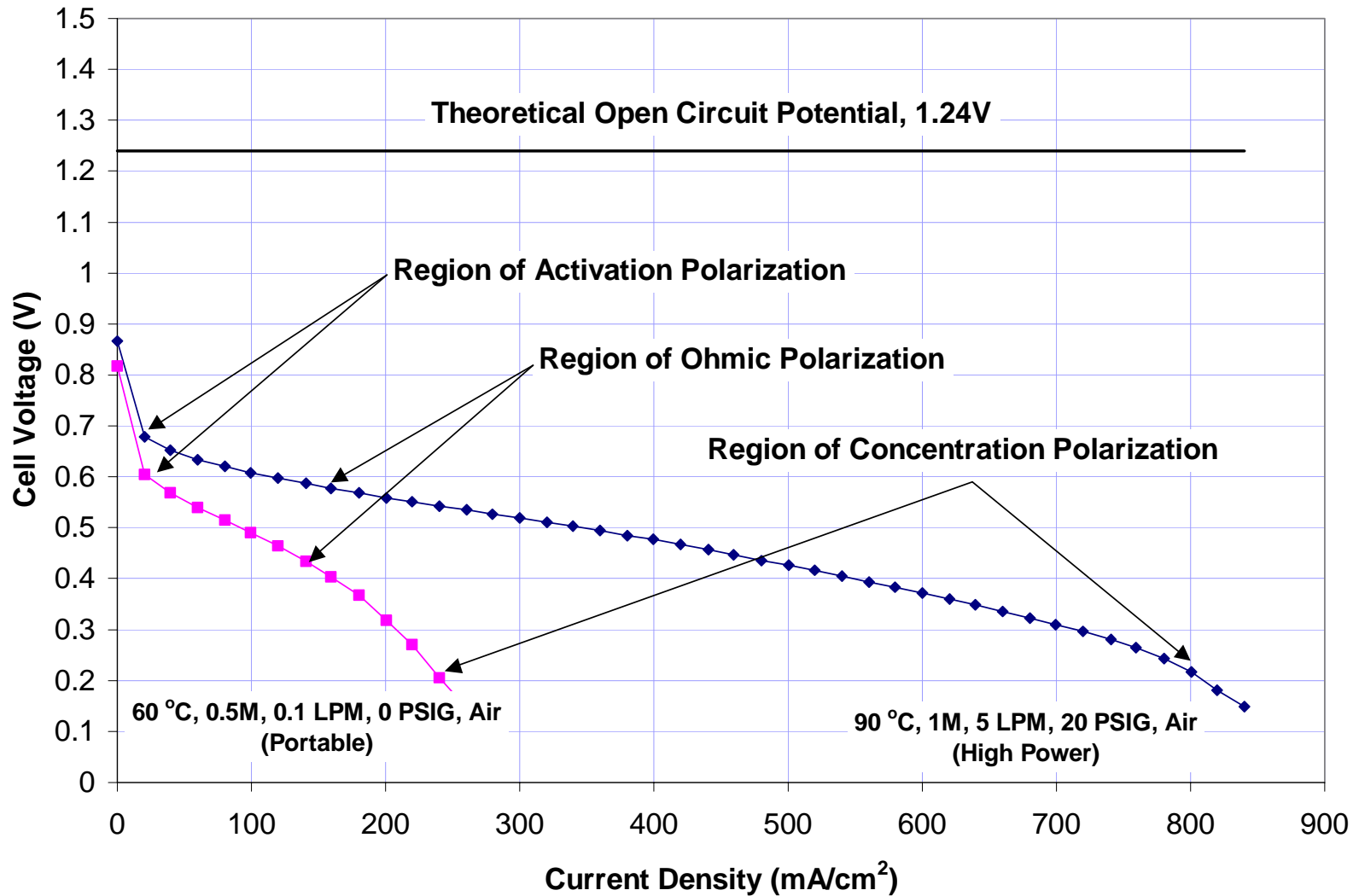
Phase I Project Schedule



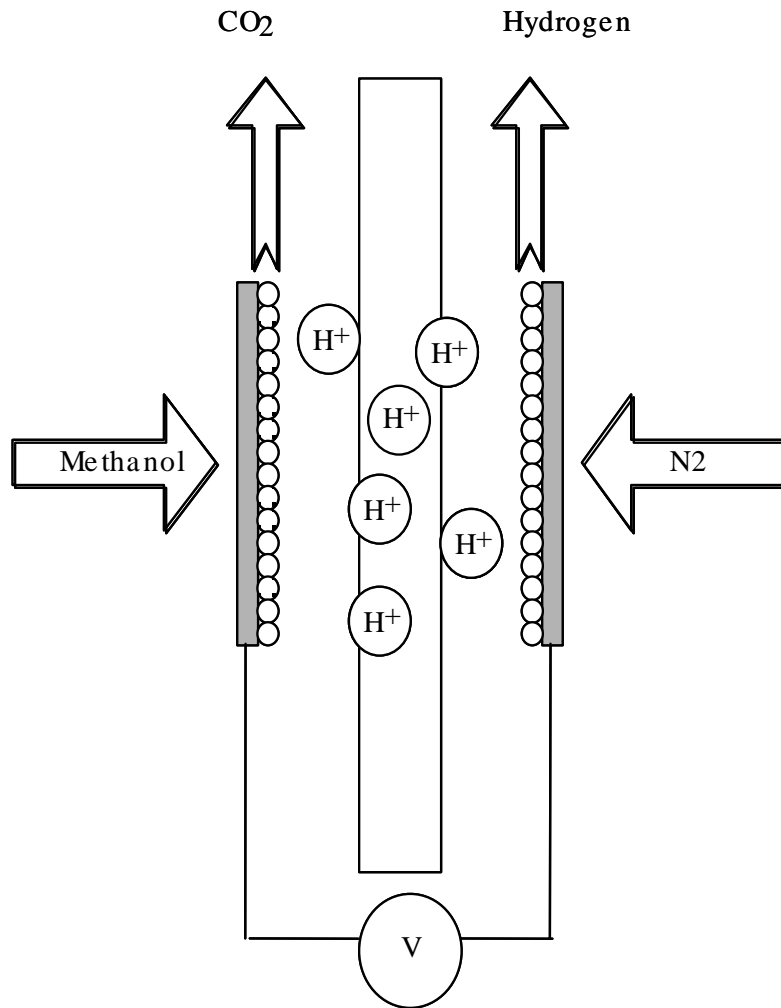
DMFC MEA Testing Techniques: Testing Schematic



DMFC MEA Testing Techniques: Cell Polarization



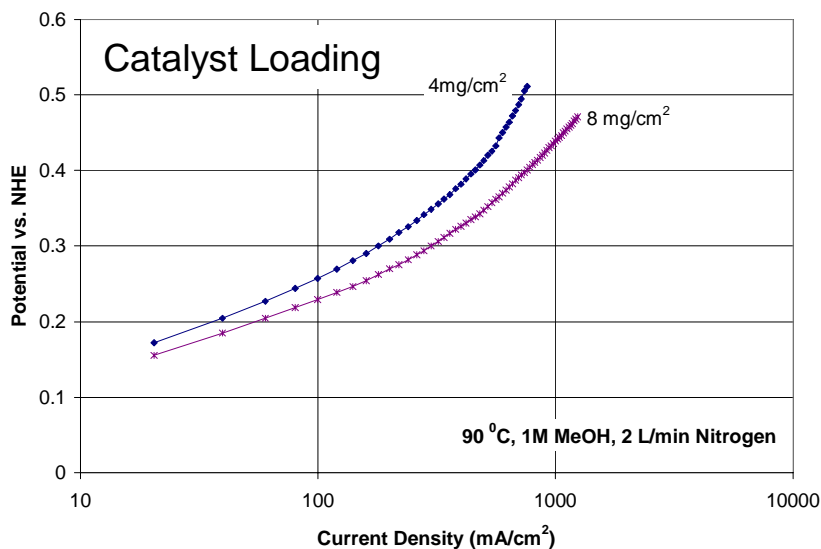
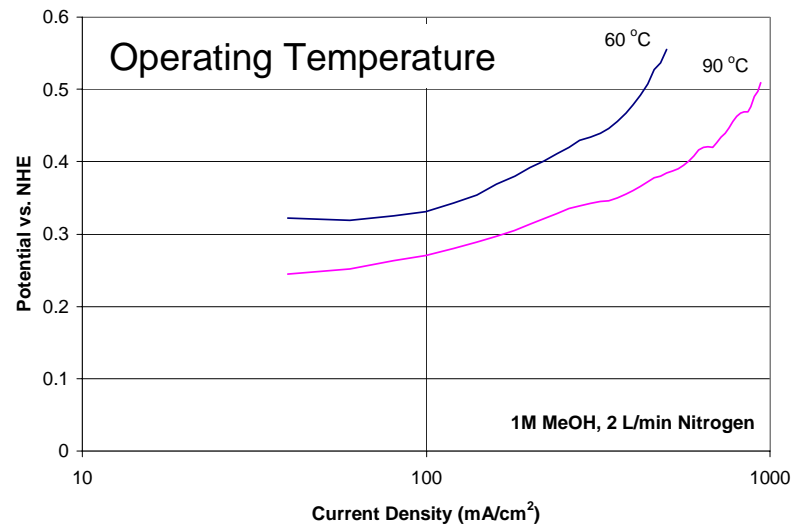
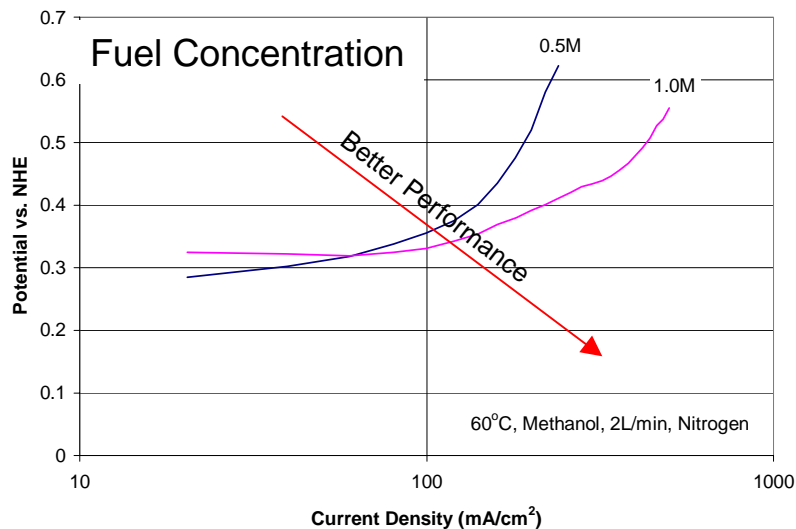
DMFC MEA Testing Techniques: Anode Polarization Subtraction



- 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 E_a vs. current density at the chosen operating temperature of the cell.
- Polarization Analysis
 - E_{cell} , at any air flow rate, can be added to E_a at the same molarity and temperature to get E_c corresponding to the flow rate.

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

DMFC MEA Testing Techniques: Factors Affecting Anode Performance

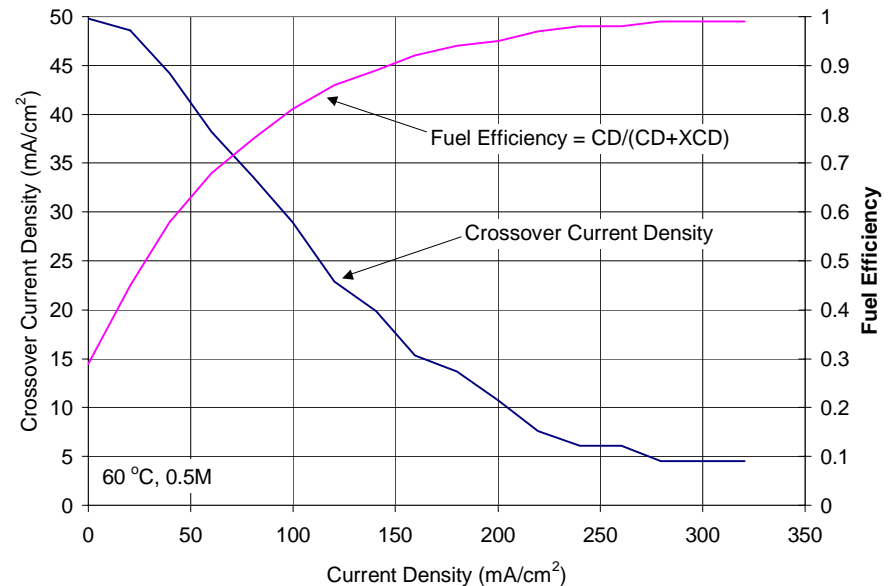
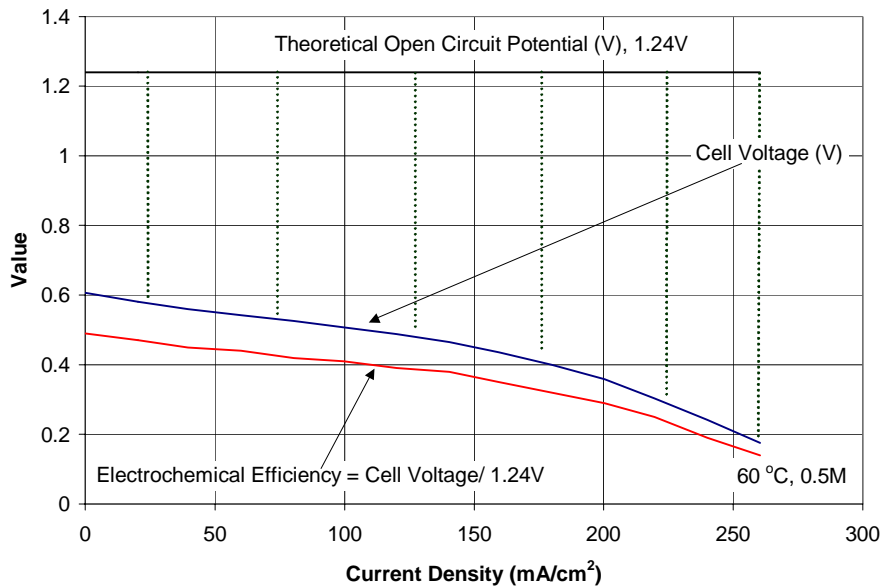


- Fuel concentration, operating temperature and catalyst loading all effect methanol oxidation on Pt-Ru catalyst

DMFC MEA Testing Techniques: Methanol Crossover

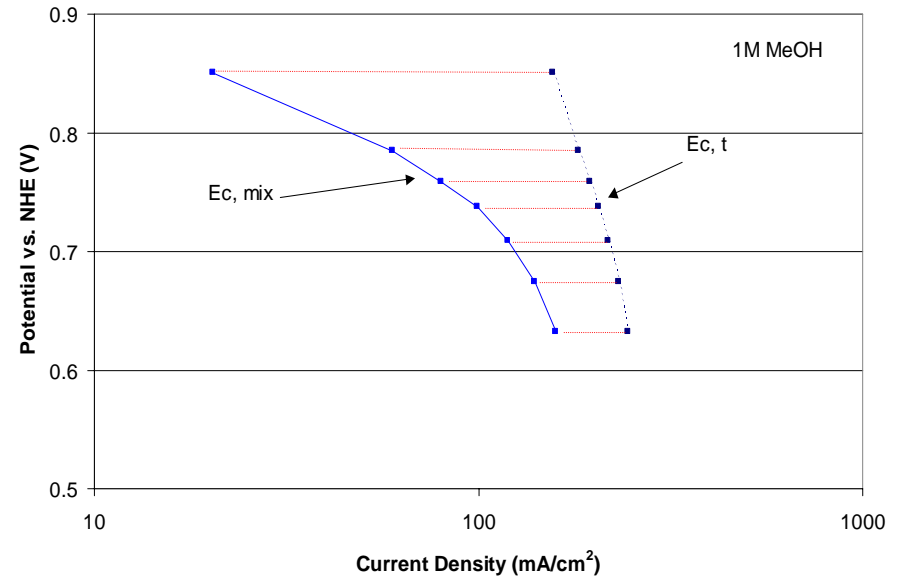
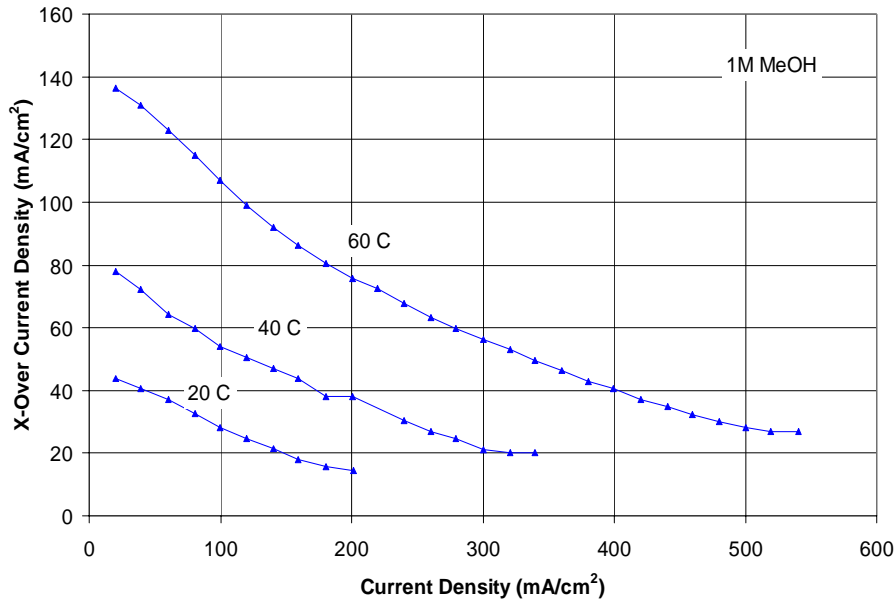
- Measuring and quantifying methanol crossover.
 - The cathode exit stream is exhausted into a CO₂ analyzer. (Horiba VIA-550)
 - An effective current is calculated from the volume % of CO₂ detected in the analyzer.
 - The current is normalized by the cell active area and reported as an crossover current density.
- Calculation
 - Convert CO₂ Volume % into a volume flow rate of CO₂.
 - Use Ideal Gas Law to calculate mole of CO₂/sec.
$$n = PV/RT$$
 - Use Faraday's Law to calculate out an effective current which can be normalized into a current density.
$$I = n F n_e$$
- Advantages of this method
 - Can see the effects of anode methanol consumption on crossover.
 - Is a true reflection of the CO₂ production in an operating cell.

DMFC MEA Testing Techniques: Efficiency Calculations



- Electrochemical Efficiency is determined by the cells deviation from its thermal neutral potential as a result of polarization. $\eta_{\text{Electrochem}} = \text{Cell Voltage} / 1.24\text{V}$
- Fuel Efficiency is determined by the ratio of applied current to total current density. $\eta_{\text{Fuel}} = CD / (CD + XCD)$
- Cell Efficiency is the product of both Electrochemical Efficiency and Fuel Efficiency. $\eta_{\text{Cell}} = \eta_{\text{Electrochem}} * \eta_{\text{Fuel}}$

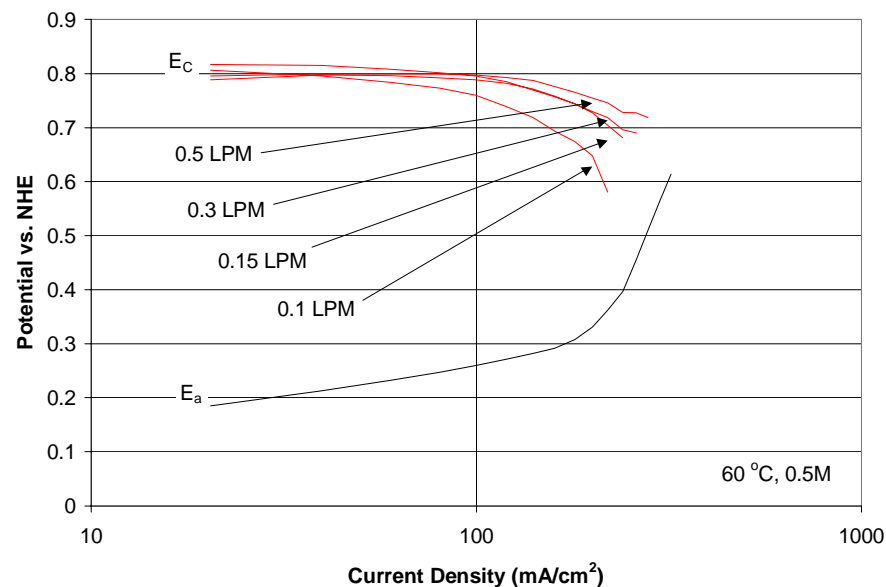
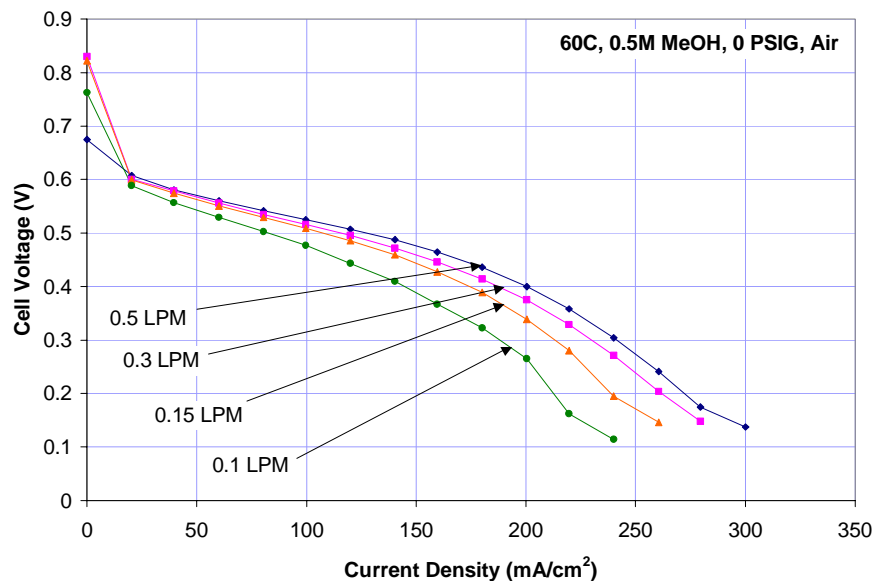
DMFC MEA Testing Techniques: Isolating The True Cathode potential



- When the effects of methanol crossover on the cathode are taken into account from an electrochemical standpoint, the true cathode potential is revealed.
- The total current applied to the cathode becomes:

$$I_{true} = I_{app} + I_{cr} \quad (4).$$
 Now $E_{c,mix}$ can simply be called E_c .
- E_c should be a constant regardless of methanol molarity.

DMFC MEA Testing Techniques: Cathode Performance



- Methanol crossover adversely effects cathode performance
 - Water produced from crossover can form a physical barrier to O₂ at the catalyst membrane interface. “Electrode Flooding”
 - Methanol is immediately oxidized at the cathode surface, thus is in competition with the protons for CO₂
- The general idea is to operate a fuel cell at the lowest possible airflow (Air Stoichiometry).

DMFC MEA Fabrication Studies: Motivation



Low Pressure 25 watt Stack ('95)



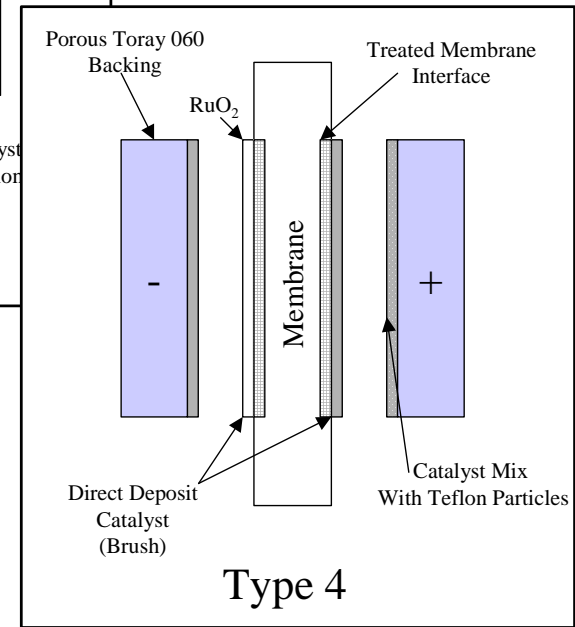
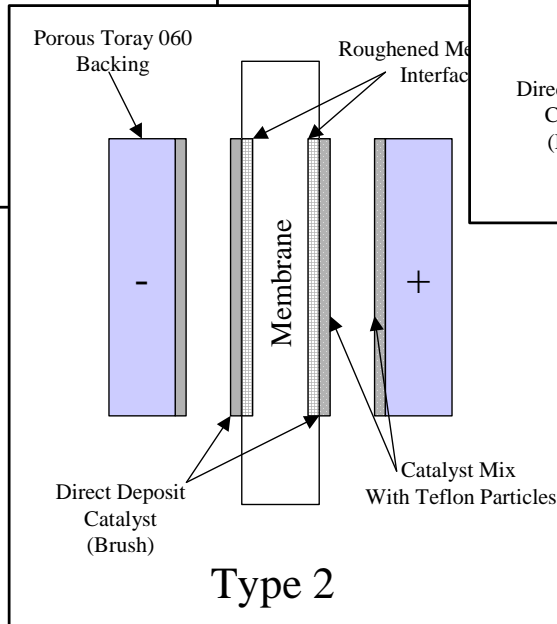
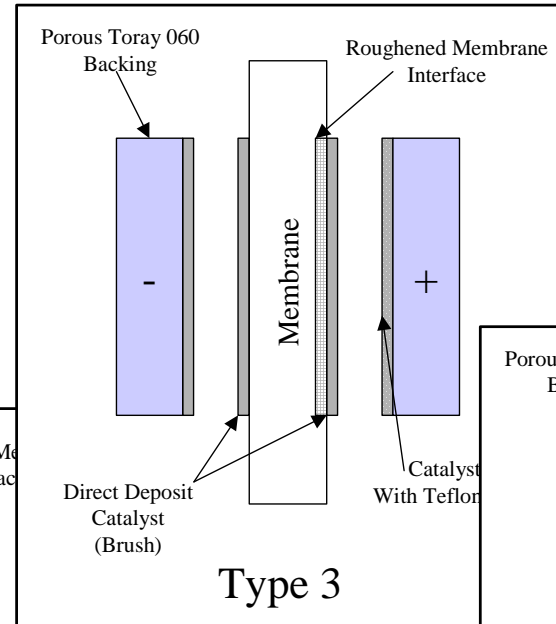
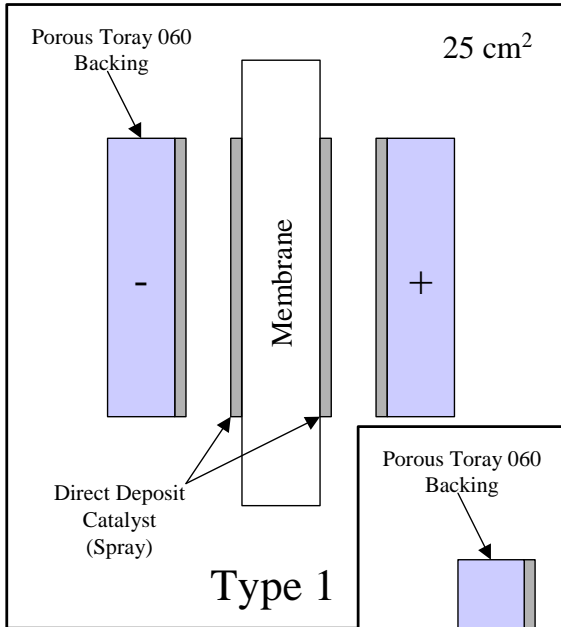
Ambient Pressure 25 watt Stack ('96)



Air-Breathing "Back-to-Back" Strip Cell ('00)

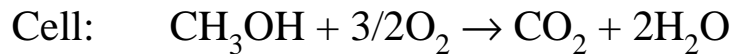
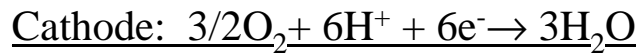
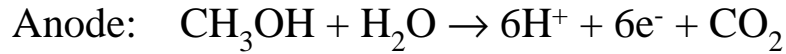
- Understanding the effects of electrode design on fuel cell performance at the low airflow rates is the motivation for this research.

DMFC MEA Fabrication Studies: Fabrication Techniques



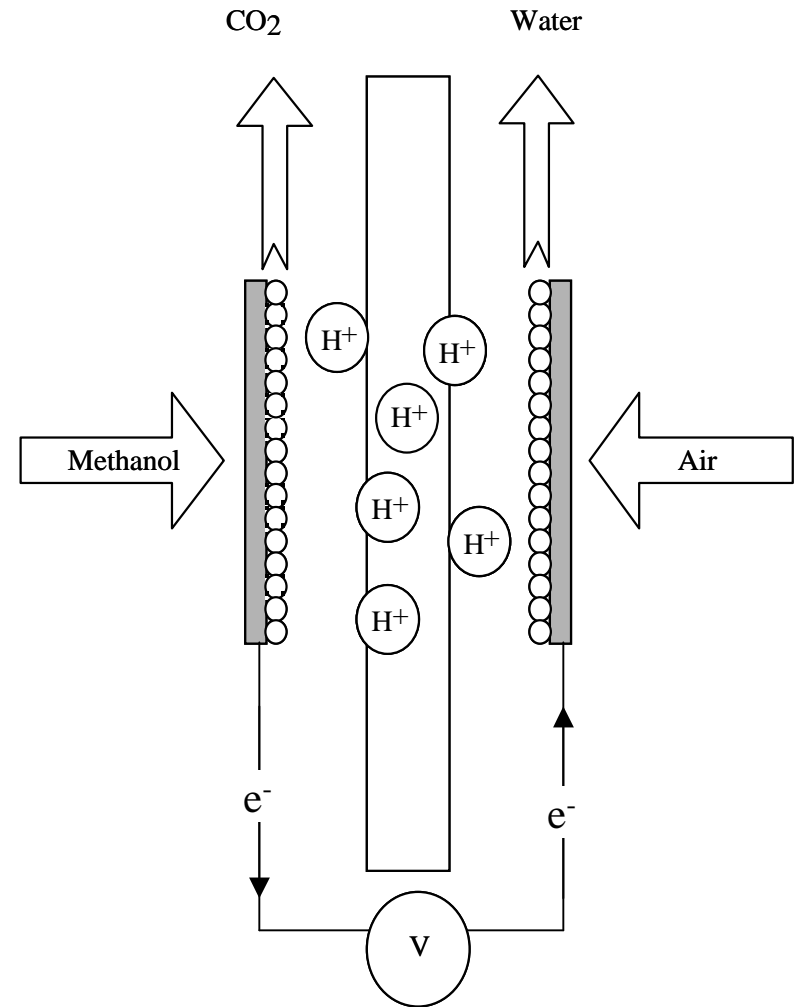
The Direct Methanol Fuel Cell

Direct Methanol Fuel Cell Reaction:



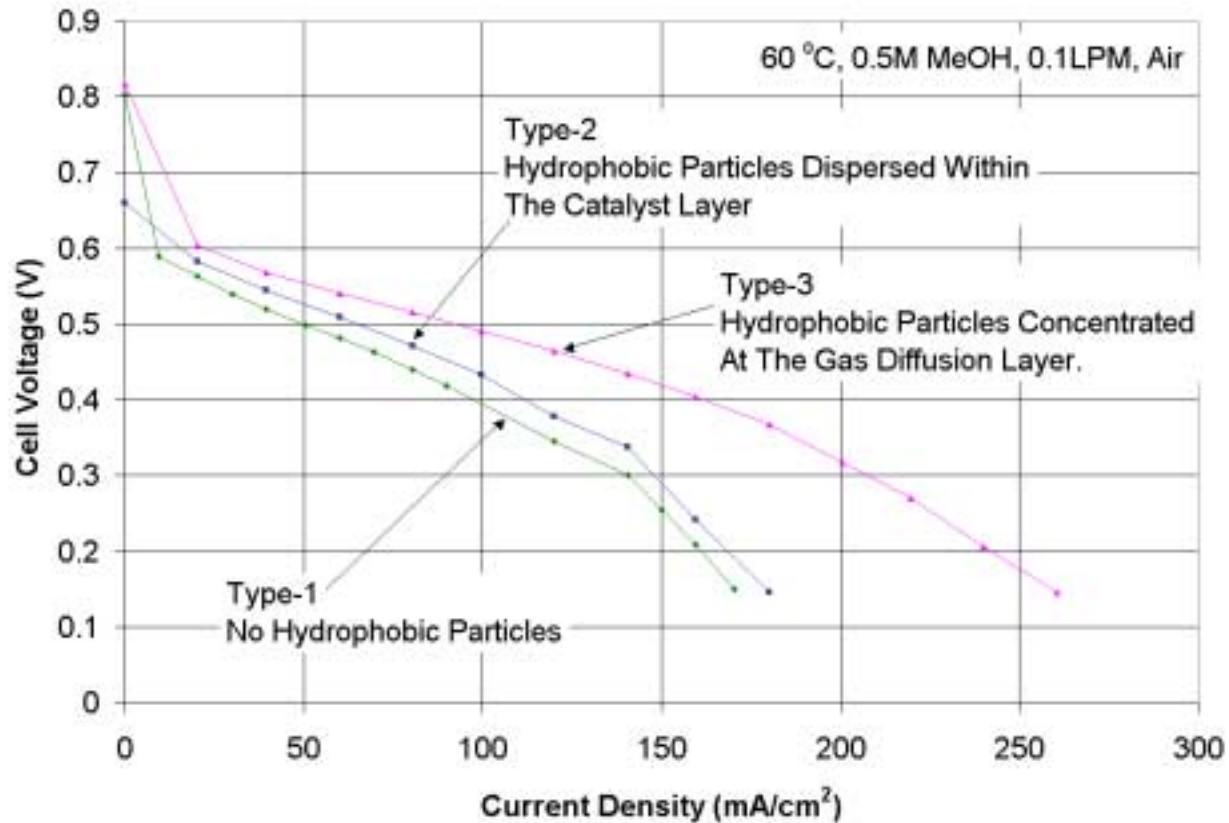
DMFC Advantages

- Safety of handling a liquid fuel versus compressed gas fuel tank (i.e. Hydrogen)
- Low methanol concentration (<3%) in the “working” fuel loop





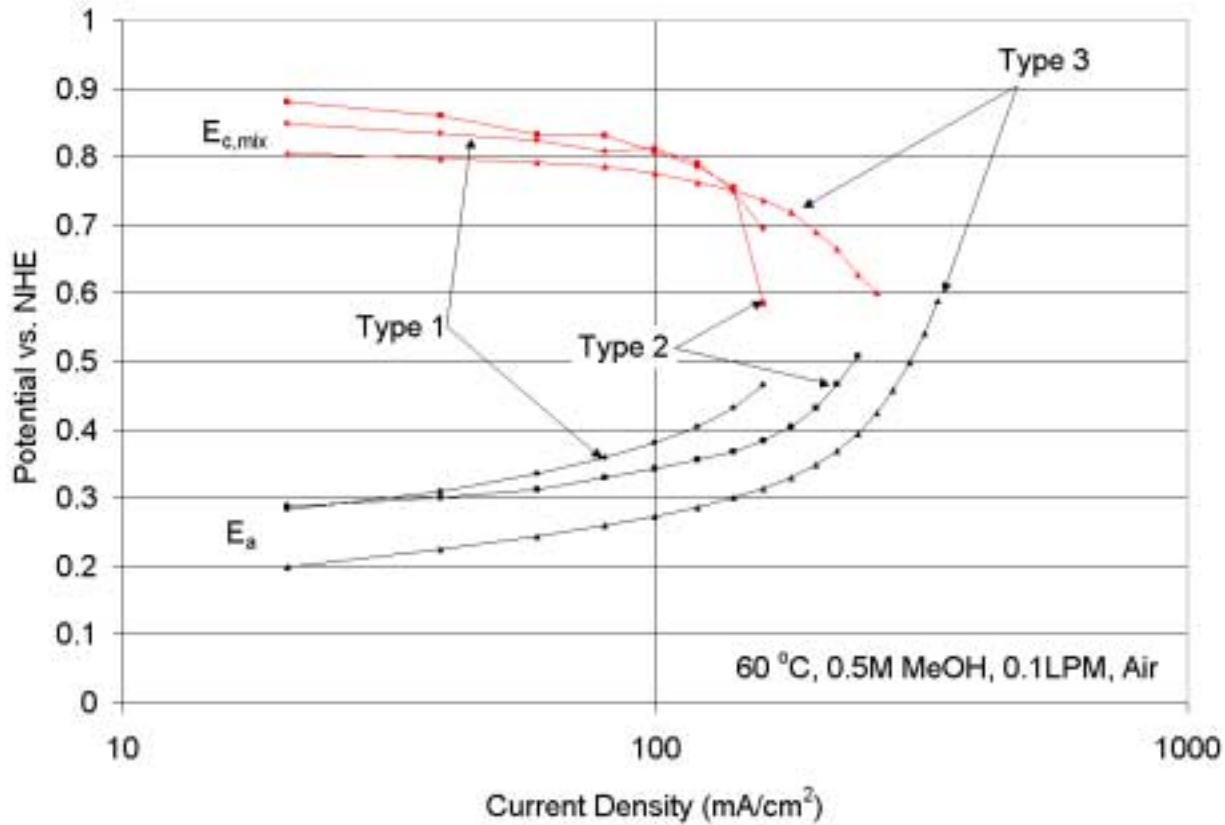
DMFC MEA Fabrication Studies: The Effect of Cathode Structure on DMFC Performance



- Hydrophobic particles have a beneficial effect on cell performance at low airflow rates.
- The location of the hydrophobic particles in the gas diffusion backing appears to be beneficial in realizing high performance.



DMFC MEA Fabrication Studies: Electrode Potentials as a Function of Applied Current Density



- Hydrophobic particles allow the oxidant easier access to the catalytic surfaces.
- Anode performance varies by application process and is dominated by electrode density or tortuosity

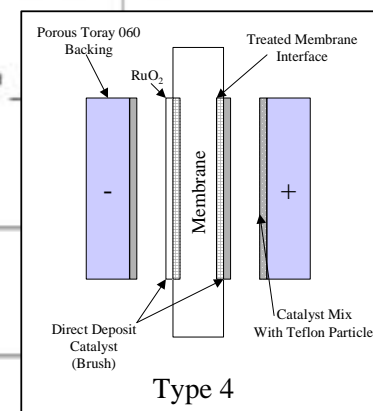
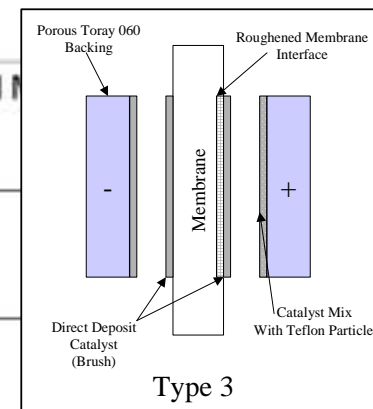
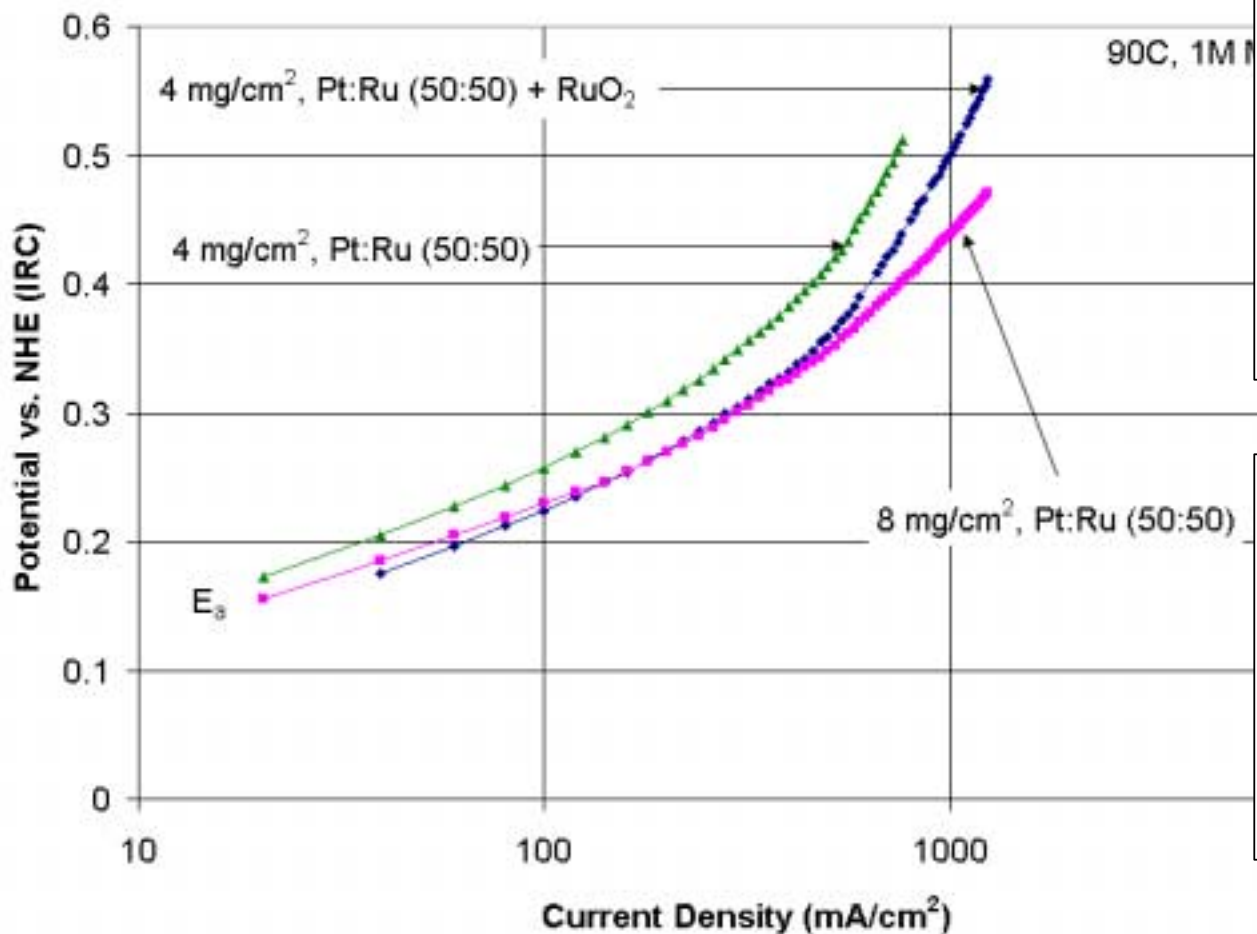
DMFC MEA Fabrication Studies: Summary of the Cell Performance for the Type 1, 2 and 3 MEAs

	<i>MEA Type</i>		
	1	2	3
<i>Peak Efficiency</i>			
Cell Efficiency (%)	23	27	29
Cell Voltage (V)	0.439	0.387	0.464
Applied Current Density (mA/cm ²)	80	120	120
Cell Power Density (mW/cm ²)	35.1	46.4	55.6
<i>Peak Power</i>			
Cell Efficiency (%)	23	25	27
Cell Voltage (V)	0.306	0.337	0.367
Applied Current Density (mA/cm ²)	120	140	180
Cell Power Density (mW/cm ²)	36.7	47.1	66.1

❖ 60 °C, 0.5M MeOH, 0.1 LPM, 0 PSIG

- Modifying the MEA electrode structure can result in an 80% increase in peak power density.
- The Type 3 MEA yields the highest performance.

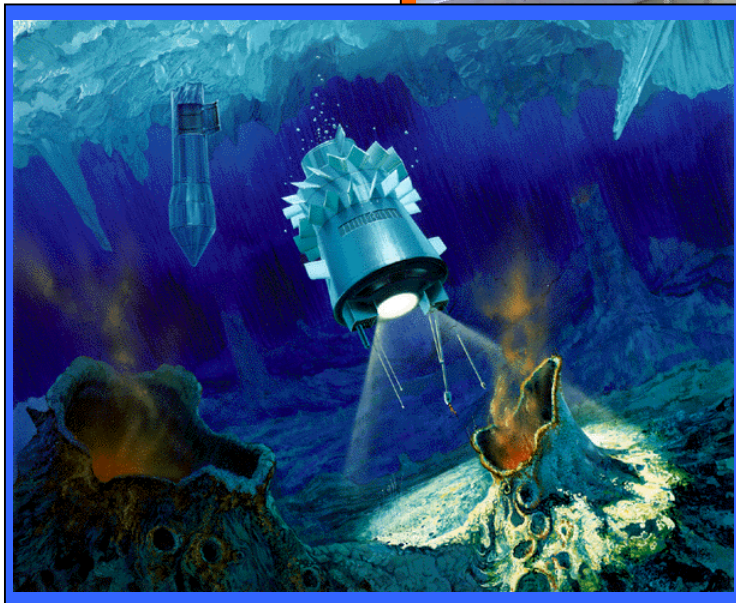
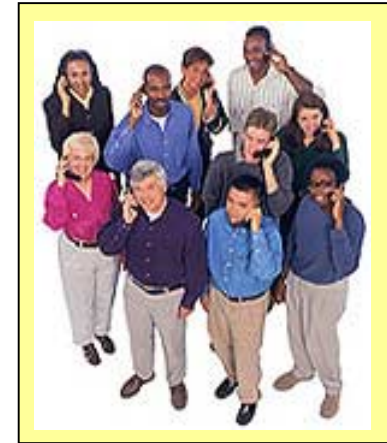
DMFC MEA Fabrication Studies: The Benefits of Hydrrous RuO_2 At The Anode Catalyst/ Membrane Interface



DMFC MEA Fabrication Studies: Conclusions

- The use of hydrophobic particles in the gas diffusion backing is key to attaining high cell performance at low airflow.
- A fuel cell operating point of 0.389 V at 180 mA/cm² is attainable at the system friendly operating conditions of 60 °C, 1.76 x Stoich.
 - Cell Efficiency: 29%
 - Cell Power Density: 70 mW/cm²
- The addition of hydrous RuO₂ to the anode/ membrane interface lowers the anode overpotential and allows for improved utilization of the catalyst.
- Electrically conductive proton conducting additives enhance the utilization of the catalyst and thus offer an alternative path to catalyst reduction.

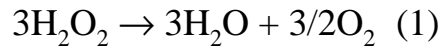
Methanol-Hydrogen Peroxide Studies: Motivation



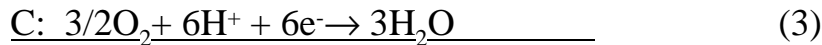
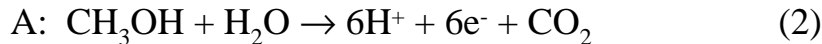
- Hydrogen peroxide can be used as an alternative oxidant for DMFC in any application which can see a limited amount of free convection air.

Methanol-Hydrogen Peroxide Fuel Cells

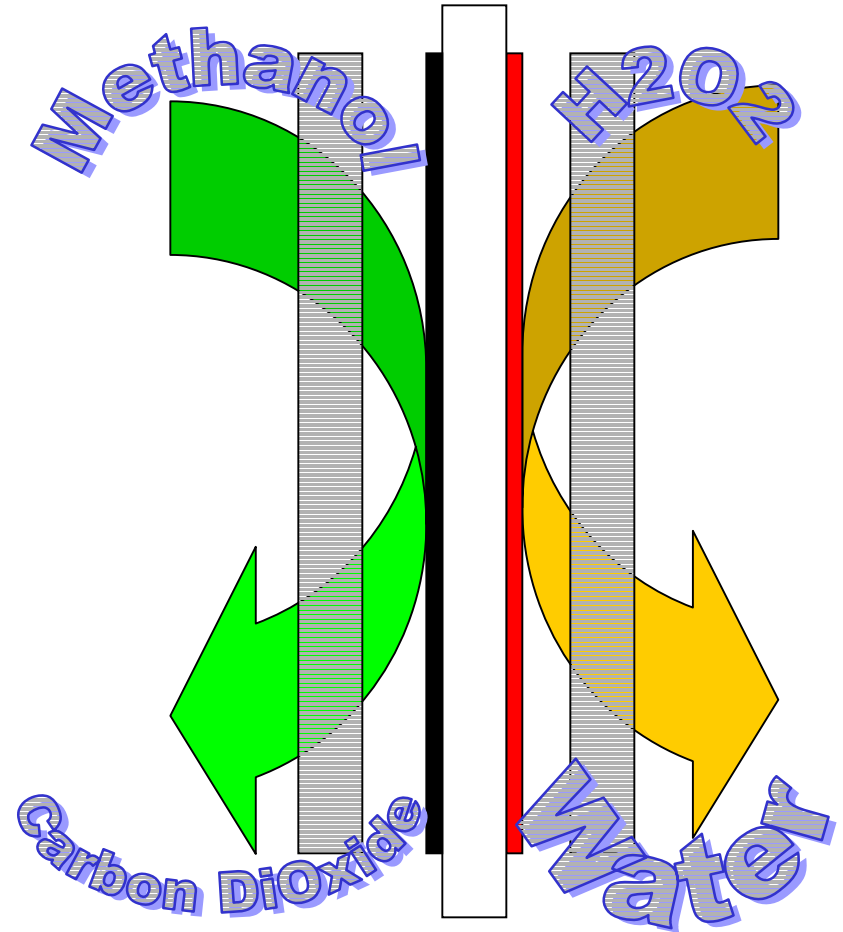
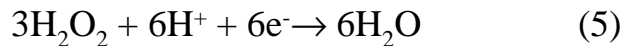
- When hydrogen peroxide is introduced to the cathode compartment of a direct methanol fuel cell it is decomposed to oxygen at the surface of the electrode backing and at the catalyst/ electrode-backing interface according to equation 1.



The fuel cell reactions are as follows:



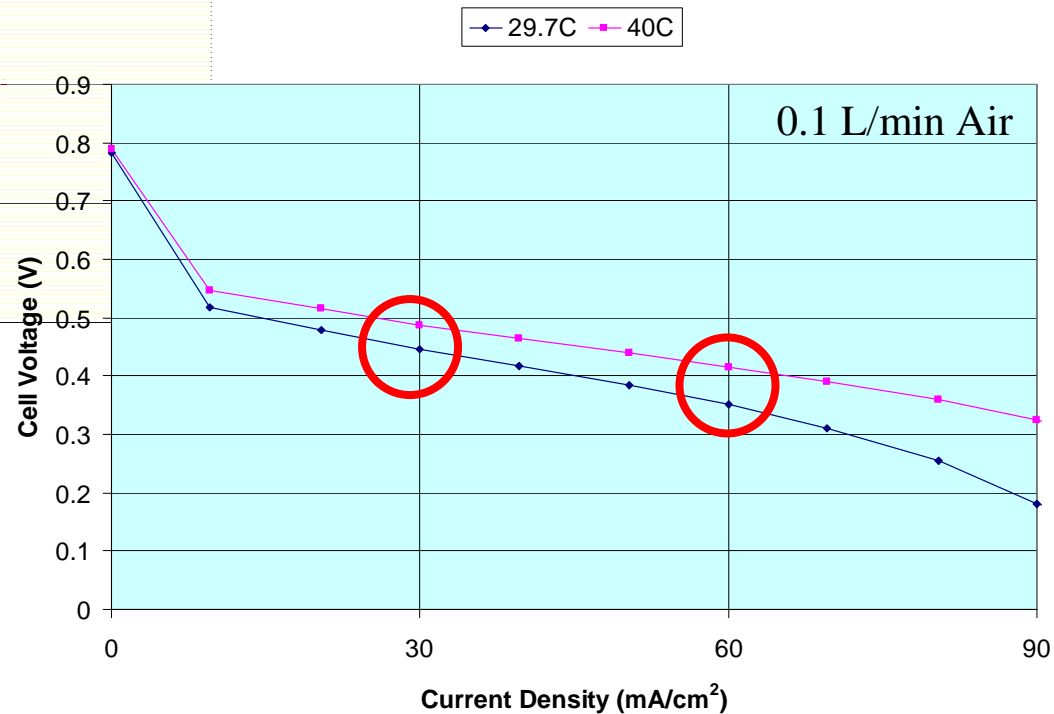
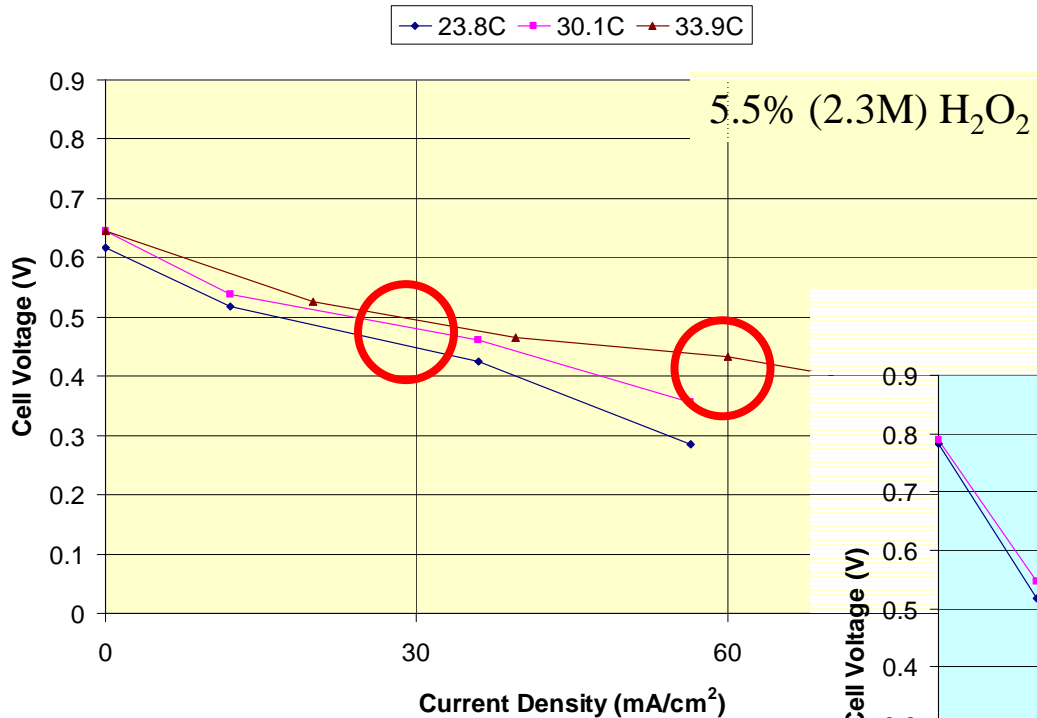
- Consumption of hydrogen peroxide is also likely to occur according to equation 5.



Methanol-Hydrogen Peroxide Studies: Experimental

- MEA Structure Tested
 - 6-8 mg/cm² Pt and Pt-Ru Catalyst Loading (Catalyst Purchased from Johnson Matthey)
 - Fabricated by direct deposit method
 - Pressed with 0% Teflon® content carbon collectors
- Experimental Matrix
 - Methanol Concentration, 0.5M
 - H₂O₂ circulation rate, 0.372 +/- 0.040 L/min
 - Cell Characterization with H₂O₂ in concentration ranges of 3-16.5%
 - Cell Characterization at 5.5% H₂O₂ at temperatures: 24, 30, and 34°C
 - Anode Polarization at 30°C
- Data Reported
 - IV-Performance
 - Half Cell Analysis
 - H₂O₂ Decomposition Analysis

Methanol-Hydrogen Peroxide Studies: Hydrogen Peroxide/ Air Comparison

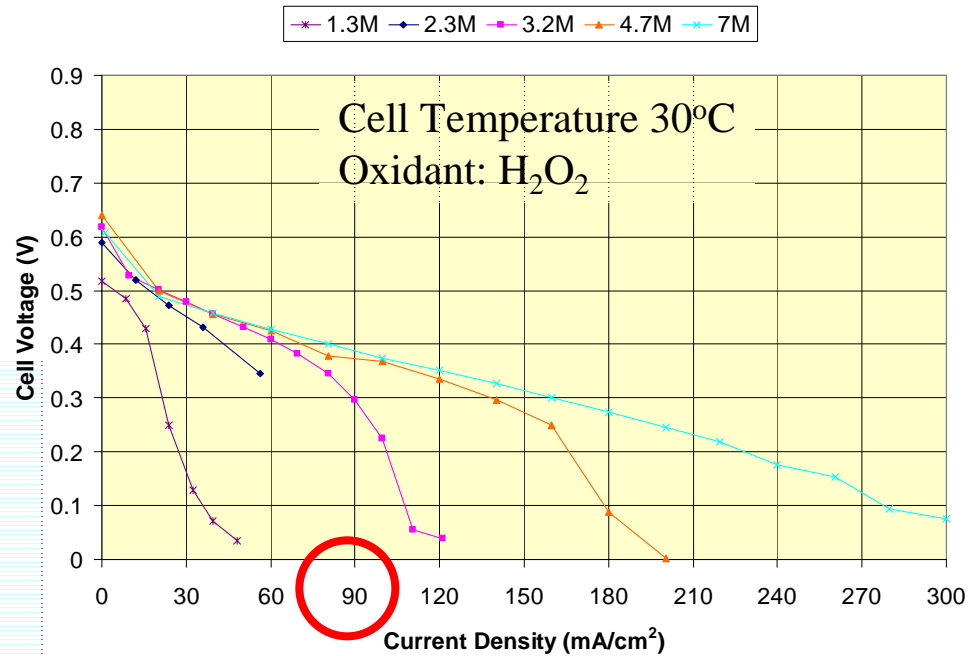
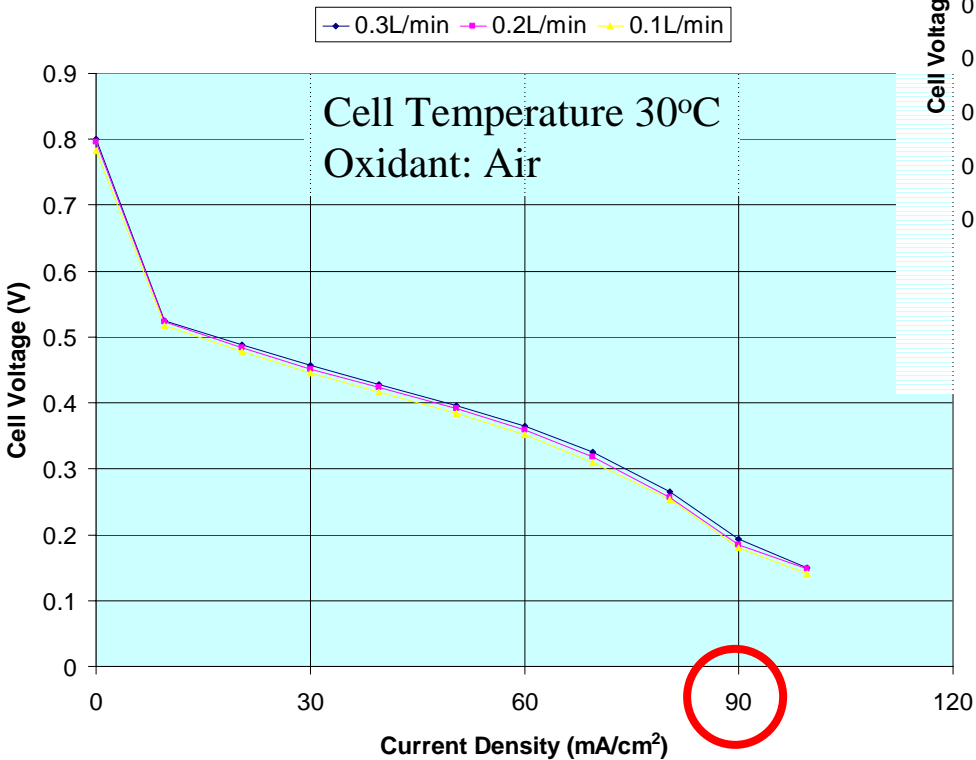


DMFC-hydrogen peroxide single cell
VI-performance is comparable to
DMFC-air at 30 and 40 °C.

H₂O₂: 0.433V, 60 mA/cm², 33.9C

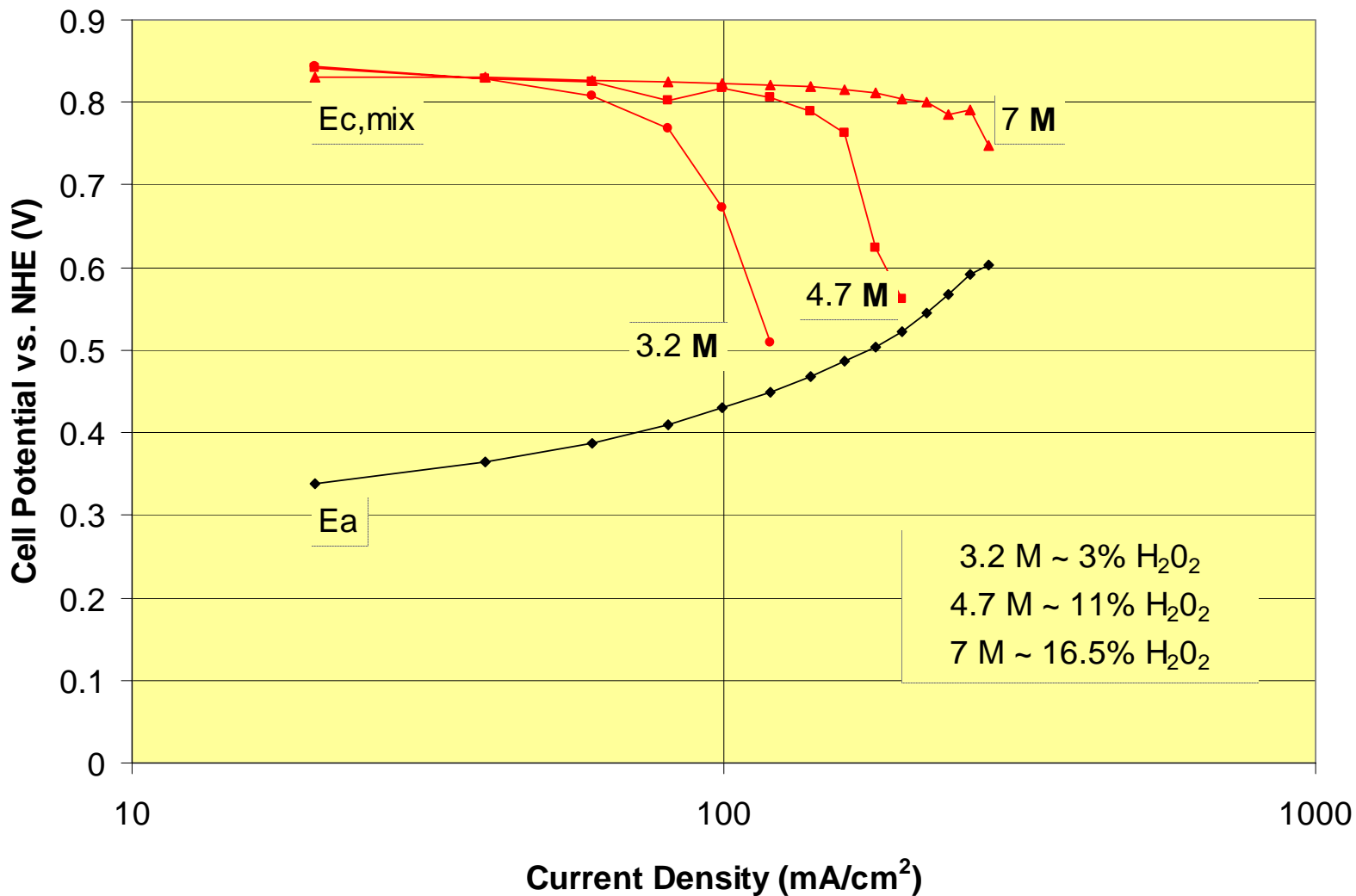
Air: 0.416V, 60 mA/cm², 40 °C

Methanol-Hydrogen Peroxide Studies: Hydrogen Peroxide/ Air Comparison

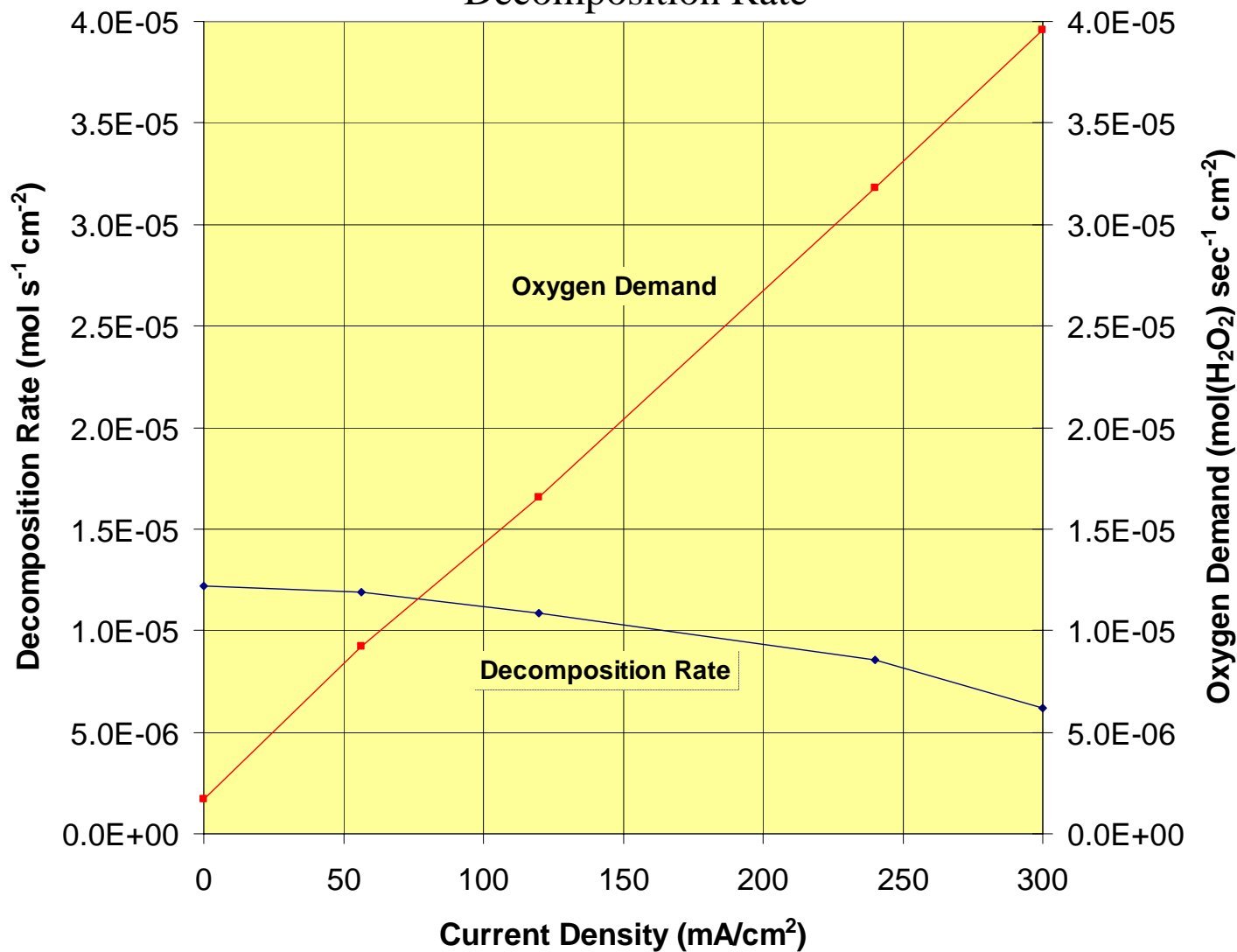


At H₂O₂ concentrations greater than 3.2M (~11%), 30 °C, cell performance is greater than that on air at all current densities.

Methanol-Hydrogen Peroxide Studies: Cathode Evaluation at 30°C

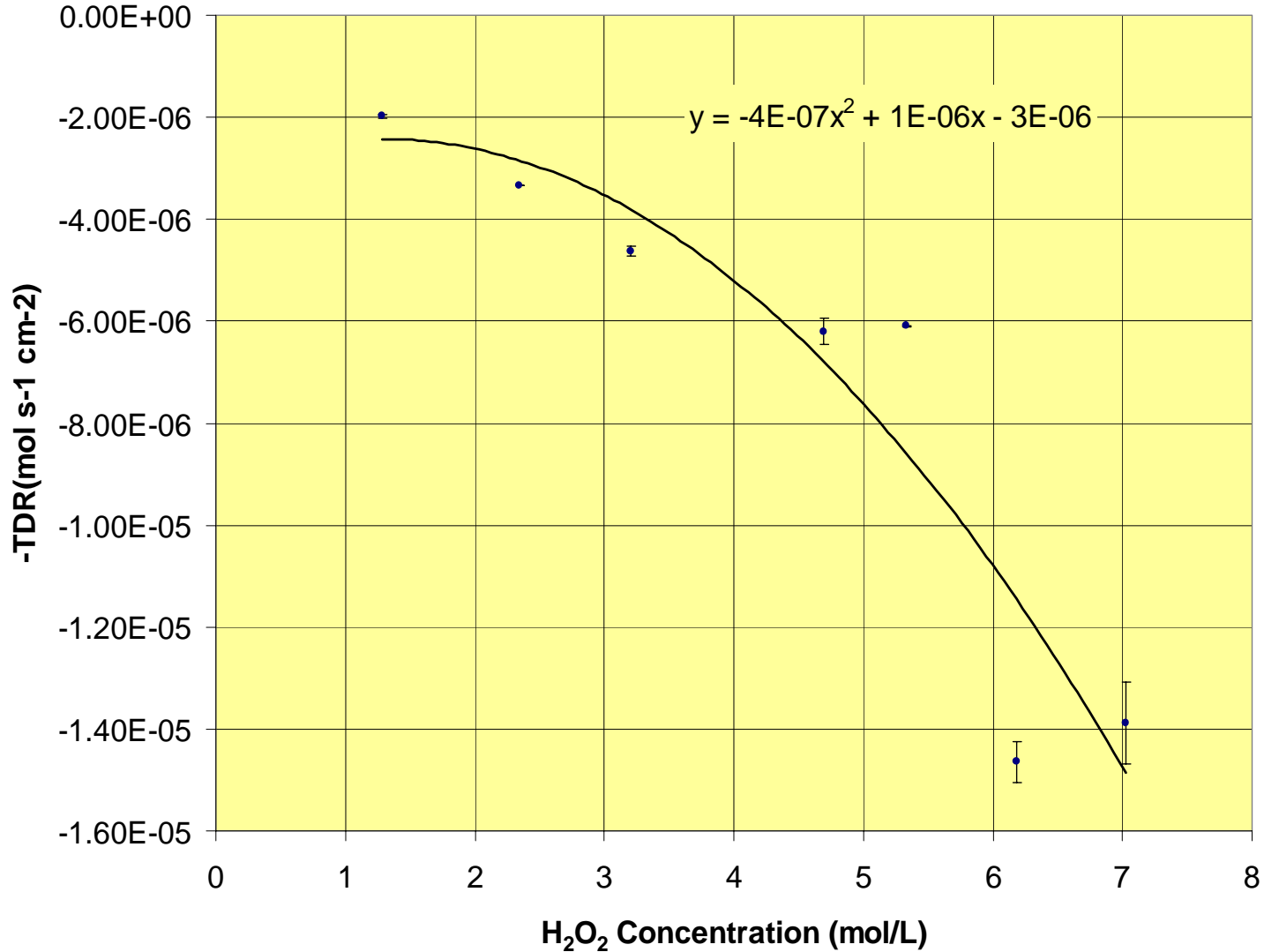


Methanol-Hydrogen Peroxide Studies: Effect of Oxygen Demand on Decomposition Rate



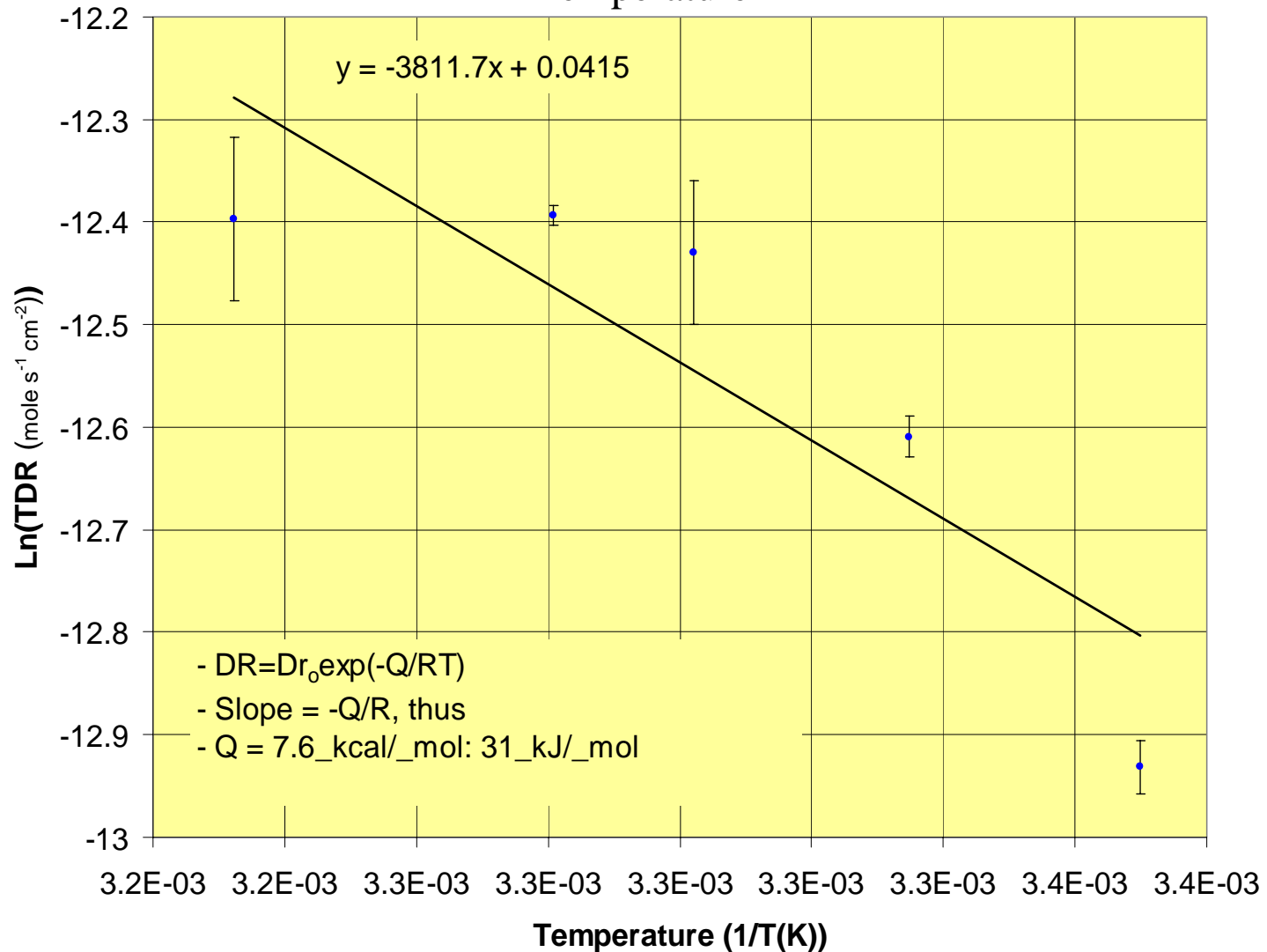


Methanol-Hydrogen Peroxide Studies: Decomposition Rate vs. Peroxide Concentration





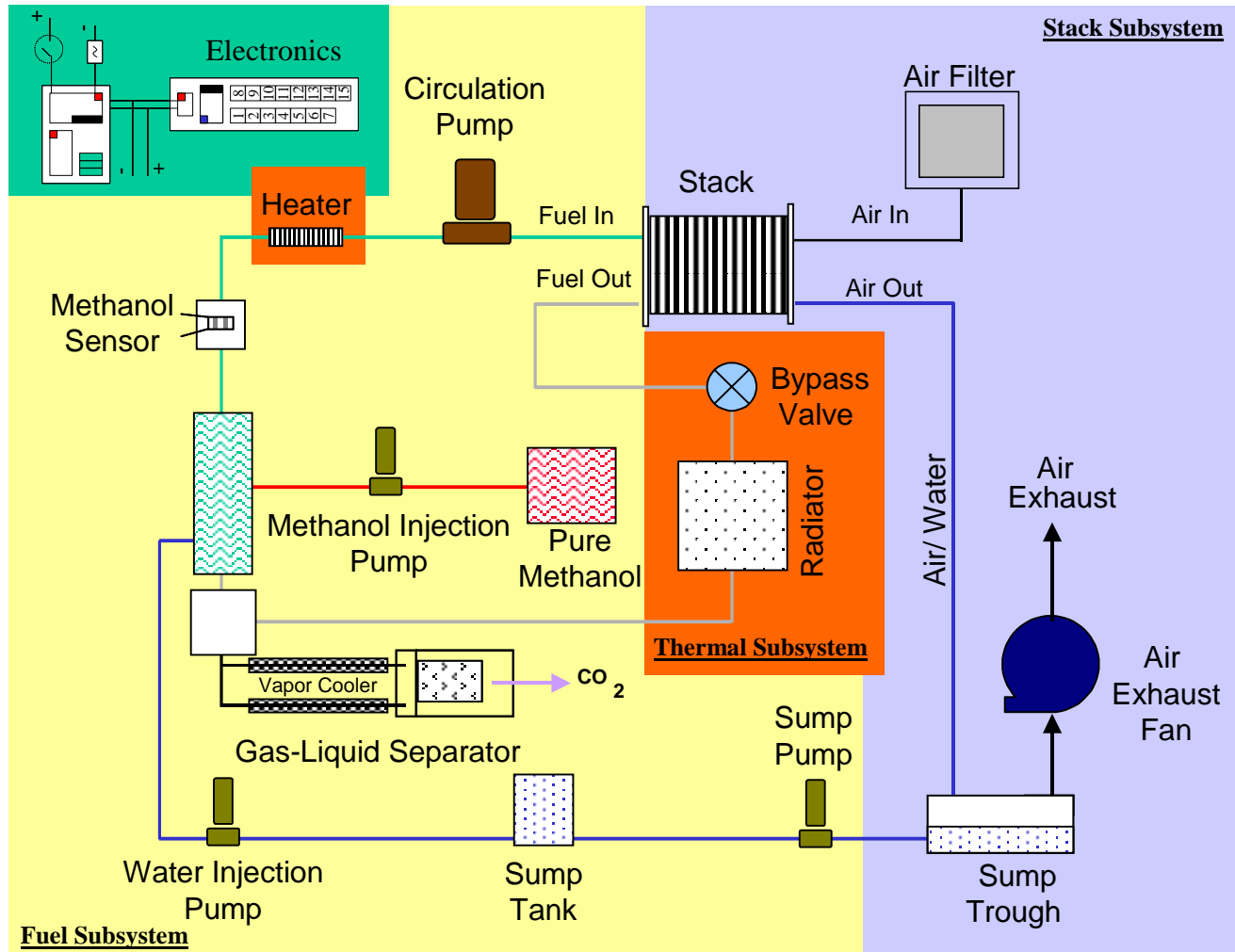
Methanol-Hydrogen Peroxide Studies: Decomposition Rate as A function of Temperature



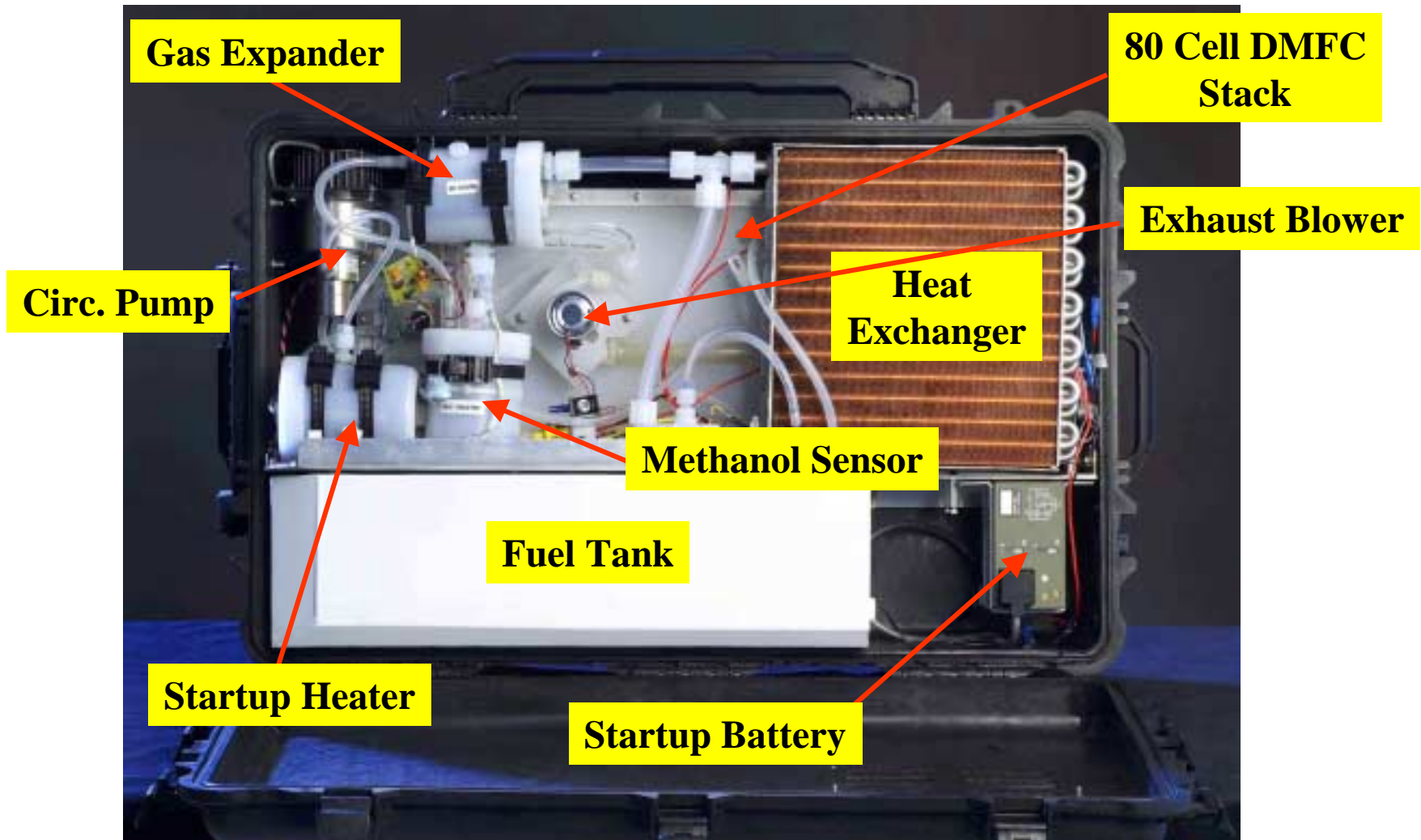
Methanol-Hydrogen Peroxide Studies: Conclusions

- Hydrogen peroxide can serve as a substitute to oxygen in DMFC reactions.
- Hydrogen peroxide can be used as a liquid oxidant or decomposed on across a catalyst bed to enrich the oxygen content of air feed.
- Concentrations of hydrogen peroxide of at least 5.5% must be used for stable performance at current densities greater than 16 mA/cm².
- Controlling Methanol Crossover is very important in H₂O₂ system because of the fixed quantity of oxidant.
- The decomposition rate of hydrogen peroxide is a thermally activated reaction with an observed activation energy 7.6 kcal/mol (31 kJ/mol)
- The decomposition rate of hydrogen peroxide appears to be a 2nd order reaction.

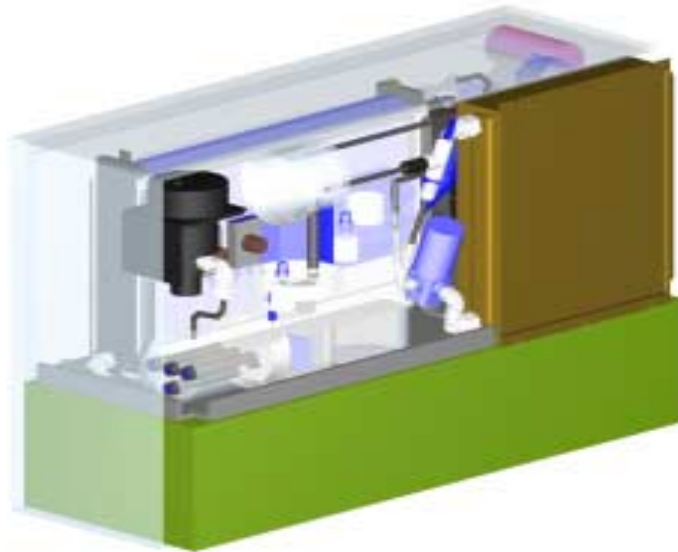
DMFC System Design



DMFC System Design: System Integration



DMFC System Design: Power Source Specifications



System Specifications

Electrical:

- Output Voltage: 24 V
- Power: 300 W
- Max Current: 12.5 A

Physical:

Power Source

- Dimensions: 31.5 in x 20.7 in x 11.5 in
- Mass: 55.6 kg (122.6 lb)
- Volume: 123 L (4.3 ft³)
- Figures of Merit: 539.5 Whr/kg, 243 Whr/L

Fuel Cell System

- System Mass: 17.7 kg (39 lb)

Fuel Tank

- Fuel: Methanol(Supplied from internal fuel tank)
- Capacity: 30000 Whr
- Tank Volume: 32 L (1.1 ft³)
- Fuel Mass: 25.2 kg (55.5 lb)

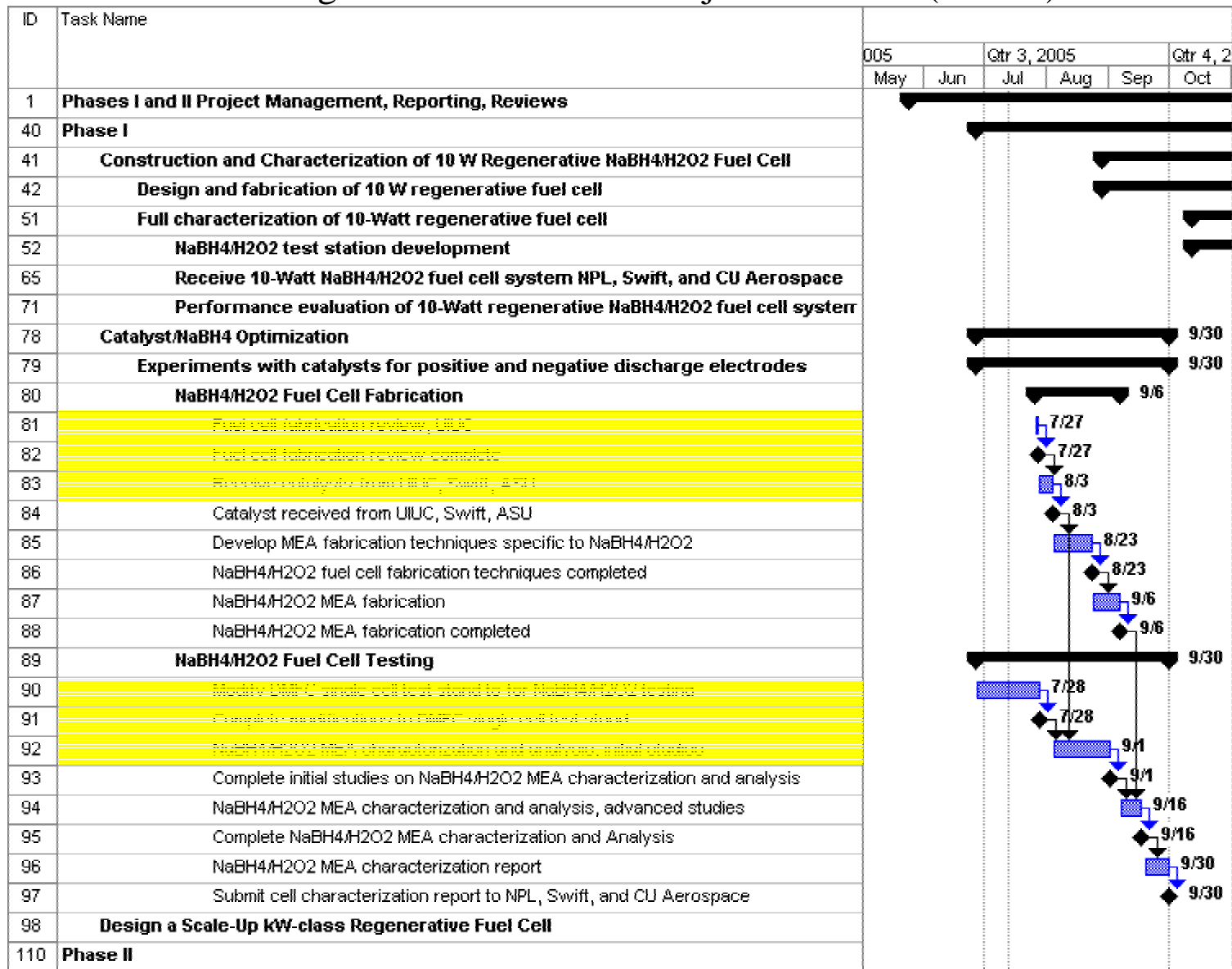
Operational Environment:

- Air Quality: High dust concentration, 20 times zero visibility (~ 5 gm/m² of ACS Coarse 30 microns dust)
- System Startup: Instantaneous when ambient temperature is greater than 5 °C (41 °F)
- Wet Storage: 5 to 70 °C (158 °F)
- Air Temperature: -17 to 45 °C (113 °F)
- Attitude Sensitivity: +/- 45° to vertical
- Shock and Vibration: Survive a three-foot drop on concrete.
- Unit must be protected during wash rack cycle.

ECP Program Status: Summary of Accomplishments

- Re-costed program
- Negotiated with UIUC to de-scope JPL deliverables
- Submitted JPL Task Proposal Revision 1 to program office
- Program on contract May 25th 2005
- Re-scheduled program
- Participated in the May 26th telecon headed by Professor Miley of UIUC.
- Participated in the June 16th telecon headed by Professor Miley of UIUC.
- Program scheduled w/JPL scheduler
- FFE in process of being populated
- Modification of DMFC Test Stand for $\text{NaBH}_4/\text{H}_2\text{O}_2$ fuel cells in progress

ECP Program Status: Phase I Project Schedule (Detail)

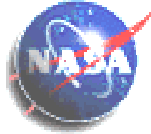




ECP Program Status: Future Work

- Receive catalyst/MEAs from UIUC and Swift
- Fabricate MEAs
- Initiate fuel cell test on standard DMFC hardware
- Fabricate $\text{NaBH}_4/\text{H}_2\text{O}_2$ test cell
 - Receive active area from UIUC
 - Test cell to fabricated out of PEEK
- Characterize MEAs fabricated from UIUC and Swift catalyst
 - Voltage-Current Performance
 - Characterize Fuel/Oxidant Utilization
 - Characterize Fuel/Oxidant Regeneration

Acknowledgements



- The data presented here was a result of DMFC research sponsored by **DARPA**.
- The work was performed at the Jet Propulsion Laboratory for the California Institute of Technology under a contract with the National Aeronautics and Space Administration.

