Combinatorial Method for Developing Cathode Catalysts for Fuel Cells

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Project ID: # FCP7

Overview

Timeline

- Start Date: October, 2004
- End Date: May, 2007
- 98% Completed

Barriers

- Low activity of non-Pt catalysts
  - 2004 Status: 8 A/cm^3
  - 2010 Target: >130 A/cm^3

Budget

- Phase II SBIR
- Total Project Funding
  - $750,000
- 2006 Funding: $246,000
- 2007 Budget: $15,000

Partners

- Illinois Institute of Technology

Need for New Fuel Cell Cathode Catalyst

- **Automotive Applications:**
  - Order of magnitude improvement over current Pt alloy based MEA's.
  - Cost – $10/kW MEA Cost
  - High Efficiency – 0.2 g/peak kW total anode/cathode loading.
  - Long Life – 10-15 years life

Project Objectives

- Develop a controlled method for accurate high-throughput evaluation of new catalyst materials.
- Scale up combinatorial approach: Sample preparation, screening system and data processing.
- Evaluate several families of catalysts for oxygen reduction activity.
- Scale up new, low-cost high-activity catalysts for evaluation in fuel cells.
- Develop instrument for efficient evaluation of multiple fuel cell components (catalysts, membranes, MEA's, etc) for general use in process development and manufacturing quality control.

Why Combinatorial Approach for Catalyst Development?

- **Barriers to rational design.**
  - Complex surface chemistry.
  - Lack of a complete understanding of the reaction processes involved.
- **Many possible catalyst permutations (not confined by equilibrium phases).**
- **Screening in parallel allows for better evaluation of relative performance.**
- **Can potentially greatly reduce the cost of optimization and accelerate the discovery of new catalysts.**

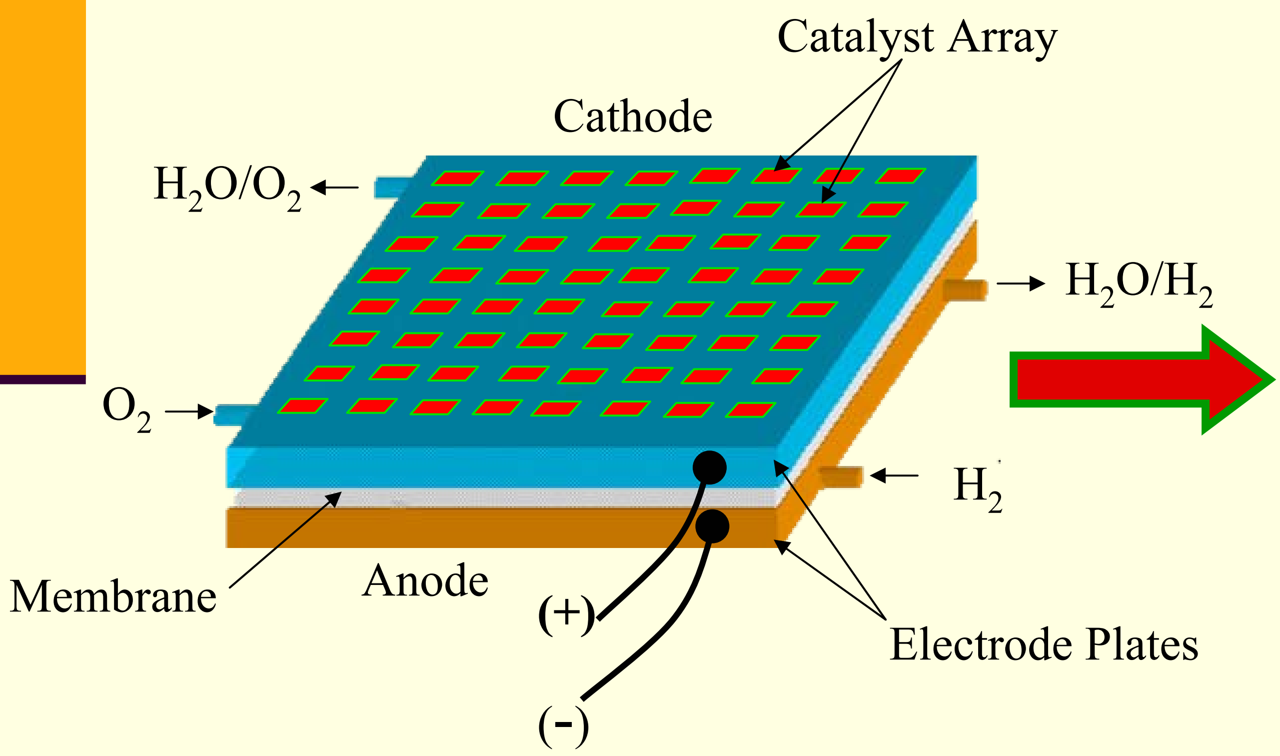
Phase II Project Catalyst Development Strategy

- **Identify best chemistry first then optimize for utilization.**
- **Control all critical parameters to determine inherent catalyst activity.**
- **Use systematic DOE techniques to design catalyst array compositions and testing condition variables.**

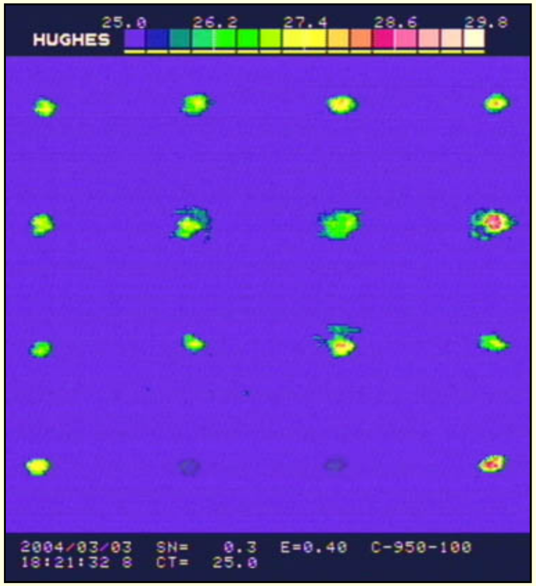
Technical Approach

Thermal Sensing

Thermal sensing allows for *in situ* monitoring of individual catalysts samples in a closed fuel cell system.



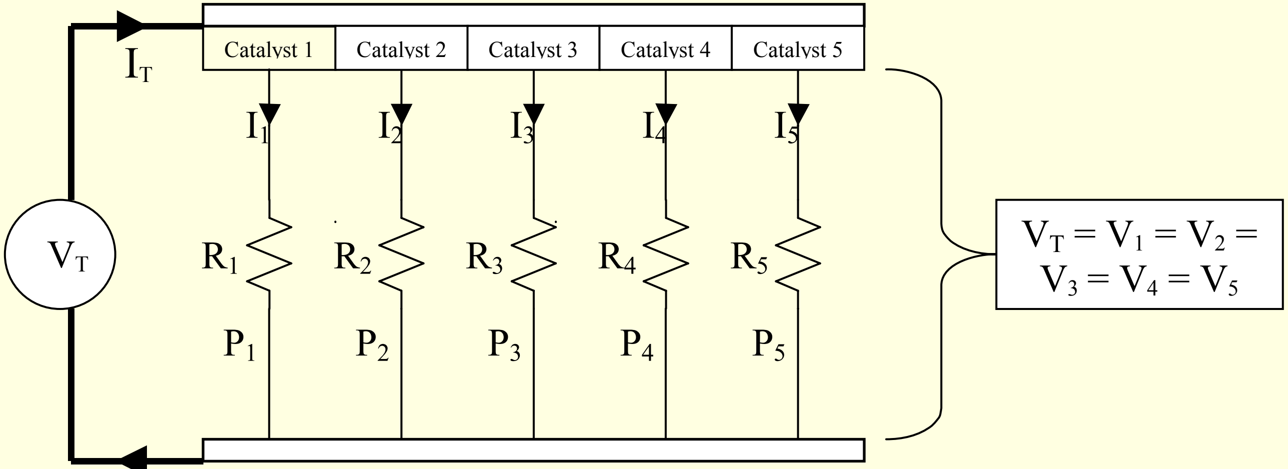
Thermal Image



Heat Generation and Catalyst Efficiency

- **Correlation between i^2R heat generated and current density.**
- **The best catalyst will generate the most heat.**
- **The current passing through each sample can be determined from dT.**

(1) $\Delta T_x \propto P_x = I_x^2 R_x = I_x V_T$



$V_T = V_1 = V_2 = V_3 = V_4 = V_5$

$I_T = I_1 + I_2 + I_3 + I_4 + I_5$

(2) $V_T = R_1I_1 = R_2I_2 = \ldots\ldots$
(3) $I_1 = (R_2/R_1)I_2, \ldots.$

Platinum/0.2V ~ 10^{-3} W/cm^2
Carbon/0.2V ~ 10^{-6} W/cm^2

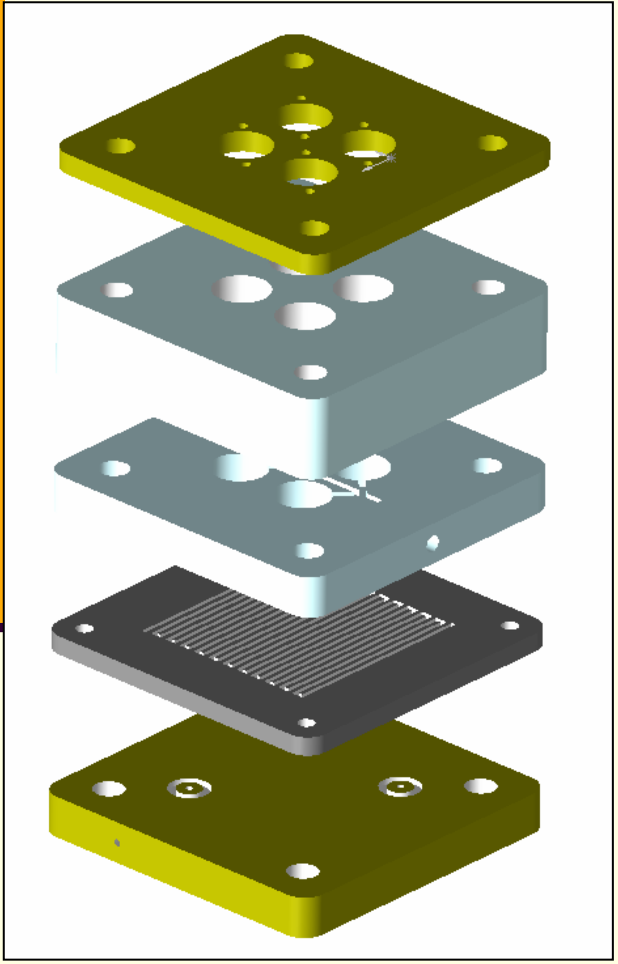
Technical Approach Advantages

- *In situ* screening under real operating conditions.
- Good control of critical parameters that affect performance.
- Great flexibility to screen any catalyst type for any fuel cell system.
- Simple, low-cost system scale-up.

Technical Accomplishments/ Progress/Results

- Further development of Gen 1 screening system design.
- DMFC version tested.
- New Gen 1 sample preparation methods.
- Prototype Gen 2 screening system developed.
- Exploration of catalyst families using Gen 1 system.
- Detailed characterization of Pd-X catalyst systems.

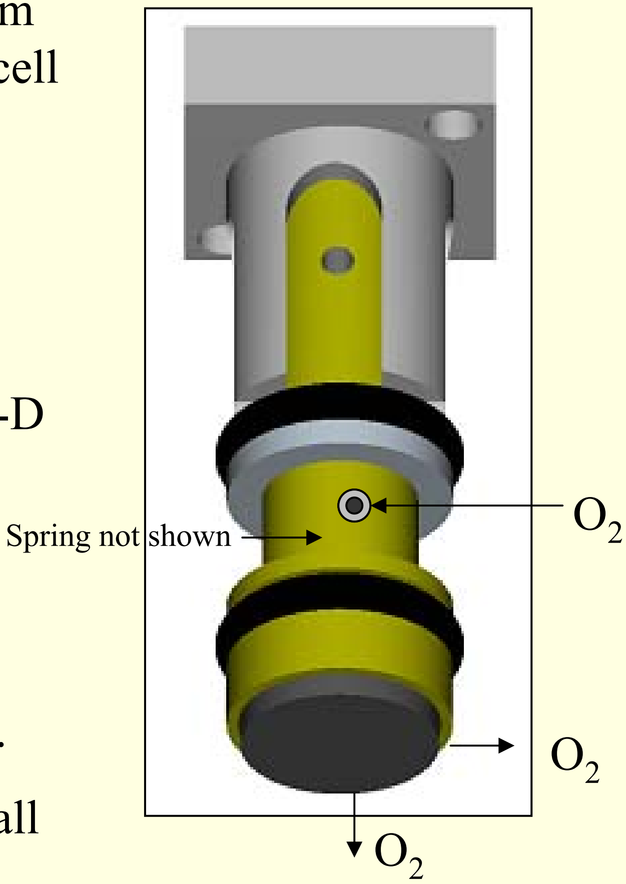
Gen 1 Fuel Cell System: Multiple Sample Rods



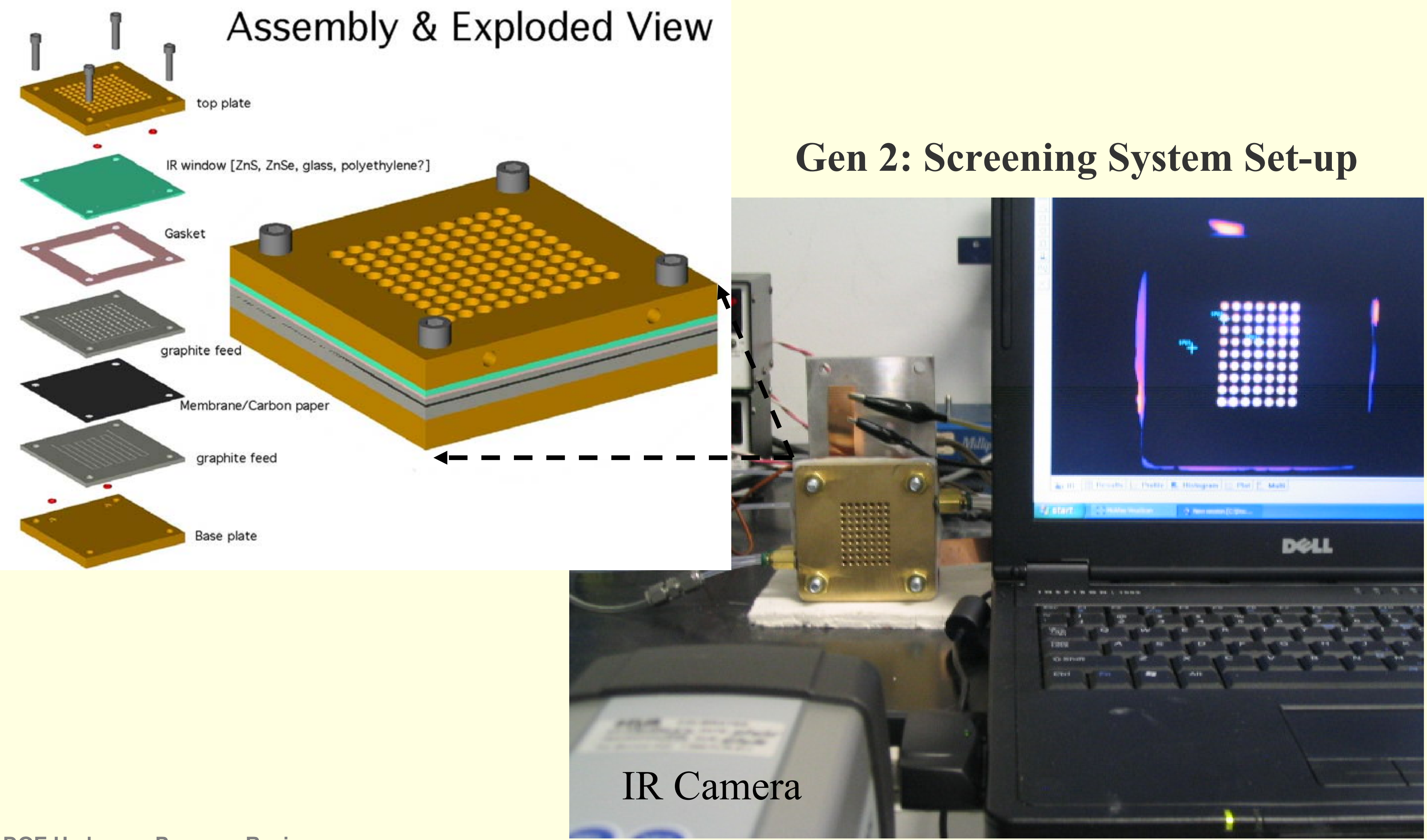
Design Innovations:

- Sample rods inserted from top side of fuel cell with cell already assembled.
- Compressed spring provides uniform contact pressure.
- Porous carbon tip and 3-D fuel flow through rod provides uniform fuel distribution to catalysts.
- Air gap minimizes heat transfer between samples.
- Catalyst prepared on small porous carbon disk.

Sample Rod



Gen 2 Fuel Cell System: Single Sample Array



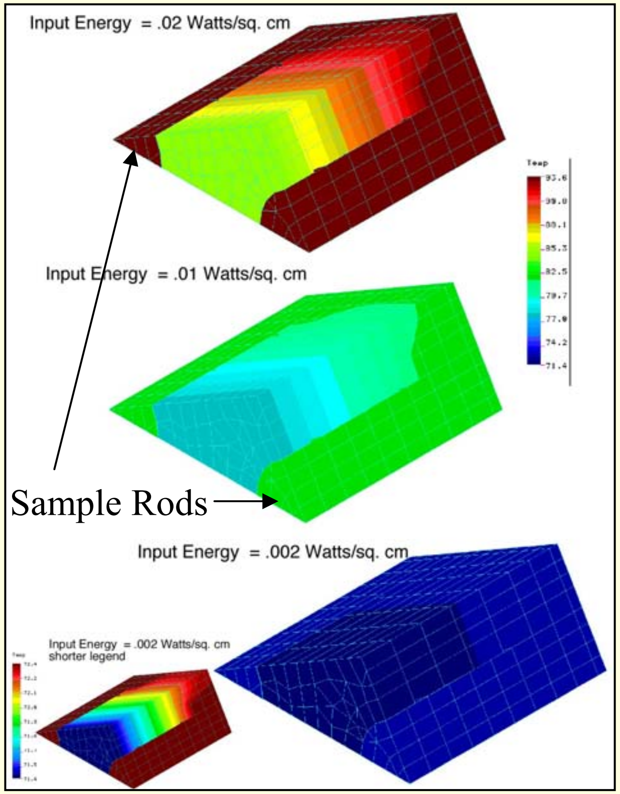
Assembly & Exploded View

Gen 2: Screening System Set-up

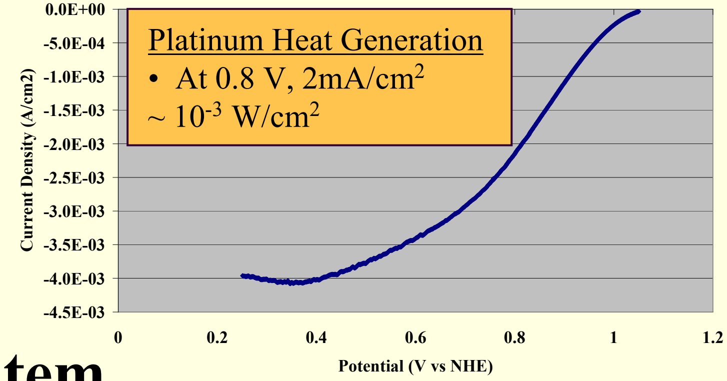
Thermal Modeling to Aid System Design

Gen 1 System

Sample Rod



Estimate Power Inputs for Models



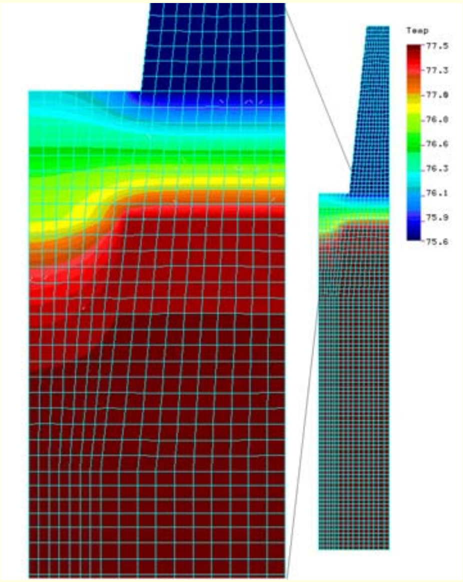
Platinum Heat Generation

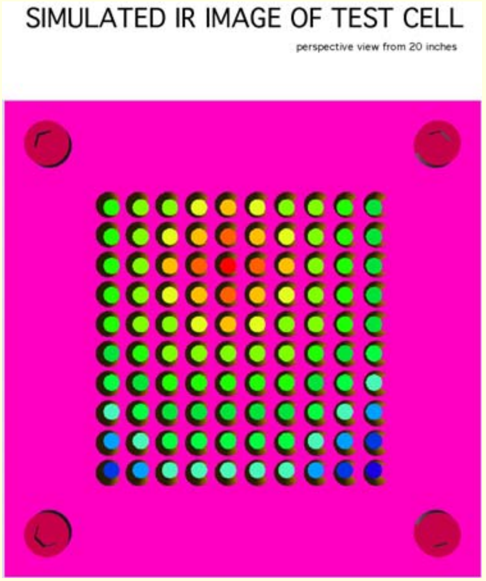
- At 0.8 V, 2mA/cm^2

~ 10^{-3} W/cm^2

Gen 2 System

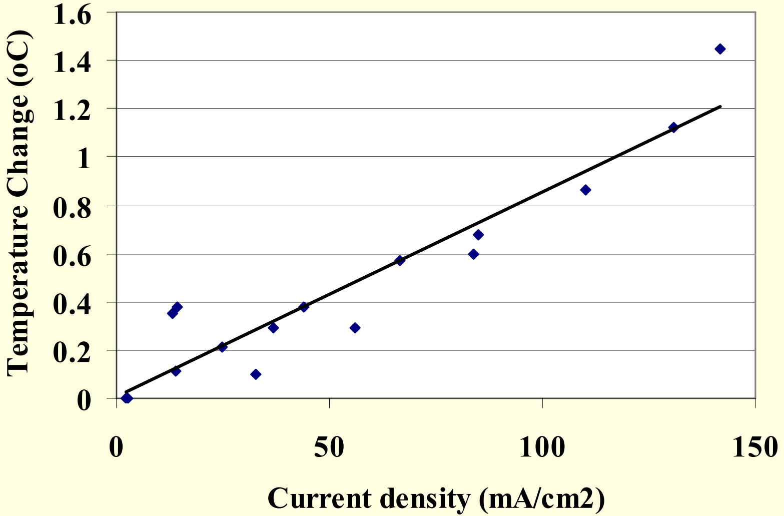
Single Window

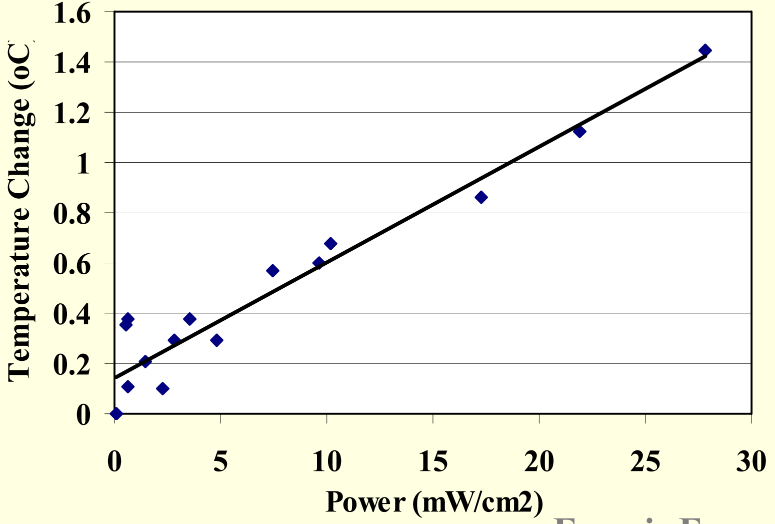




Verification of Thermal Signal Correlations

- Initial calibration of Gen 1 Fuel cell using thermal couples.
- Strong correlation between current/power density and catalyst sample temperature change.
- Sample temperature change was sufficient to detect by conventional methods.





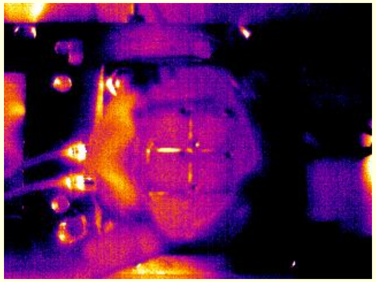
Qualifying Gen 1 System Design

- **Qualify on 4-sample array apparatus before scale up.**
- **Qualification Procedure.**
    - Demonstrate correlation between current and temperature.
    - Verify uniform fuel flow.
    - Verify uniform stack pressure.
    - Verify evaluation of constant catalyst surface area across array.
- **Scale-up to 25-sample array apparatus.**
- **Catalyst Screening.**

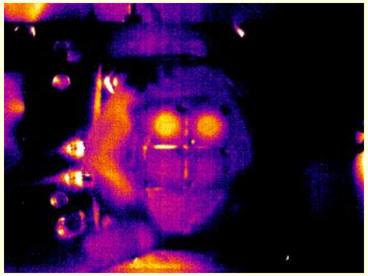
Gen 1 System: Thermal Signal Correlations

4-Sample Array – Sputter Deposition:

2x Pt (top) vs. 2x Carbon (bottom)

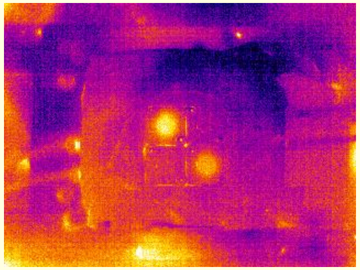


Current: 0 mA/cm^2



Current: 30 mA/cm^2

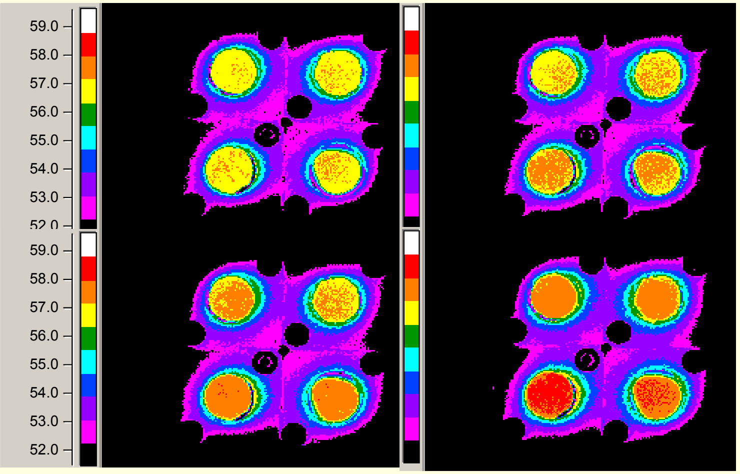
After switching right-side samples



Current: 30 mA/cm^2

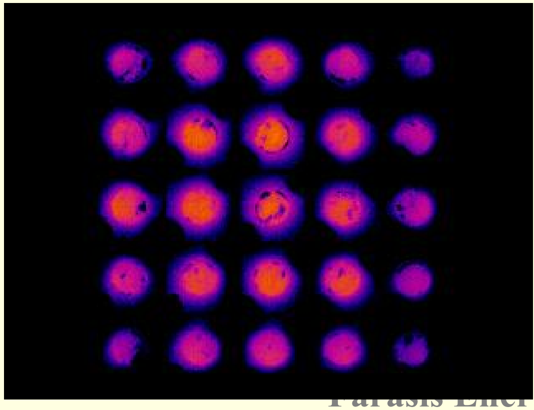
4-Sample Array – MEAs

Pt loading 0.1 – 0.4



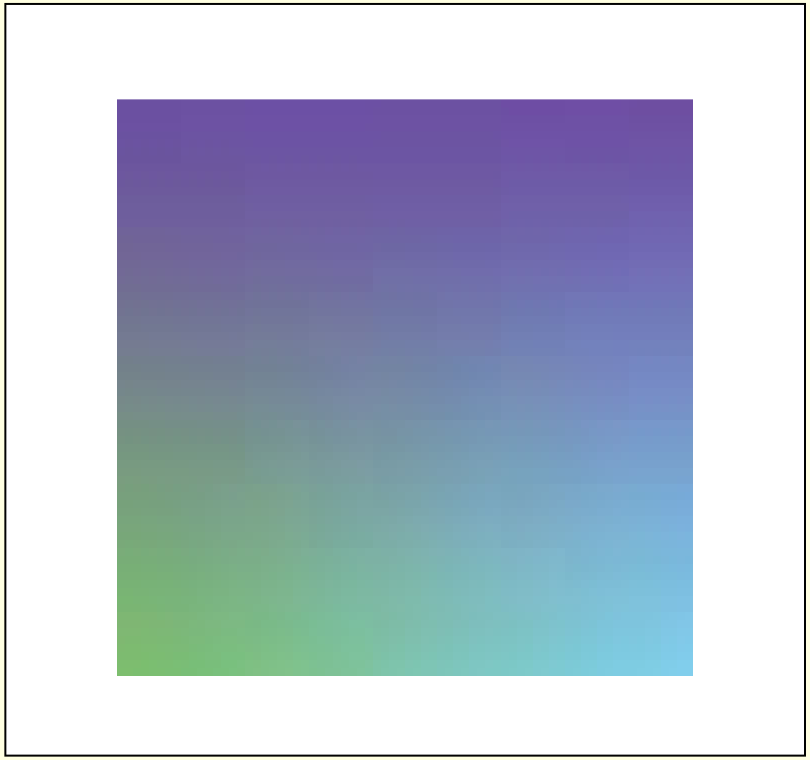
25-Sample Array – Electrodeposition:

- 55 °C Operation
- H_2/O_2
- Binary alloy array
- $\Delta T \sim 2°C$
- Hot spots-Highest current density

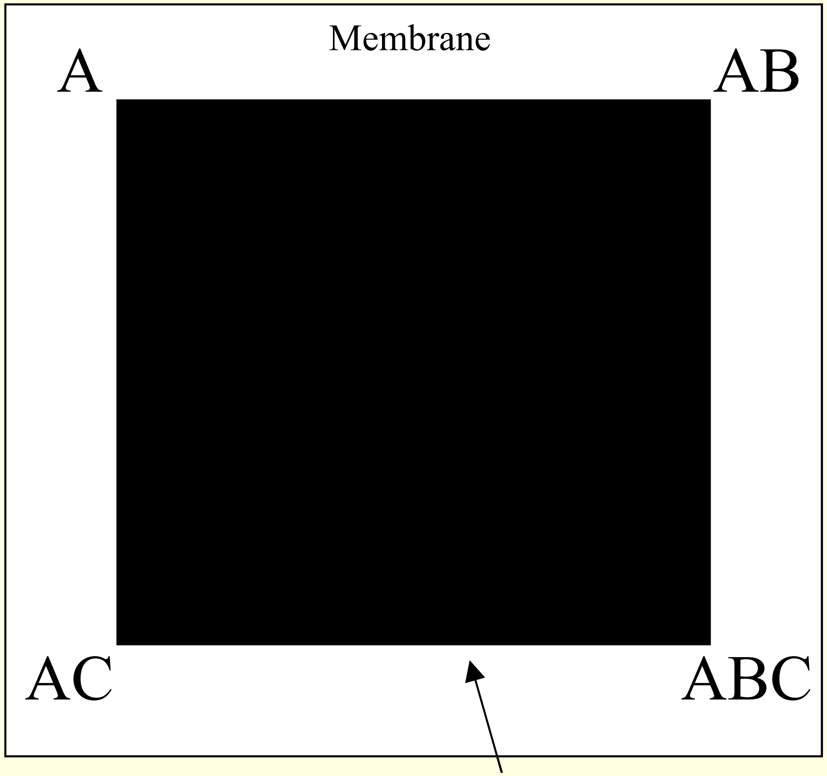


Gen 2: MEA for Combinatorial Screening

Using ink-jet technology or other methods an MEA can be prepared with a continuous compositional variation across its face (A,B,C).



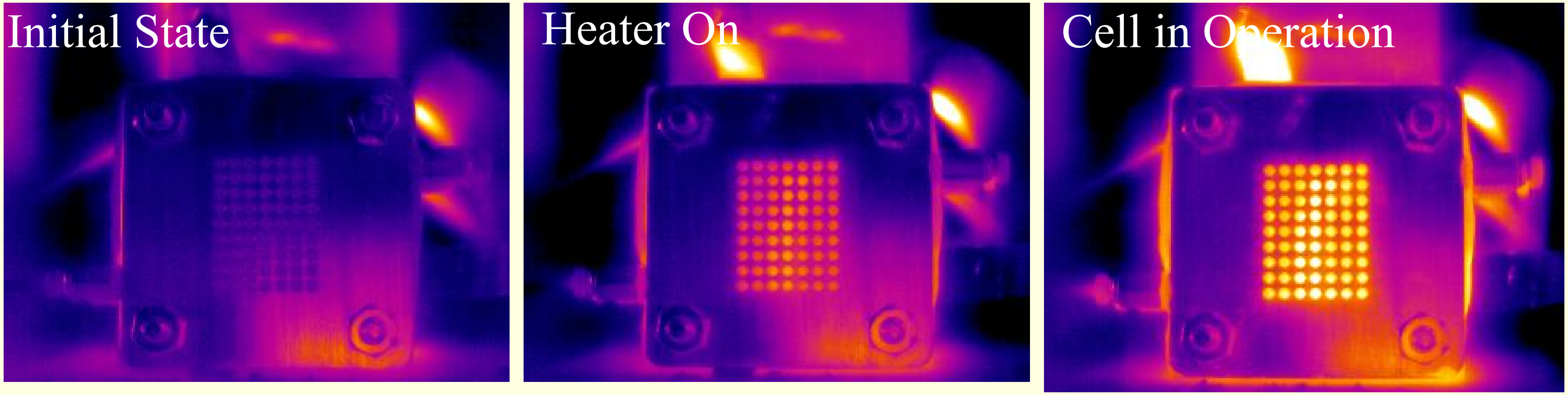
Color printing pattern



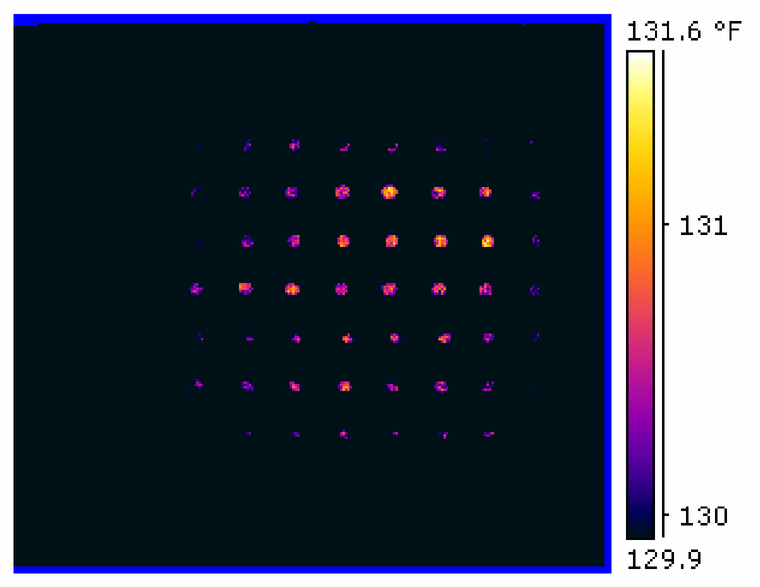
Catalyst containing electrode

Gen 2: MEA Screening Examples

Commercial MEA (Scale -27-36 °C)



Variable composition
MEA prepared at Farasis
- Conditioned over 4 hours
- Current ~50 mA/cm^2

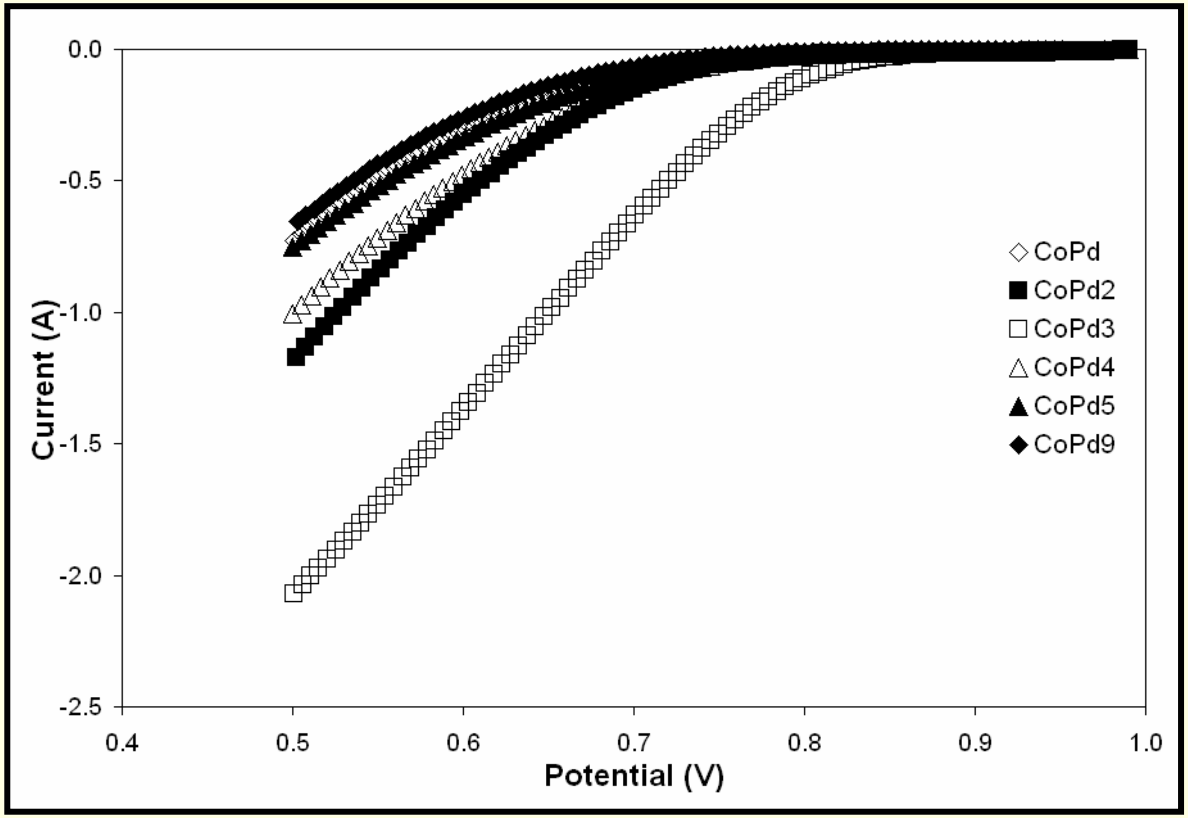


Stage 2 Catalyst Development

- **Best identified catalyst families are further characterized by conventional methods.**
- **Electrodeposited catalyst samples – CV’s, Rotating Disk.**
- **Carbon supported catalyst – MEA’s, H_2 fuel cell.**

Co-Pd Catalyst Family with High Activity

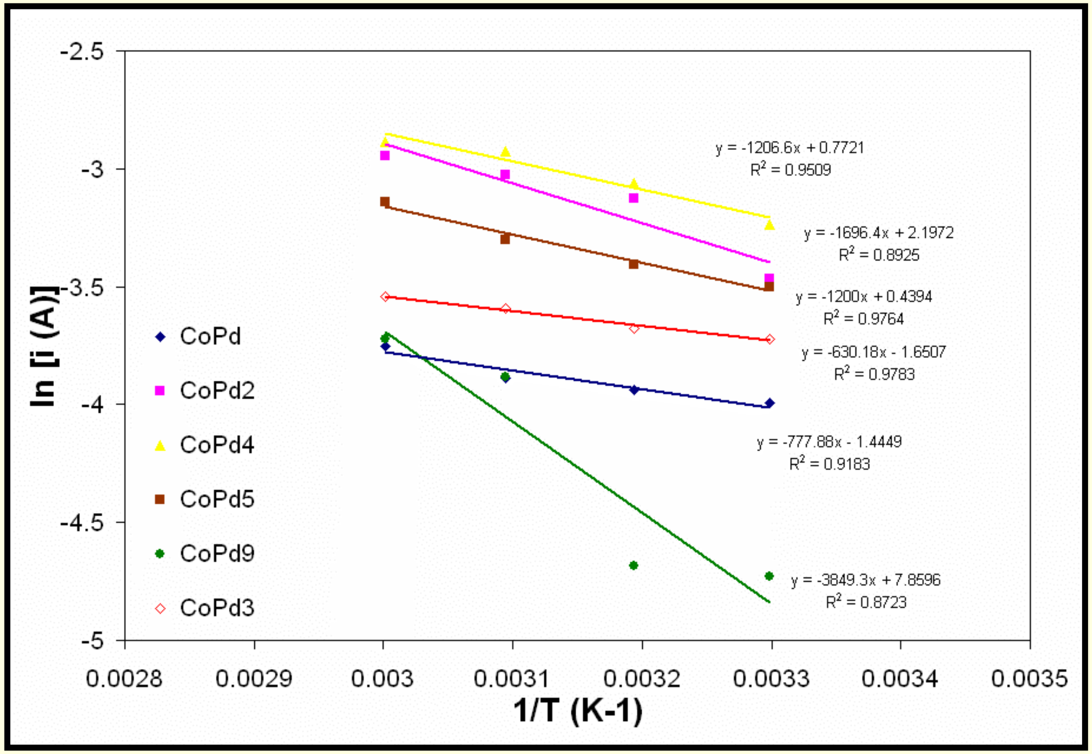
Polarization Curves for Co-Pd compositions



- Temperature: 60^{o}C
- Cathode gas: O_2
- Anode gas: H_2

$CoPd_x$ Kinetic Parameters

Arhenius Plots for the ORR in a 5 cm^2 PEMFC on $CoPd_x$ Electrocatalysts

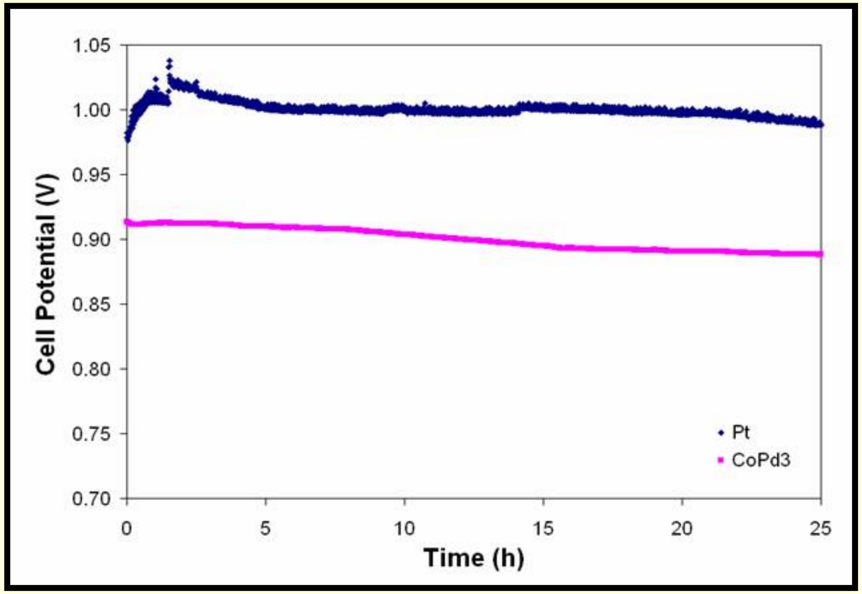


Calculated Kinetic Parameters for ORR on $CoPd_x$ Electrrocatalysts in a H_2/O_2 PEMFC

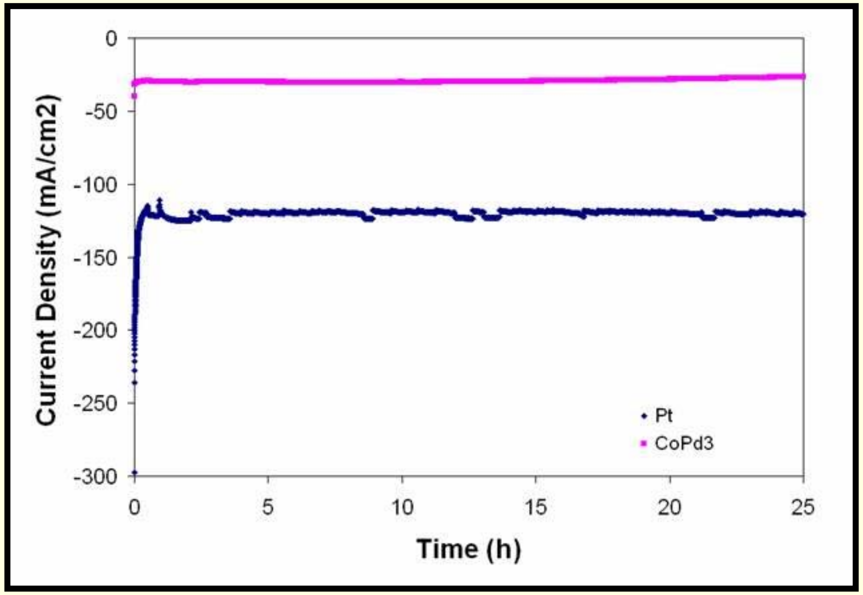
Composition	Onset Potential (V)	Activation Energy (kJ/mol)	Tafel Slope, b 60°C (mV/dec)	Exp[a/b]
CoPd	0.87	80.4	96.5	4.08E+02
$CoPd_2$	0.88	104.0	87.1	1.23E+03
$CoPd_3$	0.92	52.4	69.6	2.69E+04
$CoPd_4$	0.89	100.3	90.3	7.69E+02
$CoPd_5$	0.90	99.8	100.1	2.43E+02
$CoPd_9$	0.89	320.0	34.8	1.72E+08

Performance Stability of Pd_3Co in Hydrogen Fuel Cell

Open Circuit Voltage Pt and $CoPd_3$-cathode/ Pt-anode MEAs in a 5 cm^2 PEMFC at 60 °C.



Performance Stability of Pt and $CoPd_3$ cathode MEAs at 0.8 V, 60 °C.



- Some performance degradation of $PdCo_3$ catalyst observed.

Summary

- We have developed an easily scalable method of combinatorially screening materials for electrochemical systems based on their efficiency related thermal signature.
- We are using this system to evaluate catalysts for oxygen reduction activity.
- Materials with the greatest potential are further characterized and optimized by conventional methods.
- Our combinatorial technique and development strategy greatly increase our probability of success and decrease our discovery time.