

Combinatorial Method for Developing Cathode Catalysts for Fuel Cells

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This presentation does not contain any
proprietary or confidential information

Project ID: # FCP7

Overview

Timeline

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

Budget

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

Barriers

- Low activity of non-Pt catalysts
 - 2004 Status: 8 A/cm³
 - 2010 Target: >130 A/cm³

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.**



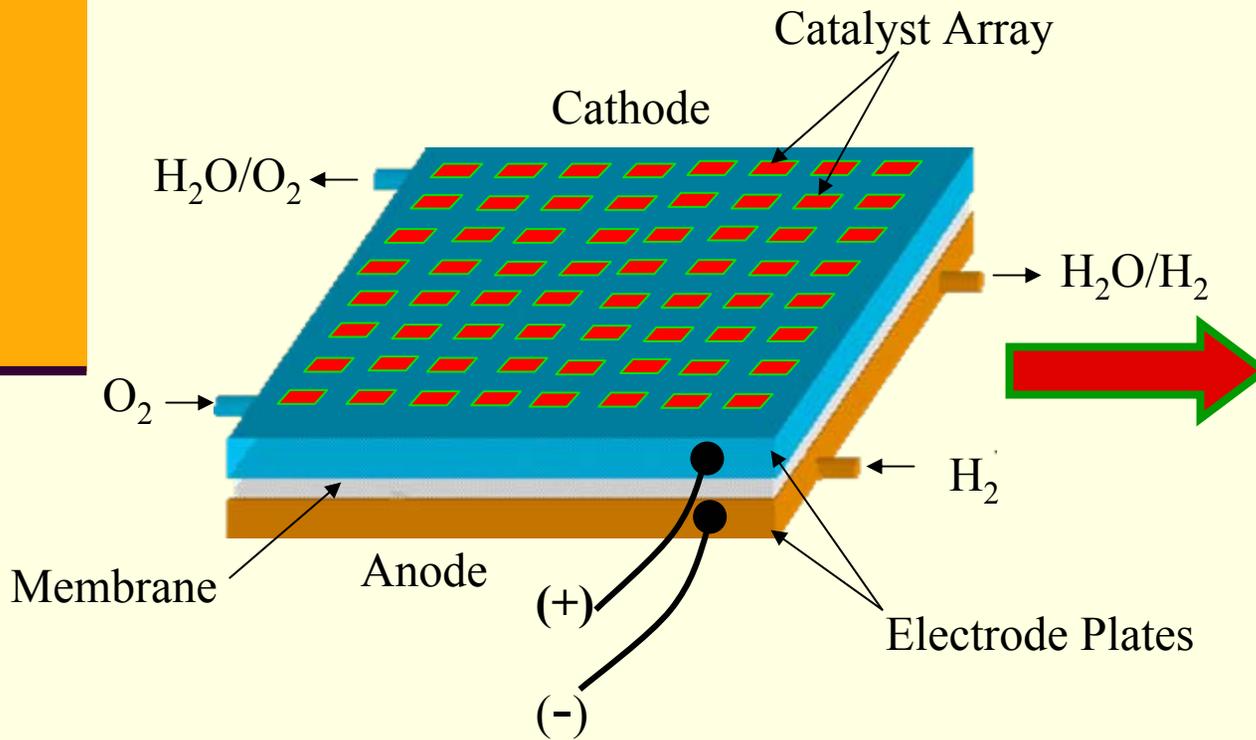
Phase II Project Catalyst Development Strategy

- **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.**

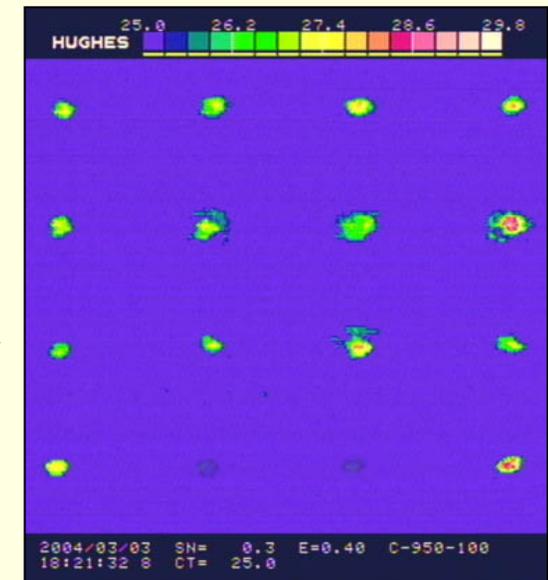
Technical Approach

Thermal Sensing

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

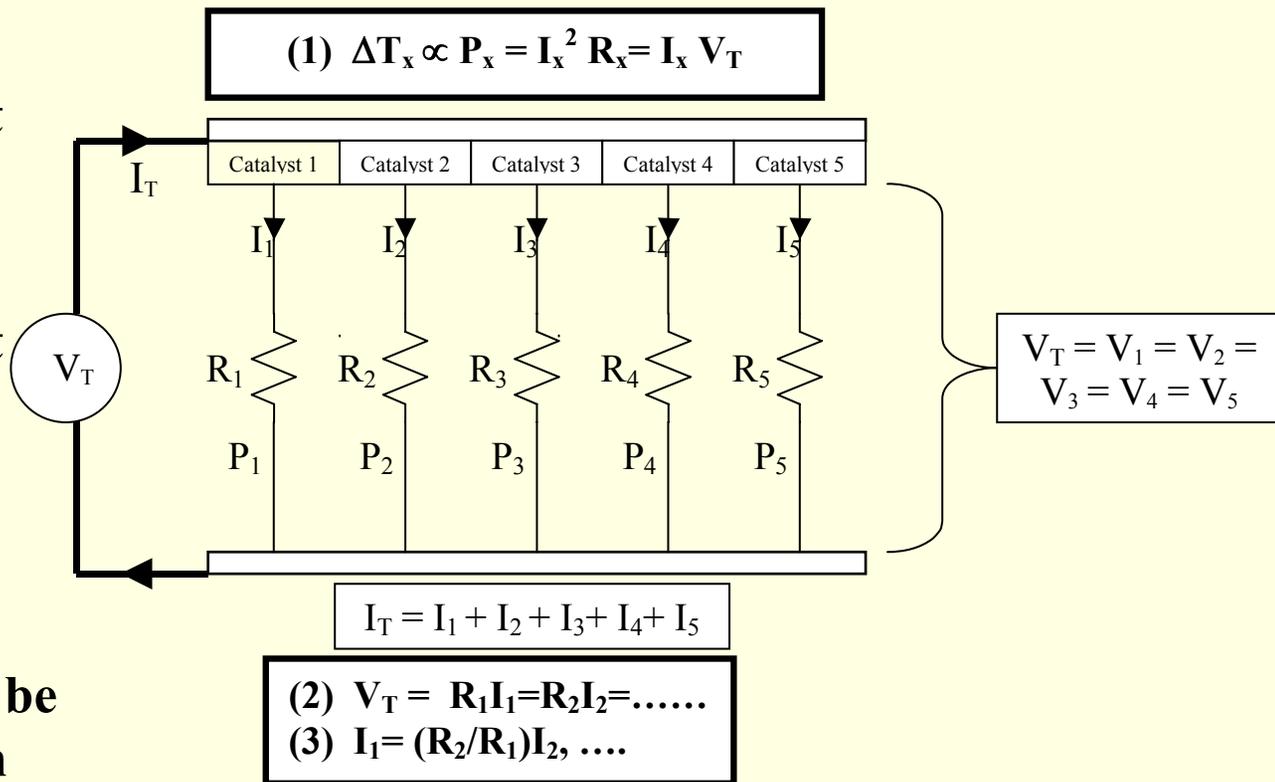


Thermal Image



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 .



Platinum/0.2V $\sim 10^{-3}$ W/cm²
 Carbon/0.2V $\sim 10^{-6}$ W/cm²

Technical Approach Advantages

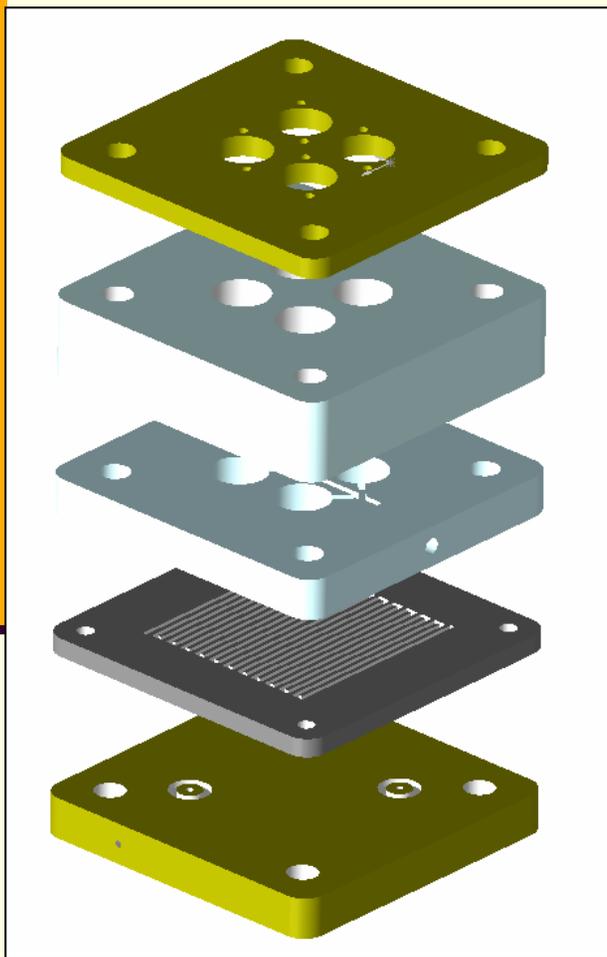
- *In situ* screening under real operating conditions.
- Good control of critical parameters that affect performance.
- Great flexibility to screen any catalyst type for any fuel cell system.
- Simple, low-cost system scale-up.



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.**

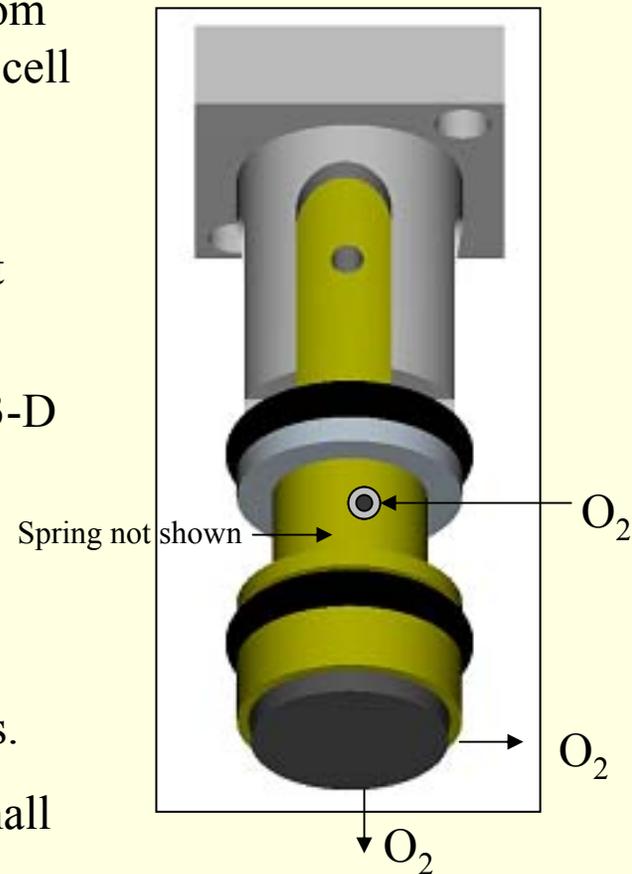
Gen 1 Fuel Cell System: Multiple Sample Rods



Design Innovations:

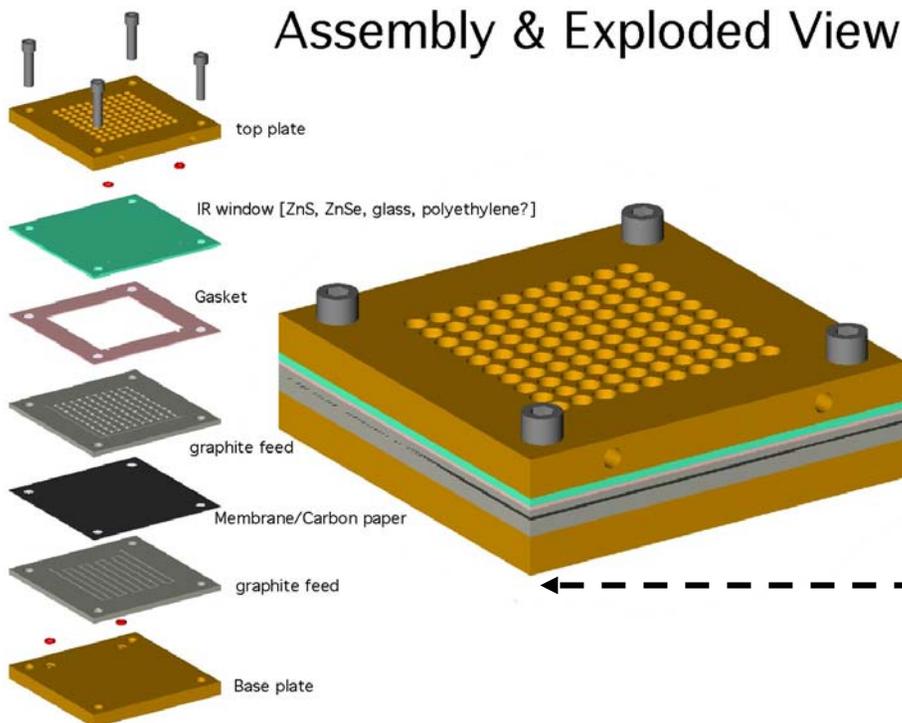
- Sample rods inserted from top side of fuel cell with cell already assembled.
- Compressed spring provides uniform contact pressure.
- Porous carbon tip and 3-D fuel flow through rod provides uniform fuel distribution to catalysts.
- Air gap minimizes heat transfer between samples.
- Catalyst prepared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

Sample Rod

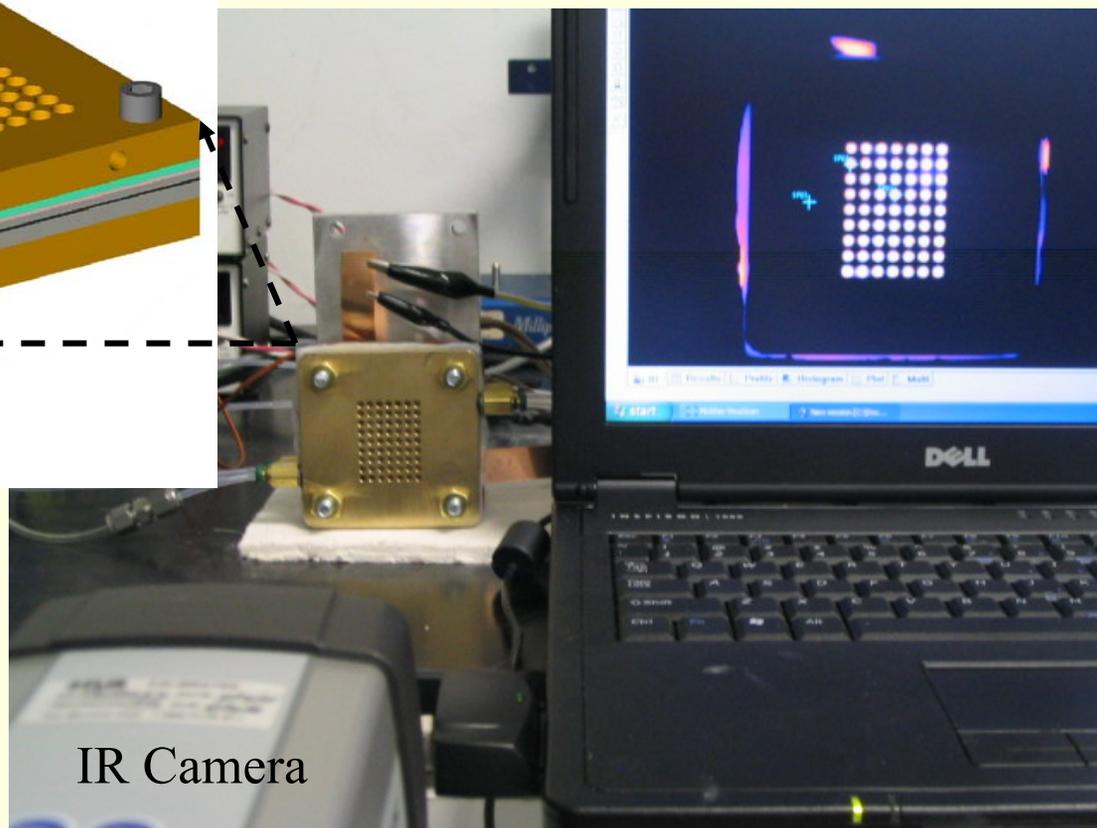


Gen 2 Fuel Cell System: Single Sample Array

Assembly & Exploded View



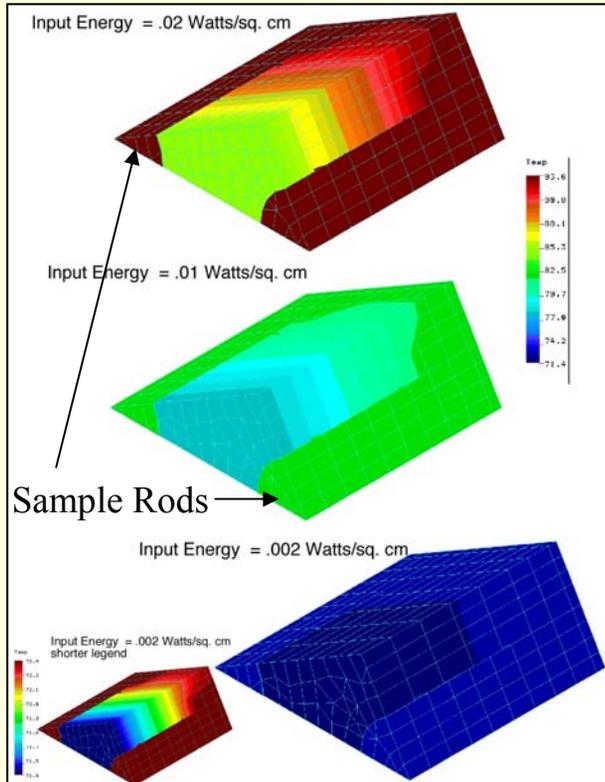
Gen 2: Screening System Set-up



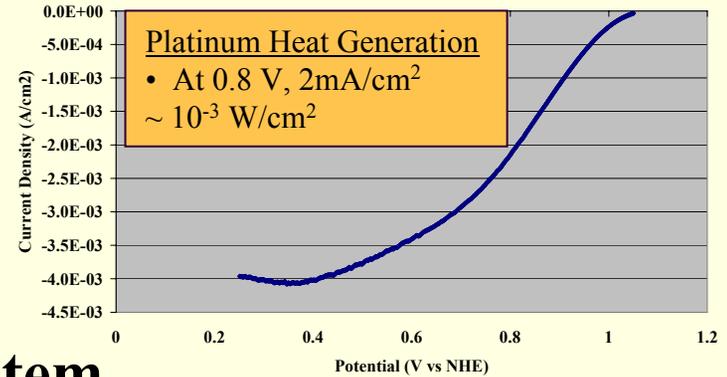
IR Camera

Thermal Modeling to Aid System Design

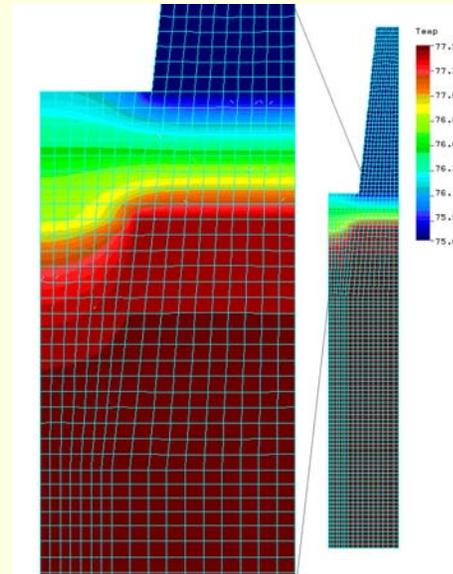
Gen 1 System Sample Rod



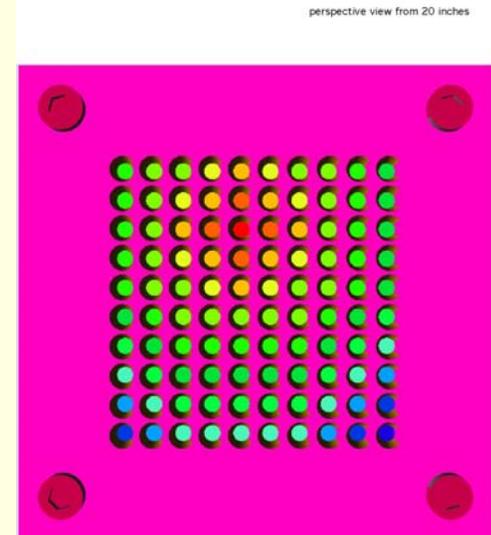
Estimate Power Inputs for Models



Gen 2 System Single Window

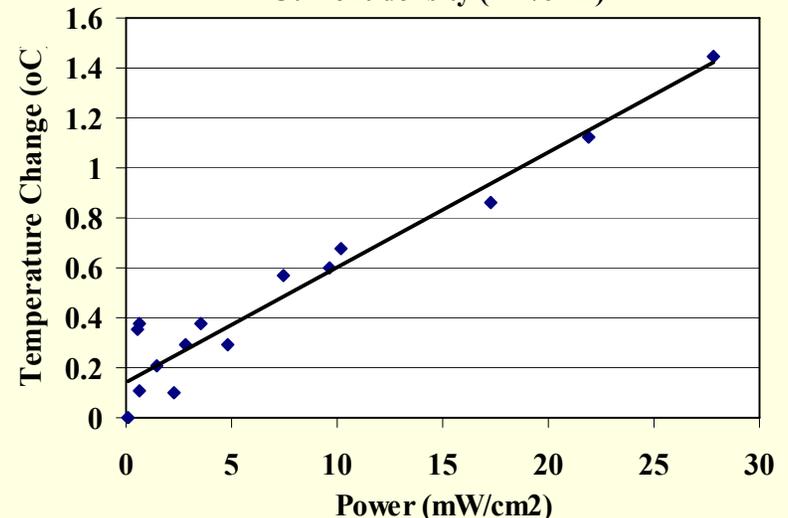
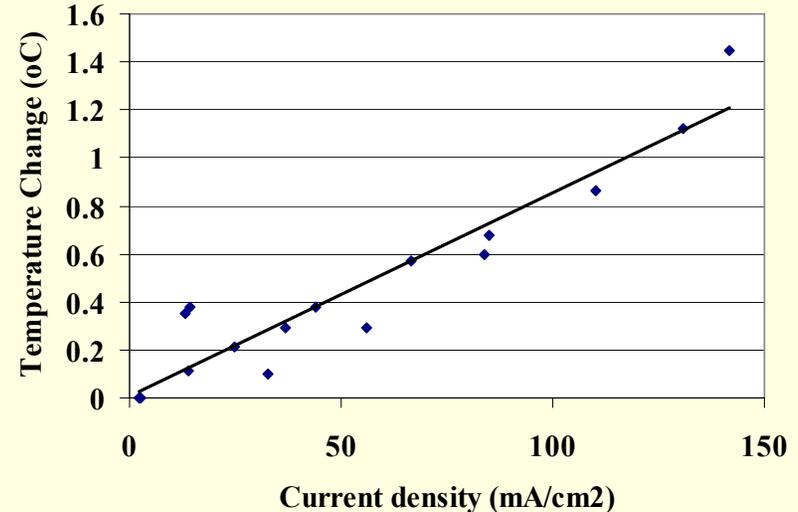


SIMULATED IR IMAGE OF TEST CELL



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.



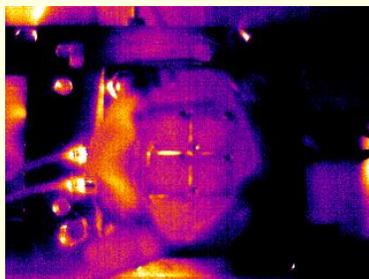
Qualifying Gen 1 System Design

- **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.**

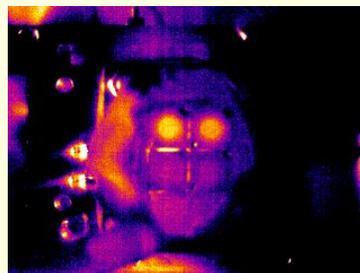
Gen 1 System: Thermal Signal Correlations

4-Sample Array – Sputter Deposition:

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



Current: 0 mA/cm²



Current: 30 mA/cm²

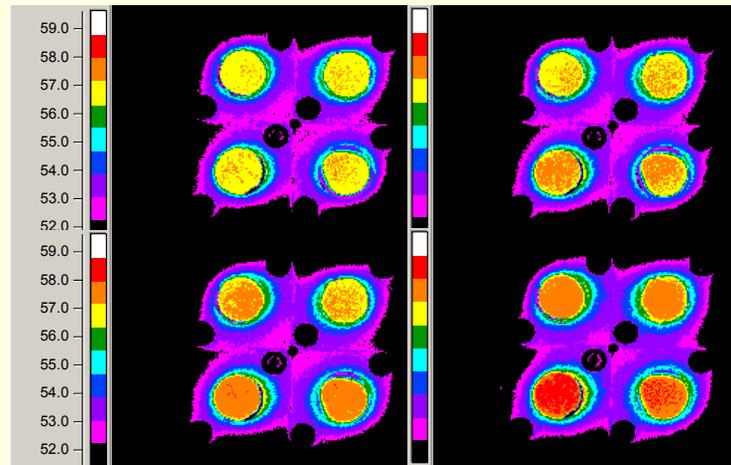
After switching right-side samples



Current: 30 mA/cm²

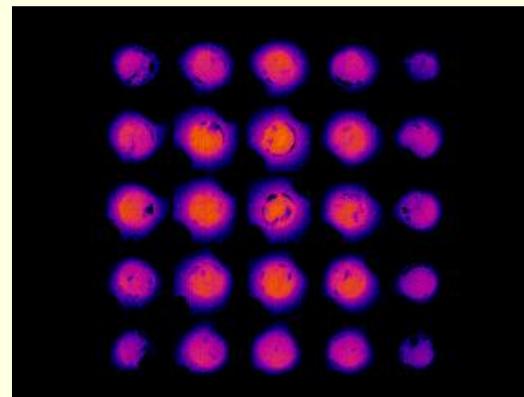
4-Sample Array – MEAs

Pt loading 0.1 – 0.4



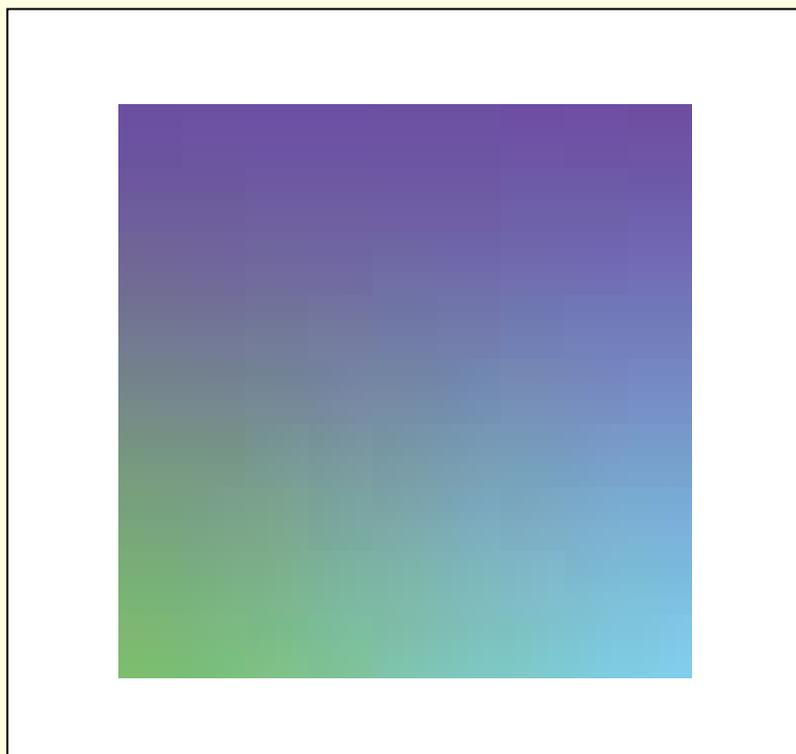
25-Sample Array – Electrodeposition:

- 55 °C Operation
- H₂/O₂
- Binary alloy array
- ΔT ~ 2°C
- Hot spots-Highest current density

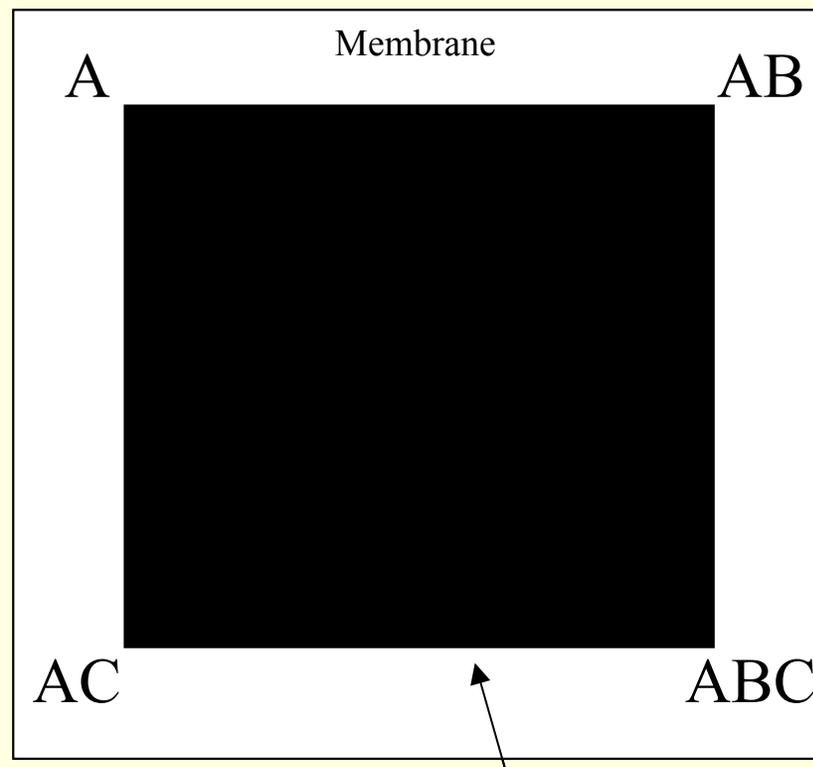


Gen 2: MEA for Combinatorial Screening

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



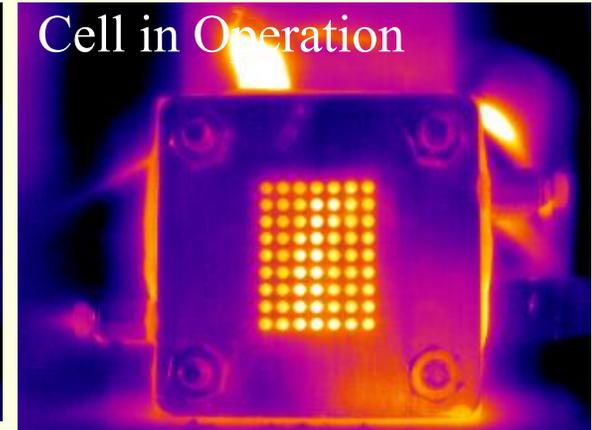
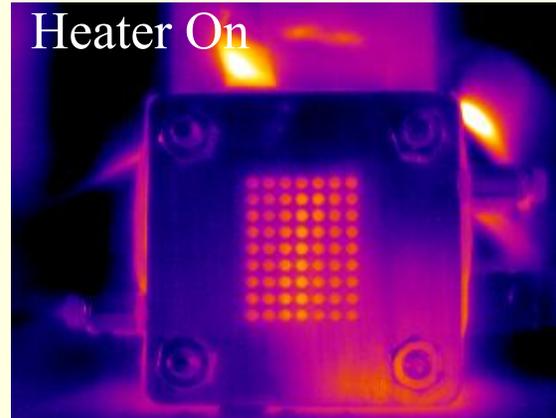
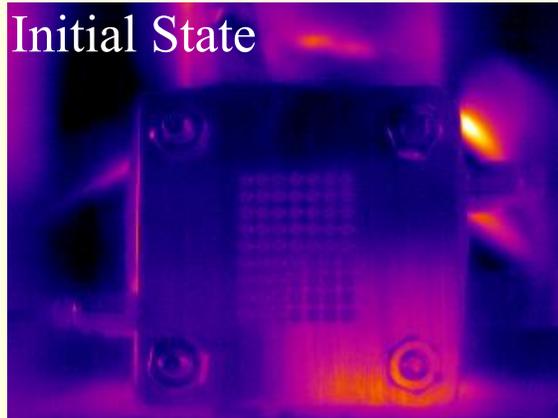
Color printing pattern



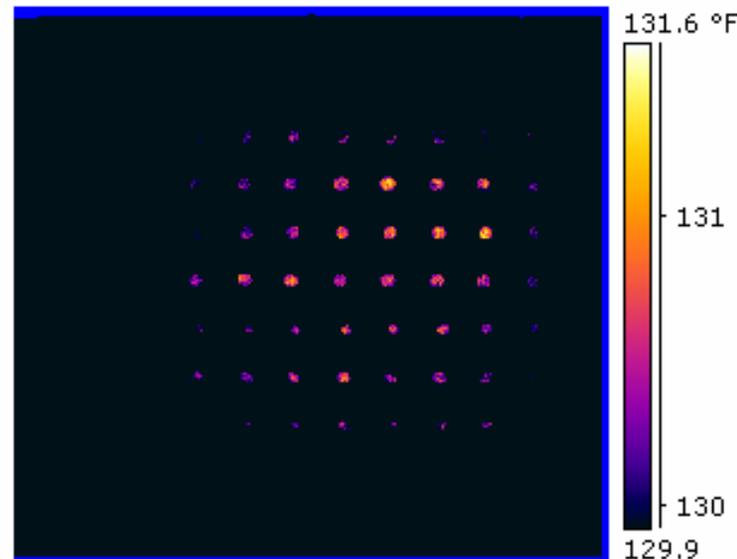
Catalyst containing electrode

Gen 2: MEA Screening Examples

Commercial MEA (Scale -27-36 °C)



- Variable composition
MEA prepared at Farasis
- Conditioned over 4 hours
 - Current $\sim 50 \text{ mA/cm}^2$

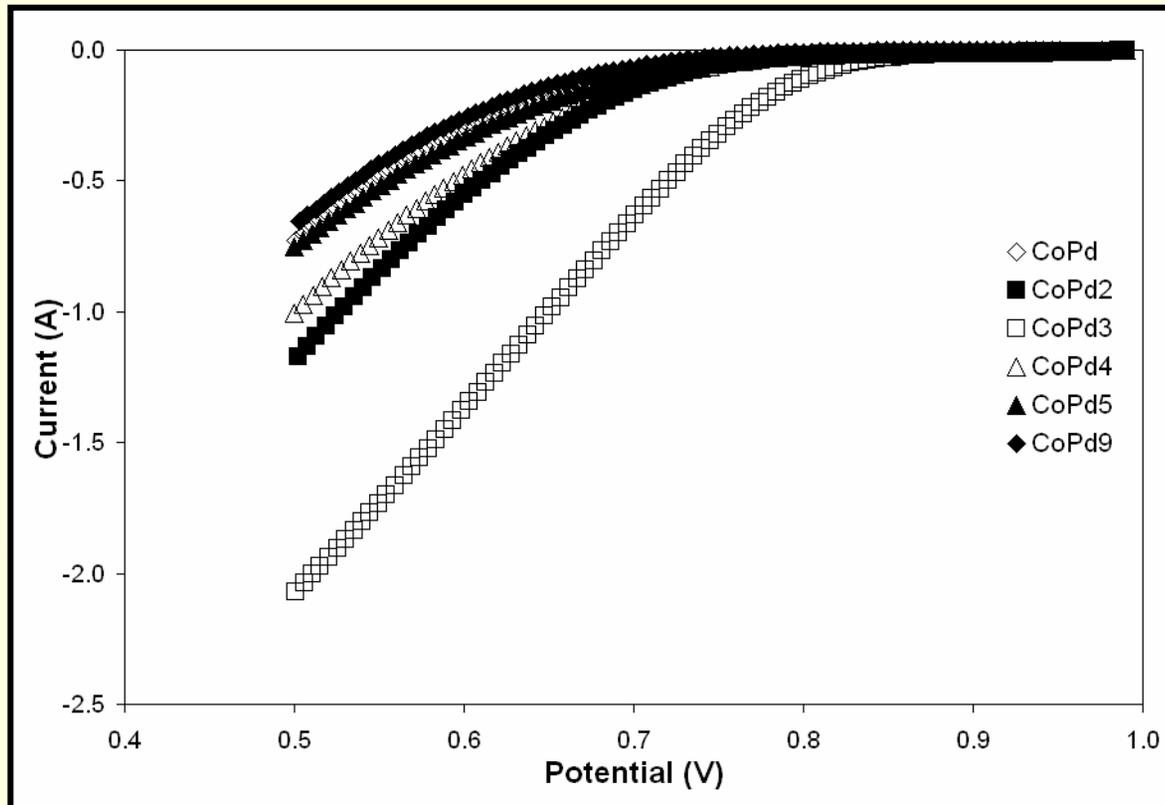


Stage 2 Catalyst Development

- **Best identified catalyst families are further characterized by conventional methods.**
- **Electrodeposited catalyst samples – CV's, Rotating Disk.**
- **Carbon supported catalyst – MEA's, H₂ fuel cell.**

Co-Pd Catalyst Family with High Activity

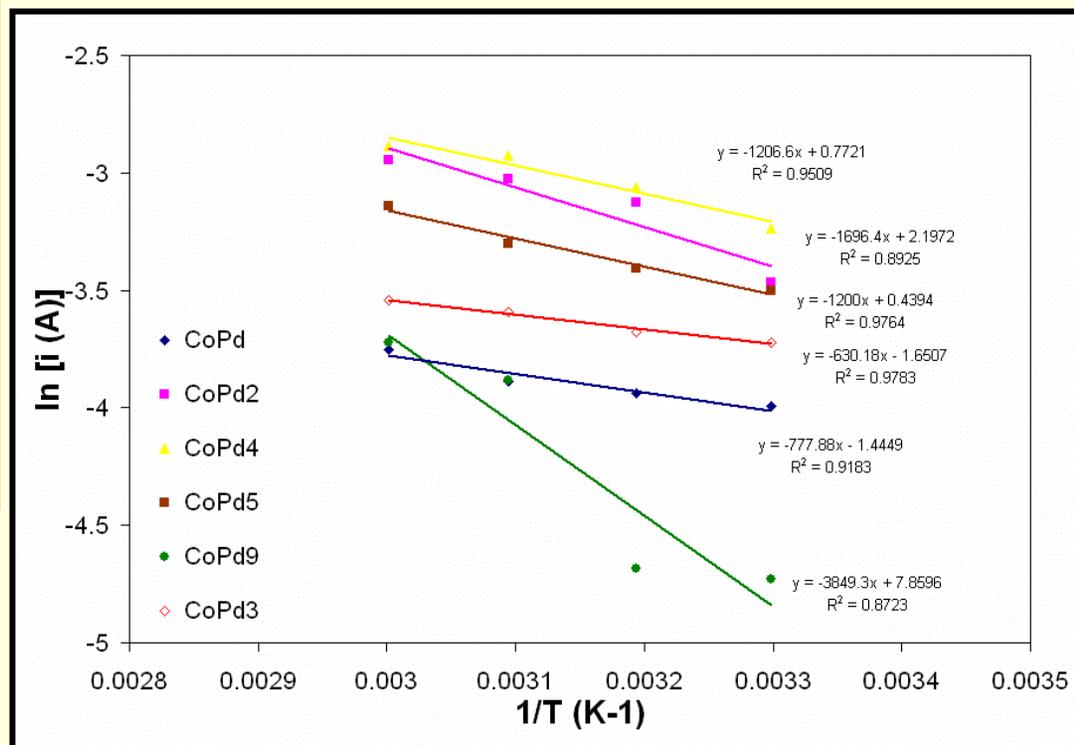
Polarization Curves for Co-Pd compositions



- Temperature: 60°C
- Cathode gas: O₂
- Anode gas: H₂

CoPd_x Kinetic Parameters

Arrhenius Plots for the ORR in a 5 cm² PEMFC on CoPd_x Electrocatalysts

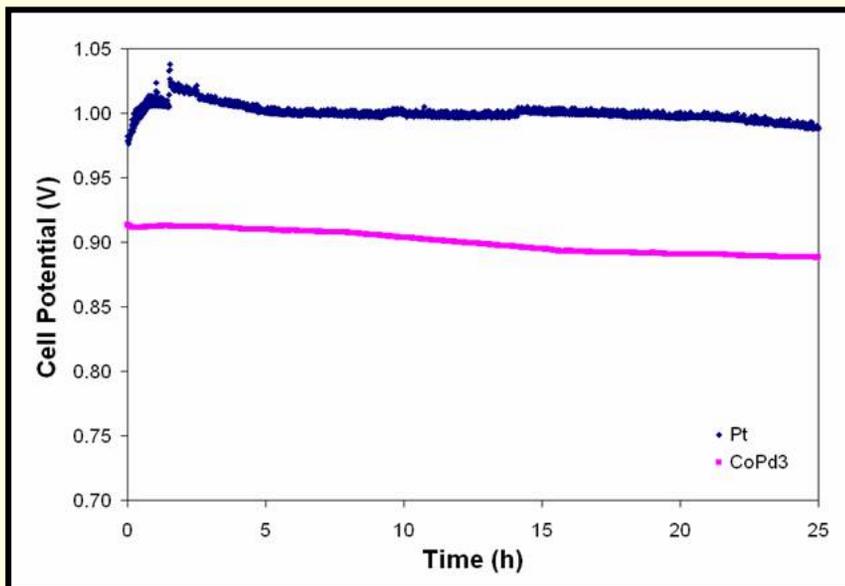


Calculated Kinetic Parameters for ORR on CoPd_x Electrocatalysts in a H₂/O₂ PEMFC

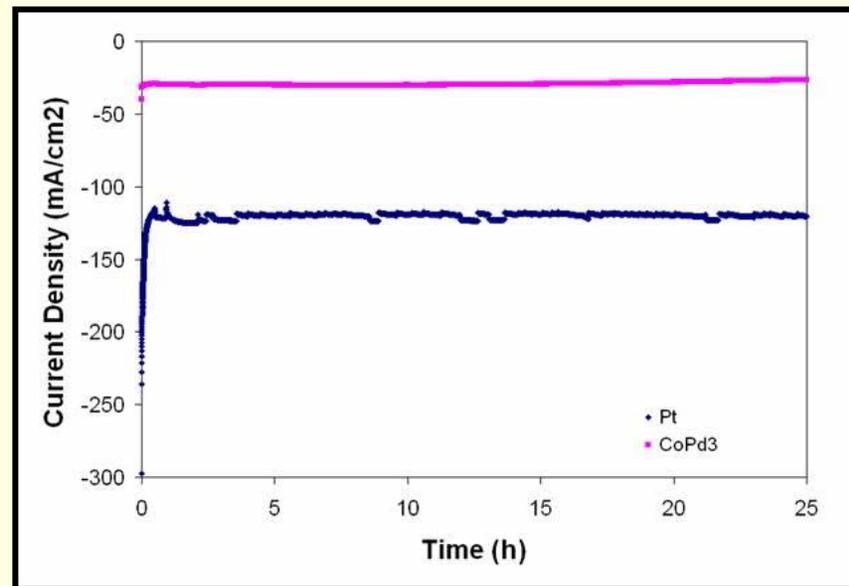
Composition	Onset Potential (V)	Activation Energy (kJ/mol)	Tafel Slope, b 60°C (mV/dec)	Exp[a/b]
CoPd	0.87	80.4	96.5	4.08E+02
CoPd ₂	0.88	104.0	87.1	1.23E+03
CoPd ₃	0.92	52.4	69.6	2.69E+04
CoPd ₄	0.89	100.3	90.3	7.69E+02
CoPd ₅	0.90	99.8	100.1	2.43E+02
CoPd ₉	0.89	320.0	34.8	1.72E+08

Performance Stability of Pd₃Co in Hydrogen Fuel Cell

Open Circuit Voltage Pt and CoPd₃-
cathode/ Pt-anode MEAs in a 5 cm²
PEMFC at 60 °C.



Performance Stability of Pt and CoPd₃
cathode MEAs at 0.8 V, 60 °C.



- Some performance degradation of PdCo₃ 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.**