

# Overview of high-throughput techniques as applied to fuel cell catalysts and electrodes

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Argonne National Laboratory

ElectroCat Workshop  
Argonne National Laboratory

July 26, 2016

# Consortium Objectives

- Accelerate the development and implementation of high activity and stable PGM-free cathode catalysts and electrodes for the:
  - **Oxygen reduction reaction** in polymer electrolyte membrane fuel cells and phosphoric acid and phosphoric acid-based fuel cells
  - **Hydrogen oxidation reaction and oxygen reduction reaction** in alkaline membrane fuel cells
- Argonne's role: Development, optimization, and implementation of combinatorial and high-throughput materials synthesis, characterization, electrode fabrication, and evaluation methodologies
- Key to realizing the full time-saving benefits of high-throughput methodology **Every step in the process needs to be combinatorial or high-throughput**
  - Discovery
  - Synthesis
  - Physical and chemical characterization
  - Catalytic activity and durability screening
  - Electrode fabrication and implementation in fuel cell



# Catalyst Discovery: Library synthesis

## ■ Model systems

- Deposition of gradients of materials by physical vapor deposition (sputtering, heating), chemical vapor deposition
- Deposition of metal salts – simultaneous chemical reduction or electrodeposition

## ■ High-throughput/robotic synthesis of realistic form of catalysts using scalable methods (Argonne case study)

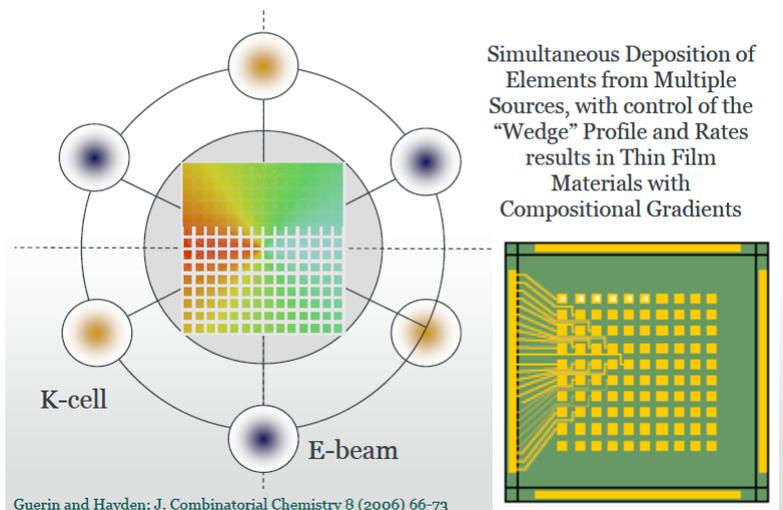
Faster  
Not scalable



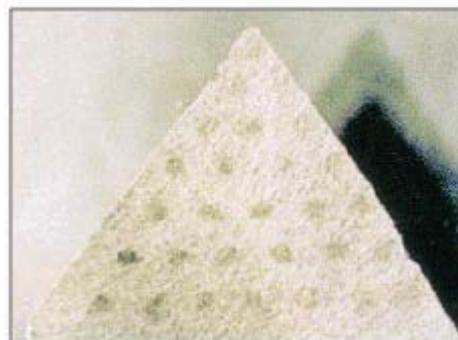
Slower  
High-surface-area

HT-PVD “Wedge Growth” of Thin Film Materials

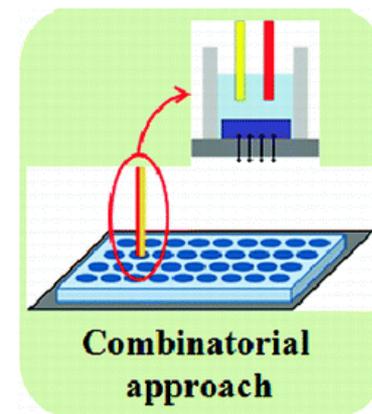
UNIVERSITY OF  
Southampton  
School of Chemistry



Guerin and Hayden, *J. Combi. Chem.*, **8** (2006) 66-73.



E. Reddington, ...E.S. Smotkin, and T.E. Mallouk, *Science*, **280** (1998).



Lee et al., *ACS Comb. Sci.*, **14** (1) (2012) 10–16.



# Catalyst Discovery: Activity Screening

- Aqueous electrolyte – stagnant electrolyte, activity measured by:
  - segmenting/insulating an electronically-conductive catalyst substrate and measuring current, common electrolyte
  - also segmenting electrolyte chamber

School of Chemistry  
 Washer jacket, WE, CE, RE, Luggin capillary, Array electrodes, Electrical contacts, IC connector, PEEK, Glassy Carbon Working Electrode, Gold Spring Pin Connector, to potentiostat.

Si Micro-Fabricated 100 Independently Addressable Gold Electrodes

Current / A  
 time t / s.

Potentiostat, Ramp-Generator and Multi-Channel Current Followers

Guerin, Hayden et. al.; J. Combinatorial Chemistry 6 (2004) 149.  
 Guerin and Hayden, J. Combi. Chem., 8 (2006) 66-73.

A. Top View – Working Electrode Array  
 B. Side View – Working Electrode Array  
 C. Side View -Electrochemical Cell

● Glassy Carbon  
 □ PEEK

■ Reference Electrode  
 | Counter Electrode (Pt)  
 — Circuit Board  
 □ PVDF  
 □ Electrolyte and Reactant

K.C. Neyerlin, et al., J. Electrochem. Soc., 156 (2009) b363-b369.

P. Strasser, et al., J. Phys. Chem. B 107 (2003) 11013. (Symyx)

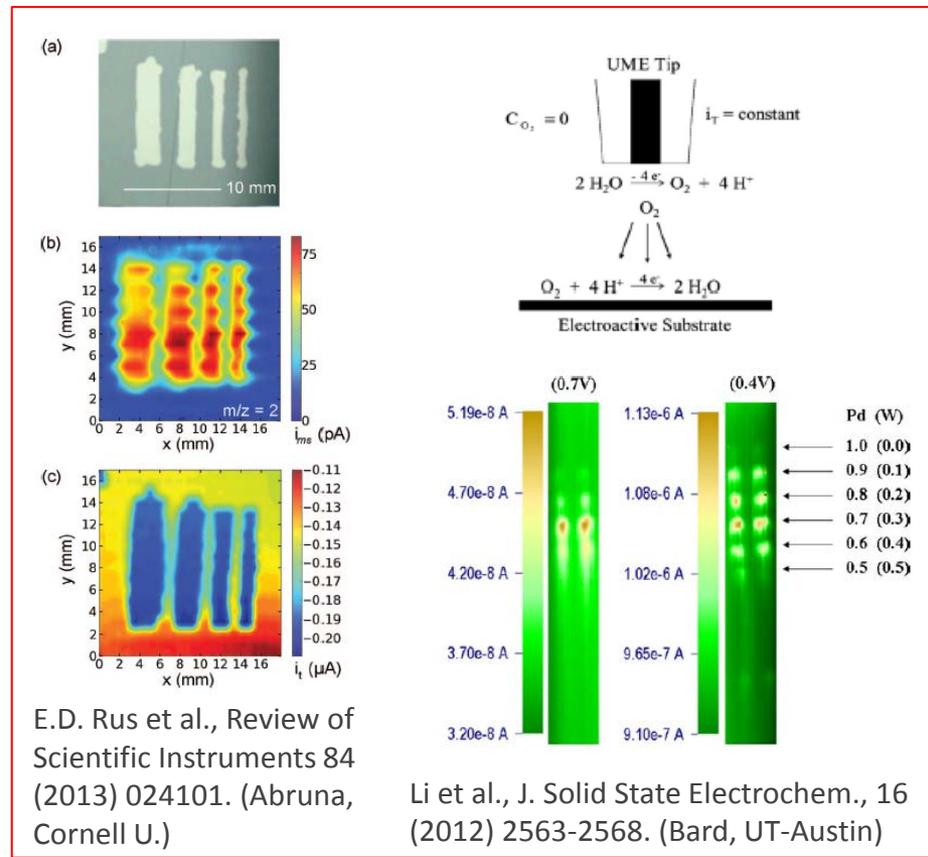
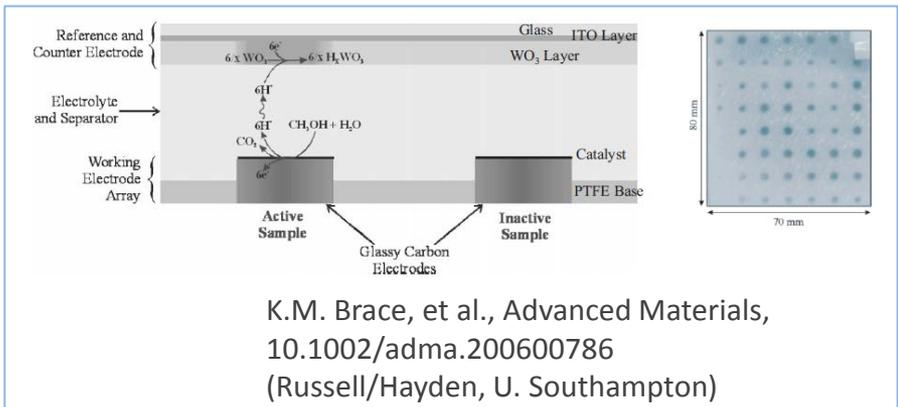
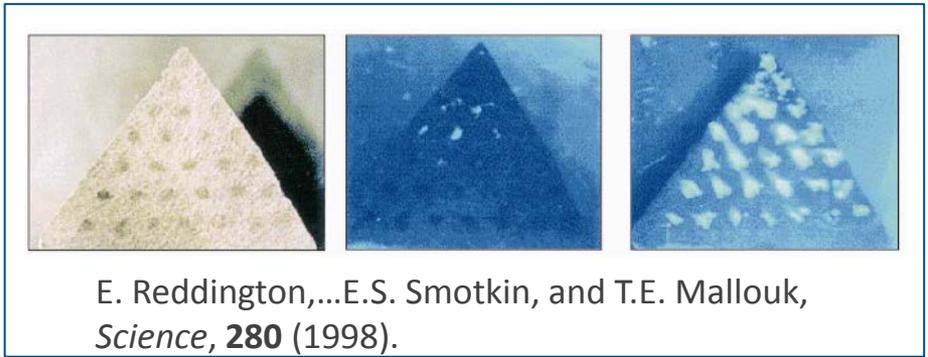
a)

□ Water Bath  
 ■ Electrolyte  
 N<sub>2</sub> for blanketing  
 PVDF  
 Water Bath Outlet  
 O-Ring  
 PEEK  
 Glassy carbon electrodes (Working)  
 PCB  
 Pt Wire (Counter)  
 Zn wire (Reference)  
 N<sub>2</sub> for blanketing  
 Water Bath Inlet

T. Sakamoto et al., J. Power Sources, 247 (2014) 605-611.

# Catalyst Discovery: Activity Screening

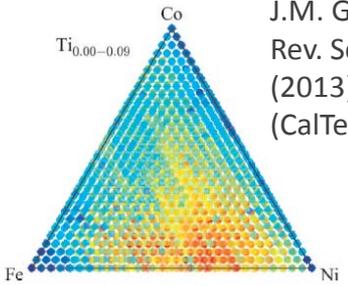
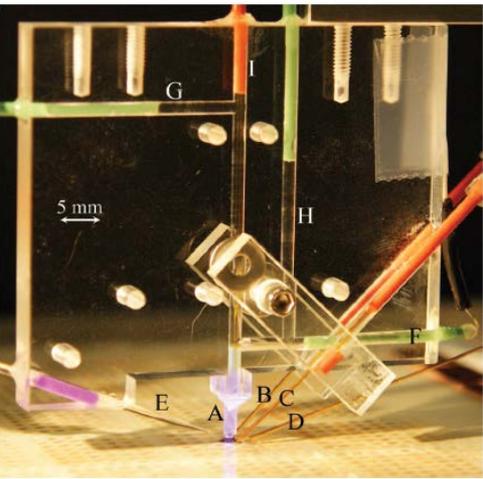
- Aqueous electrolyte – stagnant electrolyte
  - Common electrically-conductive substrate, activity measured with:
    - a solution probe (e.g., fluorescent pH probe)
    - an electrochromic counter electrode (e.g., tungsten oxide)
    - a scanning electrochemical probe (e.g., SECM)



# Catalyst Discovery: Activity Screening

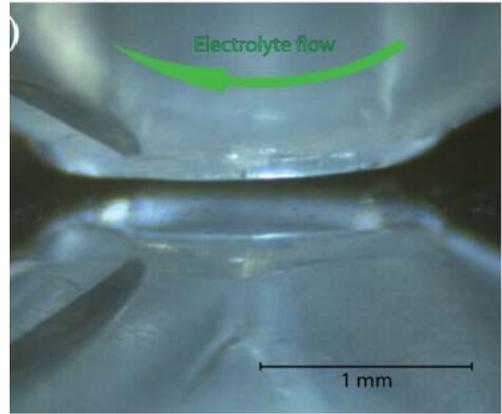
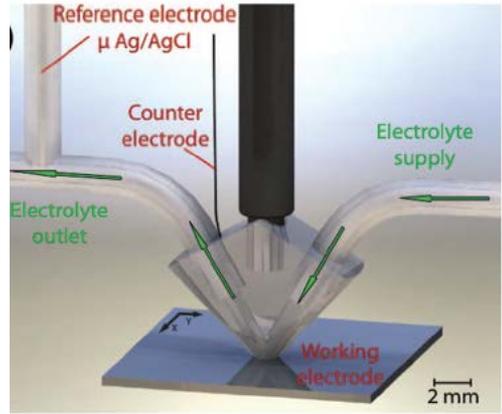
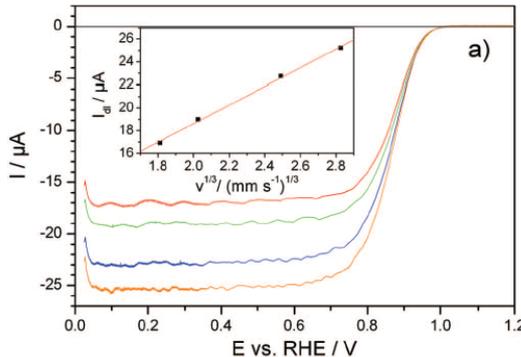
- Aqueous electrolyte – hydrodynamic
  - Common electrically-conductive substrate, activity measured with a mobile “electrochemical cell” and using current-voltage characteristics

## “Scanning Droplet Cell”



J.M. Gregoire, et al.,  
 Rev. Sci. Instrum., 84  
 (2013) 024102.  
 (CalTech)

## “Scanning Flow Cell”



A.K. Schuppert, et al., J.  
 Electrochem. Soc., 159 (2012)  
 F670-F675.  
 (Mayrhofer, Max-Planck, Germany)

# Catalyst Discovery: Activity Screening

- Aqueous electrolyte – hydrodynamic
  - Multiple separate electrically-conductive substrates; activity measured in one electrochemical cell using current-voltage characteristics

## “Multi-channel Rotating-Disk Electrode”

E.B. Easton, A. Bonakdarpour, J.R. Dahn, *Electrochem. Solid-State Lett.*, 9 (1006) A463-A467.

T. He, et al., *J. Power Sources*, 165 (2007) 87-91. (Honda, U.S.A.)

## Channel Flow Double Electrode

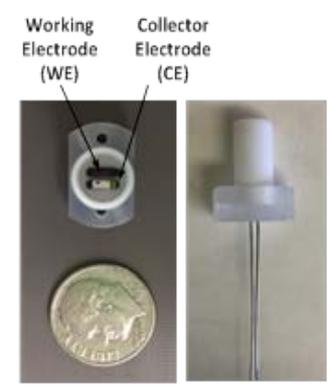
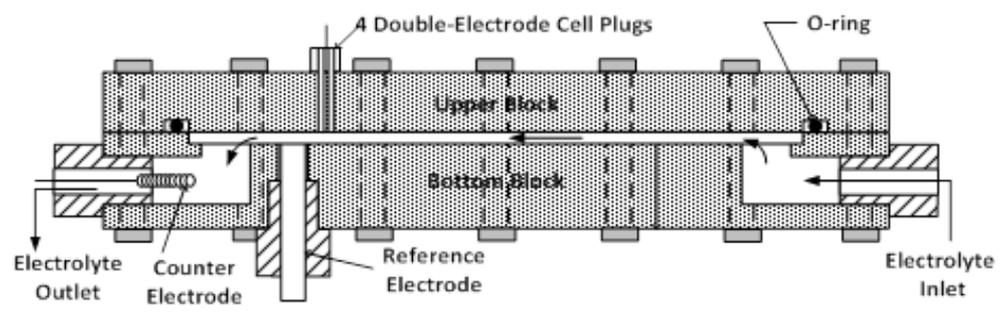
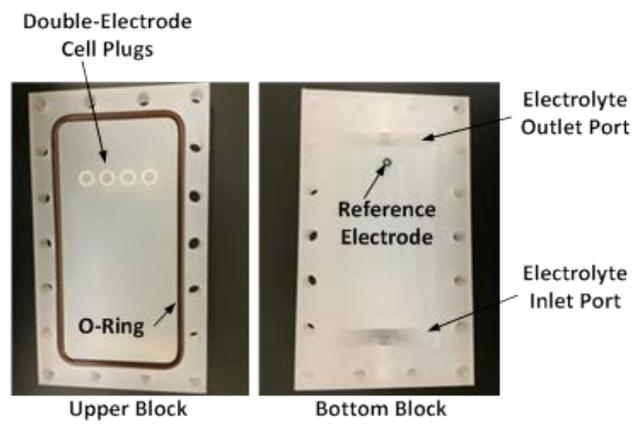
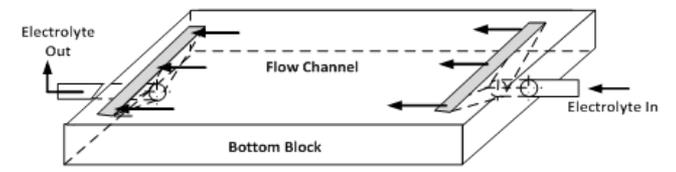
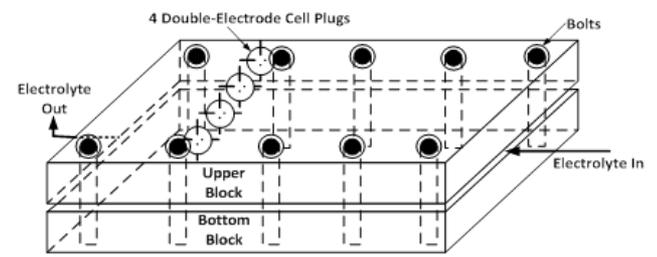
H. Yano, et al., *J. Phys. Chem. C*, **112** (2008) 8372. (M. Watanabe and Eiwa Corporation, Japan.)

# Issues with the Eiwa cell design addressed with ANL cell design

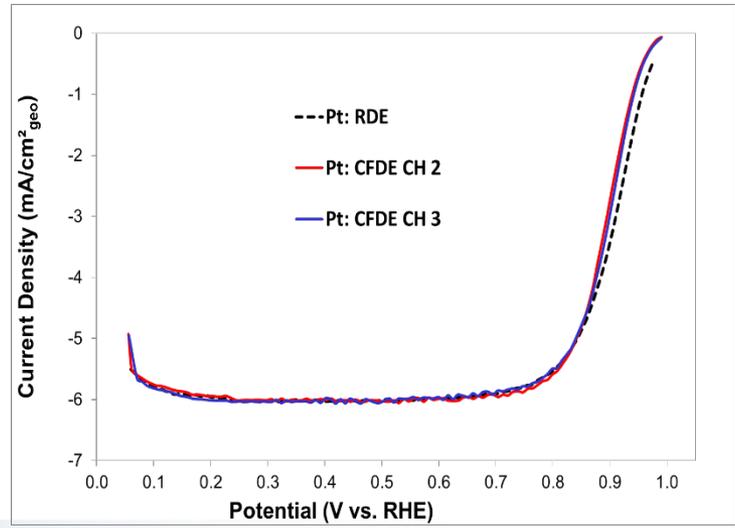
- Bubbles easily trapped in the reference electrode port, causing faulty, high working electrode potentials leading to spikes and noisy voltammograms. In severe cases the catalysts are damaged leading to the loss of catalytic activity
- Electrodes are permanently fixed onto the flow plates. If an electrode is damaged and needs to be polished the entire bottom plate of the CFDE must be polished
- Very high  $iR$  drop between working and reference electrodes ( $>1$  k $\Omega$  resistance)
- Due to the lack of aligning mechanism for assembling and disassembling the flow cell, the process is difficult and time consuming.
- These issues were addressed with Argonne's flow cell design
  - Micro-reference electrode flush with top surface of channel ( $\sim 50$   $\Omega$  Working-Ref resistance)
  - Removable electrodes
  - Aligning pins for cell assembly
  - Cell can be operated in any vertical position



# Argonne's four-channel CFDE cell



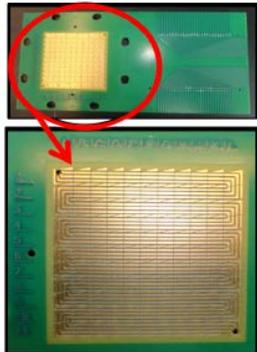
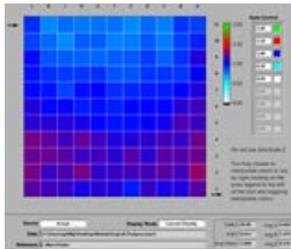
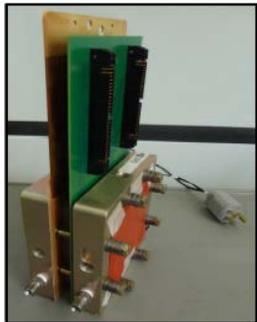
ORR, 18  $\mu\text{g-Pt}/\text{cm}^2$  TKK  
 46 wt% Pt/C catalyst, 0.1 M  $\text{HClO}_4$ ,  
 $\Delta E_{1/2}$  (RDE-CFDE) < 9 mV



# Catalyst activity screening and fuel cell implementation

- Continuous electrode and gas diffusion layer
  - Segmented flow field – segmented bipolar plate
- Electrically isolated electrodes, gas diffusion layers, and bipolar plates
  - Separate gas diffusion electrodes on continuous membrane

## Segmented Cell Hardware



**Guido Bender,  
National Renewable  
Energy Laboratory**

“The Spatial Performance Effect of Electrode Defects in PEMFC,” G. Bender, W. Felt, M. Ulsh; ECS Fall Meeting, Honolulu, HI; October, 2012.

## Array Fuel Cell



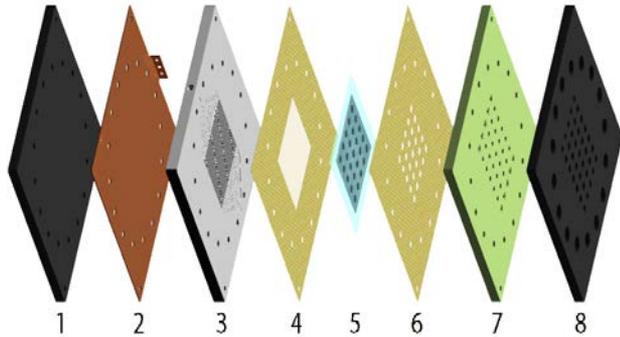
**Gene Smotkin,  
NuVant Systems**



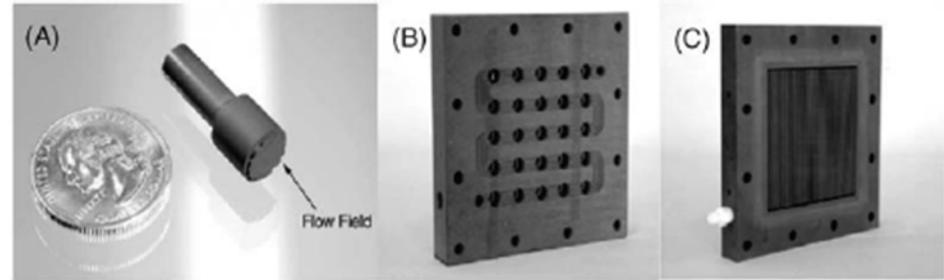
“High-throughput screening of fuel cell electrocatalysts”, E .S. Smotkin, J. Jiang, A. Nayar, and R. Liu, Appl. Surf. Sci., 252 (2006) 2573-2579.

# NuVant Array Fuel Cell

Array Fuel Cell (AFC) developed in DOE-FCTO SBIR Project,  
2005-0017-DE-F602-03ER8374



1. Al end plate; 2. Cu current collector; 3. Graphite flow field; 4. Teflon gasket; 5. Array MEA 6. Array side Teflon gasket; 7. Electronically insulating parallel flow field plate with 25 embedded graphite flow field sensors; 8. Array-side Al end plate.



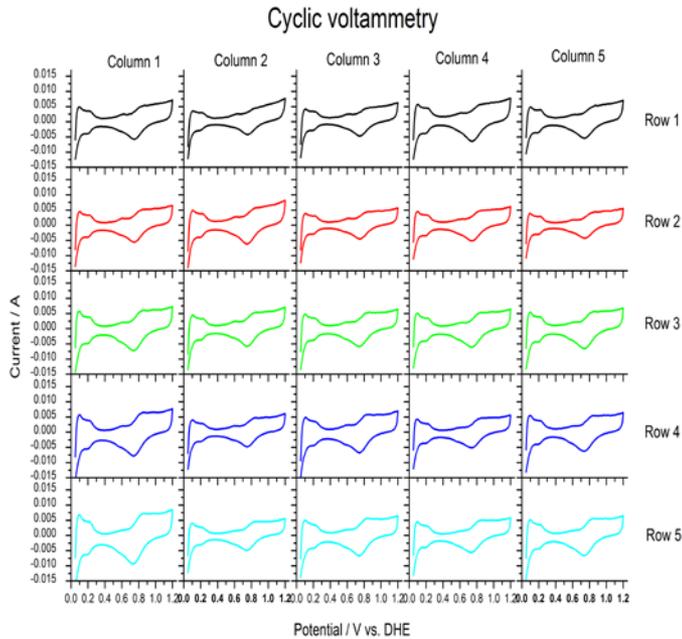
Flow field sensors embedded into  
“component 7”



Array MEA (Nafion 117)  
Bottom side is standard  
100 cm<sup>2</sup> active area GDL.  
Top side are catalytic disc  
areas under disc GDLs.  
Segmented flow field,  
catalytic areas and GDLs.

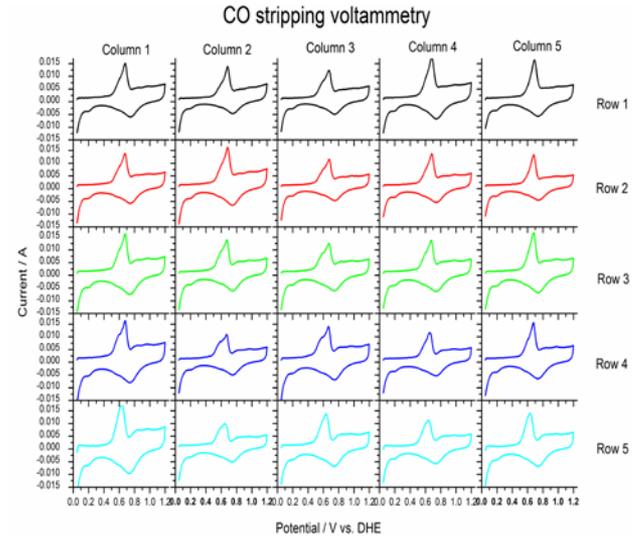


# Array fuel cell cyclic voltammetry and fuel cell performance

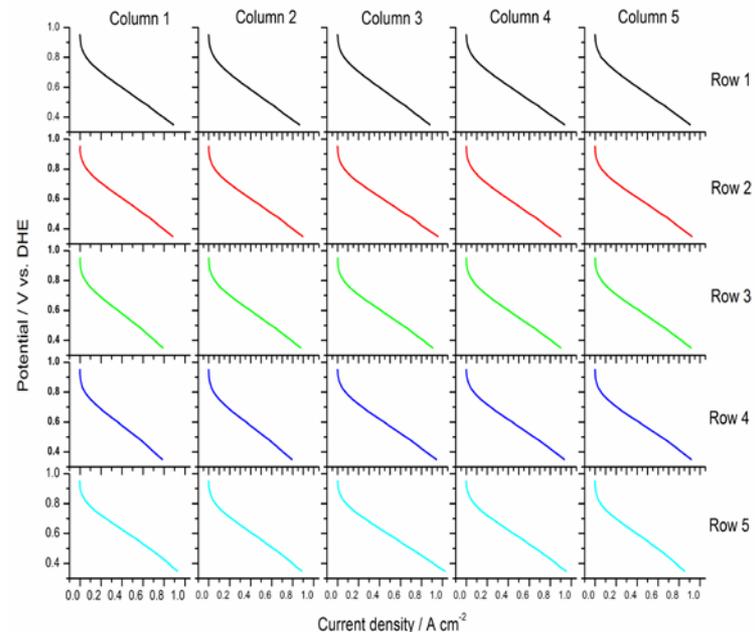


CVs of 25 electrodes made of 40 wt. % Pt/C catalyst cycled between 0.05 and 1.2 V vs. DHE. Scan rate 100 mV/s. Cell temp. 60°C, Humidifier temp. 70°C. Hydrogen flow rate: 100 SCCM. Nitrogen flow rate: 50 SCCM for each parallel flow field.

ORR polarization curves using row switching. Carbon cloth GDLs. 40 wt % Pt/C catalyst at the array cathode/working electrodes. 40 wt % PtRu/C at counter/reference electrode. Cell temp. 60°C. H<sub>2</sub> flow: 100 SCCM. O<sub>2</sub> flow rate/column: 50 SCCM. Polarization curves obtained one row at a time to mitigate down stream dilution. The column flow fields are isolated from each other.



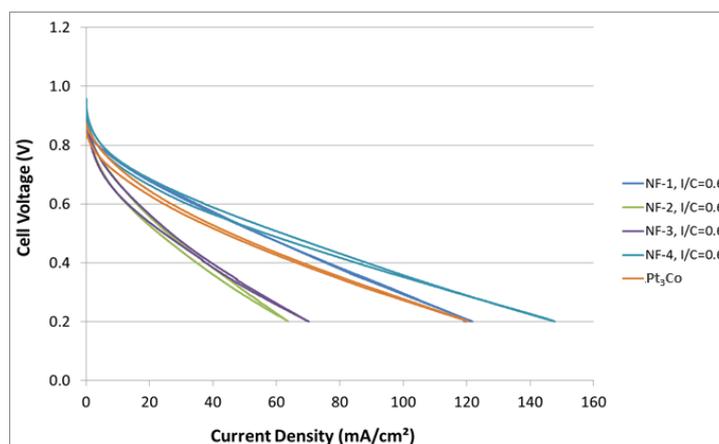
## Oxygen Reduction Reaction - Polarisation curve experiment



# High-throughput optimization of electrode composition

- Utilize robotic system to prepare and deposit catalyst-ionomer-solvent inks onto gas diffusion layers or decals:
  - Inks are made by weighing and dispensing the catalyst powder, solvent, and ionomer solutions at varying ratios into vials using the robotic system and mixed using sonication and magnetic stir bars
  - Characterize agglomerate structure of inks using dynamic light scattering
  - Inks dispensed in circular spots directly onto a heated 1.27 cm<sup>2</sup> gas diffusion layers or decals using the micropipette liquid dispensing unit of the robotic system
  - Hot-press decals or gas diffusion electrodes onto a single membrane/anode assembly.
- To be developed: automated way to uniformly deposit inks onto gas diffusion layers, blanks, and glassy carbon electrodes (e.g., ink-jet printer technology)

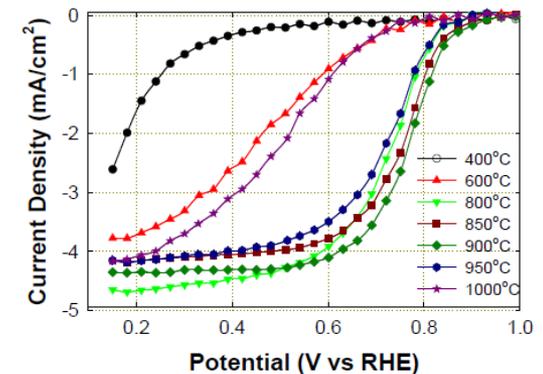
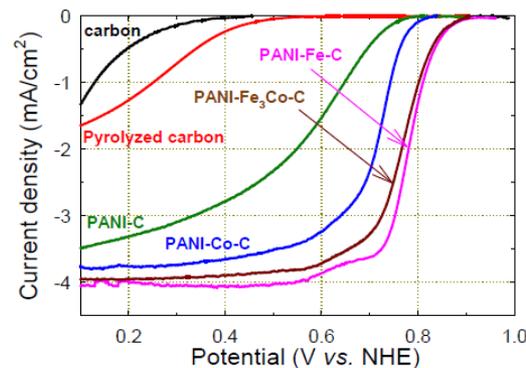
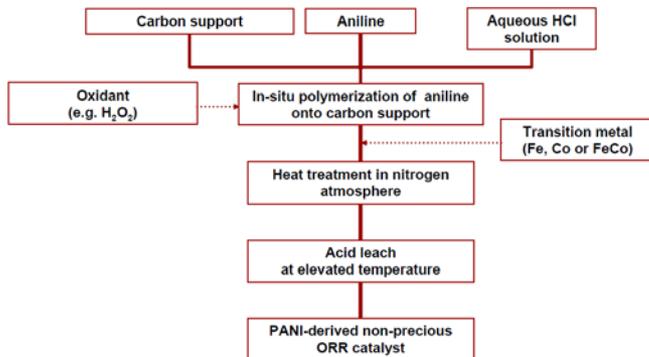
T=60°C, H<sub>2</sub>/Air, 100 kPa(abs.), Cathode PGM loading: 0.1 mg-Pt/cm<sup>2</sup> for Pt<sub>3</sub>Ni nanoframe (NF) and 0.53 mg-Pt/cm<sup>2</sup> for Pt<sub>3</sub>Co



Inks deposited  
by a human  
for this MEA!

# High-throughput/robotic synthesis of high-surface-area PGM-free catalyst (ANL-LANL One Year Lab Call Project)

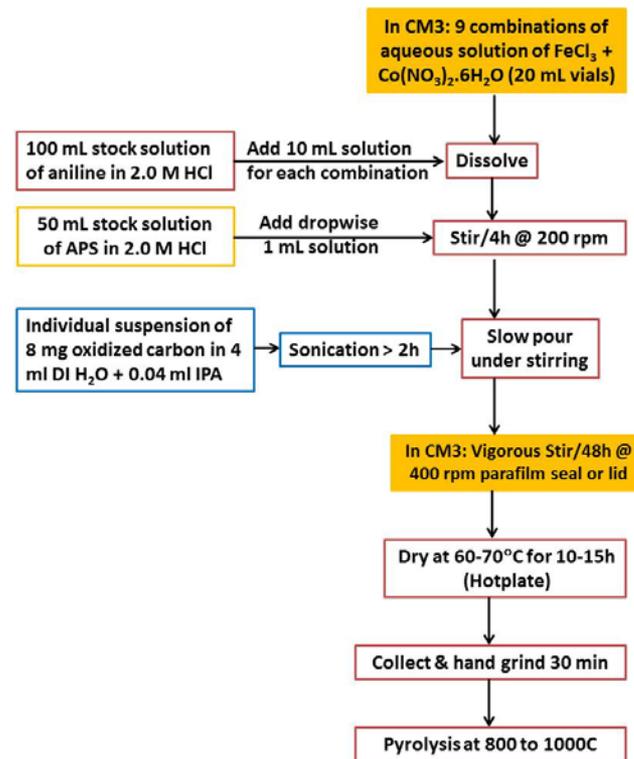
- Overall Approach: Develop and utilize capability for high-throughput synthesis and oxygen reduction reaction (ORR) activity testing of iron, cobalt, polyaniline-based catalysts pioneered by Los Alamos National Laboratory (P. Zelenay, FC-003, “Advanced Cathode Catalysts”, 2007-2011)
- Argonne Tasks:
  - Rapid throughput synthesis of catalyst precursor composites
  - Rapid throughput pyrolysis of catalyst precursors
  - Rapid throughput physical and chemical characterization of catalysts
  - Develop a cell/method for high throughput screening of ORR and ORR activity stability of catalysts in a hydrodynamic aqueous cell
  - Verify validity of high-throughput hydrodynamic cell design and performance using RDE
  - Utilize hydrodynamic cell to screen ORR activity of catalysts made by high-throughput synthesis techniques



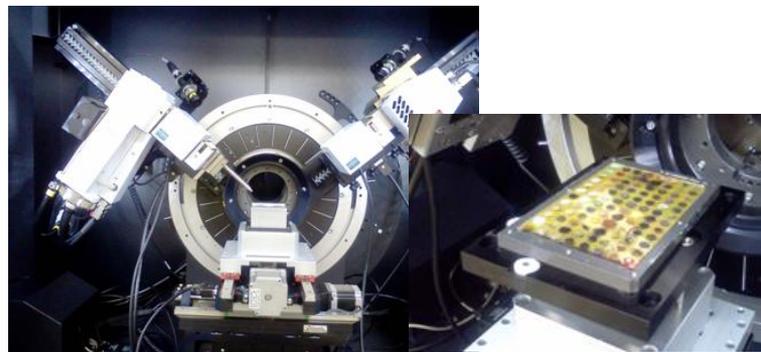
# Example: High-throughput synthesis and characterization of PANI- $\text{Fe}_x\text{Co}_y$

- Synthesis of the powder catalyst precursor was executed on a robotic platform (CM3, FreeSlate Inc.)
- Eleven samples, nine PANI-Fe-Co compositions and two replicates, with the same total amount of metal ( $\text{Fe}+\text{Co}=0.0012$  moles) were synthesized
- High-throughput X-ray diffraction (D8, Bruker AXS) was performed after pyrolysis from  $800^\circ\text{C}$  to  $1000^\circ\text{C}$  and on final catalysts

Robotic platform



HT X-ray Powder Diffraction



# High-throughput PGM-free catalyst synthesis and phase composition characterization

## Nine Fe to Co ratios

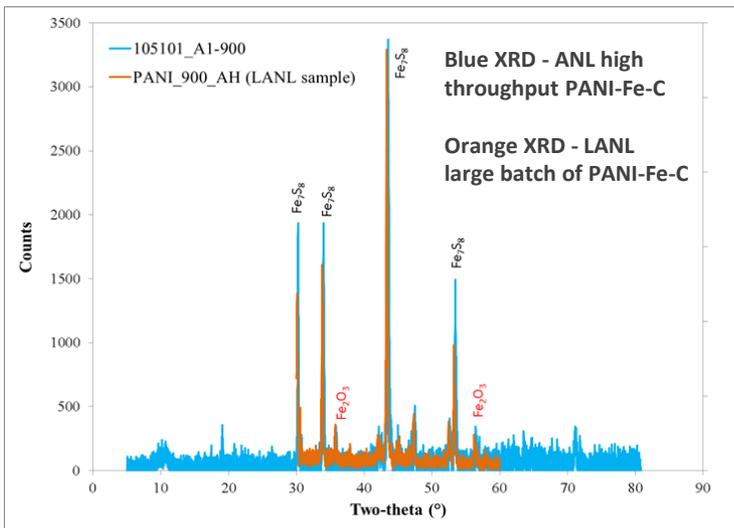
Moles Fe in ratio	Moles Co in ratio
1	0
4	1
3	1
2	1
1	1
1	2
1	3
1	4
0	1

**Forty-five variants**

**Five pyrolysis temperatures:  
800, 850, 900, 950, 1000°C**



(Left) Nine metal salt precursor solutions with iron to cobalt ratios shown in Table (Cobalt only on left and Iron only on right).  
(Right) The iron only solution during polymerization of the polyaniline.



**Highlight: Argonne's HT process produces PANI-Fe-C powder with same phase composition as large single batch synthesized at LANL**

See back-up slides for XRD's of other PANI-Fe,Co-C compositions

# Methods for HT acid treatment and washing of PGM-free catalyst precursors

Acid treatment at elevated temperature

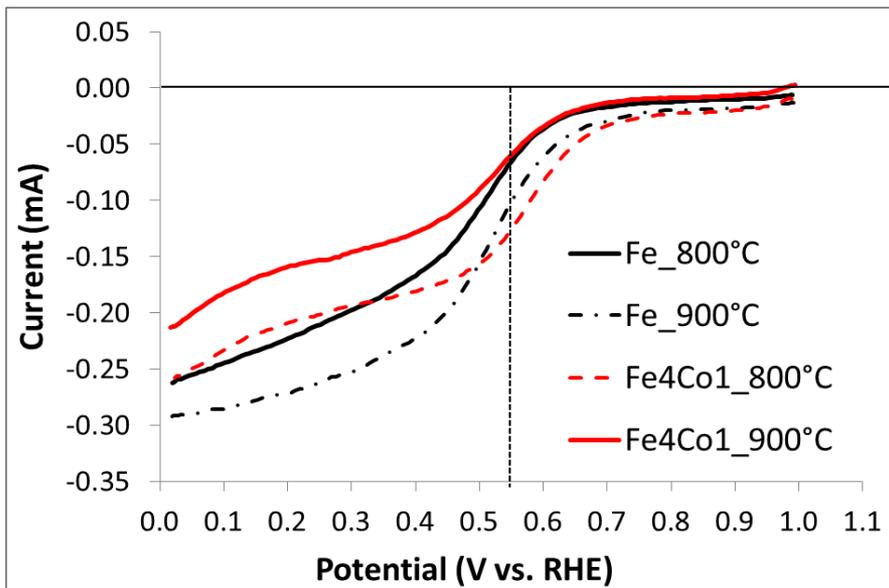
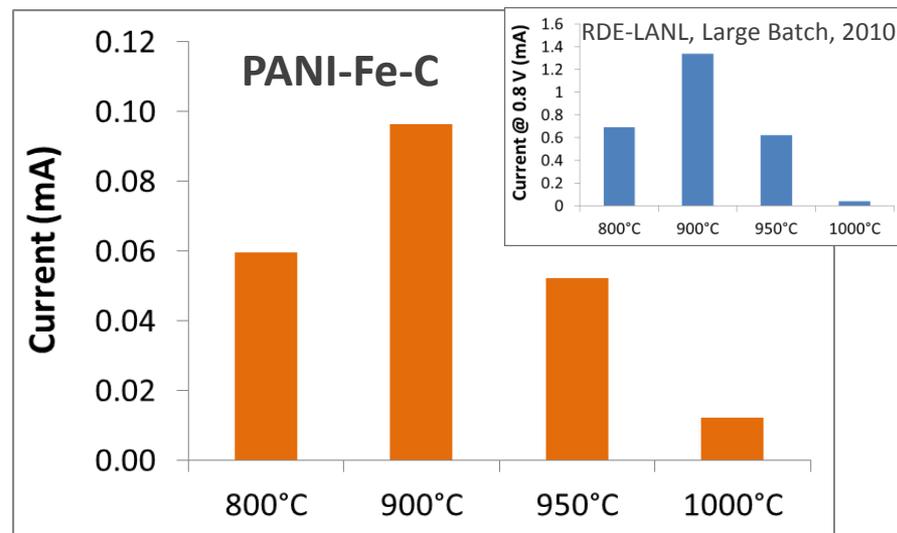
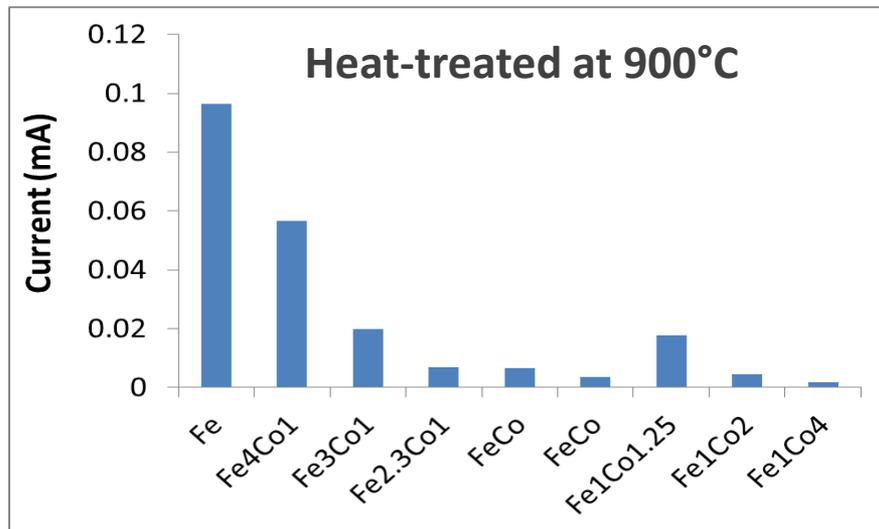


Centrifuging (replaces filtering)



- Acid treatment and washing steps can be high throughput
- Pyrolysis step can be high throughput
- Slow step in catalyst processing is catalyst grinding
  - This step can be mechanized as well

# ORR activity trends for HT PANI-Fe,Co-C using four-channel double electrode cell



- **Highlight:** Achieved excellent agreement of activity trends, determined using CFDE, for HT small batch samples prepared in this project with trends observed using RDE for large batches prepared by LANL (Zelenay, FC-003)
- **Highlight:** Identified a new PANI-Fe,Co-C composition with higher ORR activity than the previously-identified best in this class: Fe<sub>4</sub>Co<sub>1</sub> pyrolyzed at 800°C

# Next steps for high-throughput synthesis, activity screening, characterization, electrode development

- Catalyst synthesis and activity screening:
  - Full automation of PGM-free catalyst synthesis steps, including grinding step
  - Automation of uniform deposition of ink on glassy carbon electrodes
  - Addressing issues with lack of diffusion-limited current in hydrodynamic measurements of PGM-free catalyst ORR activity
  - Addressing high overpotentials observed in **PGM-free** electrocatalyst ORR voltammograms versus those observed in RDE
- Catalyst characterization:
  - High-throughput pyrolysis with in situ effluent analysis and X-ray absorption (XAFS) characterization of species
  - High-throughput XAFS characterization for metal species present in cathode catalyst layer and changes in species during ORR in fuel cell
  - Combinatorial characterization of ORR activity using CFDE cell with downstream electrochemical and on-line ICP-MS detection of dissolved catalyst components for stability characterization
  - In situ/in operando high throughput analysis of species formed, catalyst particle size evolution, and carbon agglomerate structure using XAFS and X-ray scattering

## Next steps (continued)

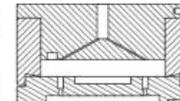
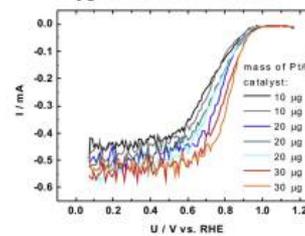
- Electrodes/MEA:
  - Complete robotic synthesis and characterization of agglomerate structure of catalyst-ionomer inks (light scattering of dilute inks; X-ray scattering of concentrated inks)
  - Complete robotic fabrication of catalyst-ionomer decals and *ex situ* characterization of ionic and electronic conductivities of ink layers on decals as a function of T and RH
  - Complete robotic characterization of porosity and diffusivity of catalyst-ionomer decals
  - **Attaining high performance in high current density region for array fuel cell**
  - “High throughput” tomography with automated image analysis and output of structural parameters to cathode catalyst layer structure-transport-performance model
- Identify and utilize other high-throughput synthesis and screening techniques developed at other labs
- Apply techniques to other classes of catalysts developed within ElectroCat



# Back-up slides



### Multielectrode Teflon Cell Oxygen Reduction Reaction



## Multielectrode Teflon electrochemical nanocatalyst investigation system

Nejc Hodnik <sup>a,b,\*</sup>

<sup>a</sup> Max-Planck-Institut für Eisenforschung GmbH, Max-Planck Str. 1, 40237 Düsseldorf, Germany

<sup>b</sup> National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

MethodsX 2 (2015) 204–210

- University of Cape Town, Center for Catalysis Research, Jack Fletcher



# Combinatorial Electrochemistry: A Highly Parallel, Optical Screening Method for Discovery of Better Electrocatalysts

Erik Reddington, Anthony Sapienza, Bogdan Gurau, Rameshkrishnan Viswanathan, S. Sarangapani, Eugene S. Smotkin,\* Thomas E. Mallouk\*

SCIENCE • VOL. 280 • 12 JUNE 1998



**Fig. 1.** Pt-Rh-Os ternary array in 6 M aqueous methanol (pH 6) quinine indicator. **(Left)** Image in white light. **(Center)** Fluorescence image at low overpotential, identifying the most active region of composition space. **(Right)** Fluorescence image at high overpotential, where methanol oxidation occurs at every spot in the array.

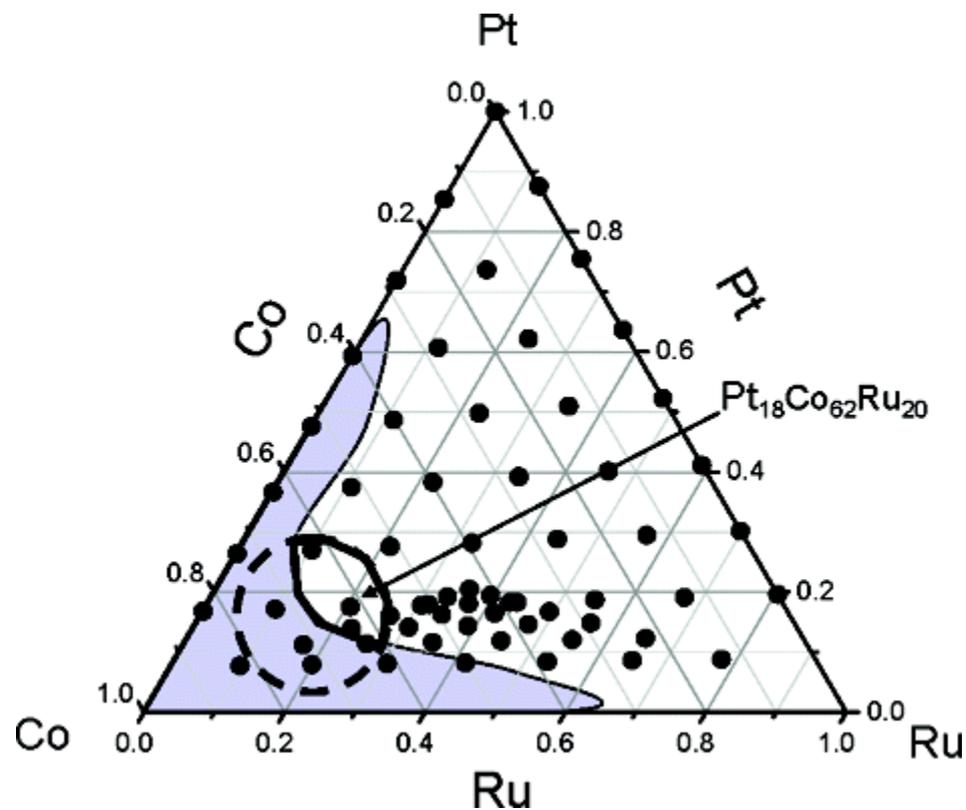
## Peter Strasser\*

Department of Chemical and  
Biomolecular Engineering,  
University of Houston, Houston,  
Texas 77204-4004

*J. Comb. Chem.*, **2008**, *10* (2), pp  
216–224

**DOI:** 10.1021/cc700166p

Publication Date (Web): February  
08, 2008



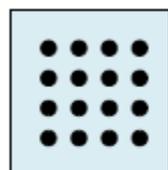
## Combinatorial Study of High-Surface-Area Binary and Ternary Electrocatalysts for the Oxygen Evolution Reaction

K. C. Neyerlin,<sup>a,\*</sup> Greg Bugosh,<sup>a</sup> Rhys Forgie,<sup>a</sup> Zengcai Liu,<sup>a,\*</sup> and Peter Strasser<sup>a,b,\*\*,z</sup>

<sup>a</sup>Department of Chemical & Biomolecular Engineering, University of Houston, Houston, Texas 77204, USA

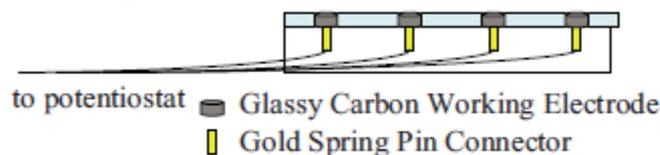
<sup>b</sup>Institut fuer Chemie, Technische Universitaet Berlin, 10623 Berlin, Germany

A. Top View – Working Electrode Array



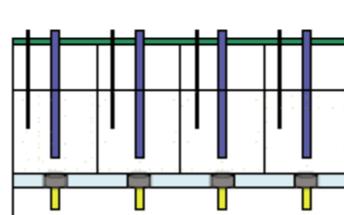
- Glassy Carbon
- PEEK

B. Side View – Working Electrode Array

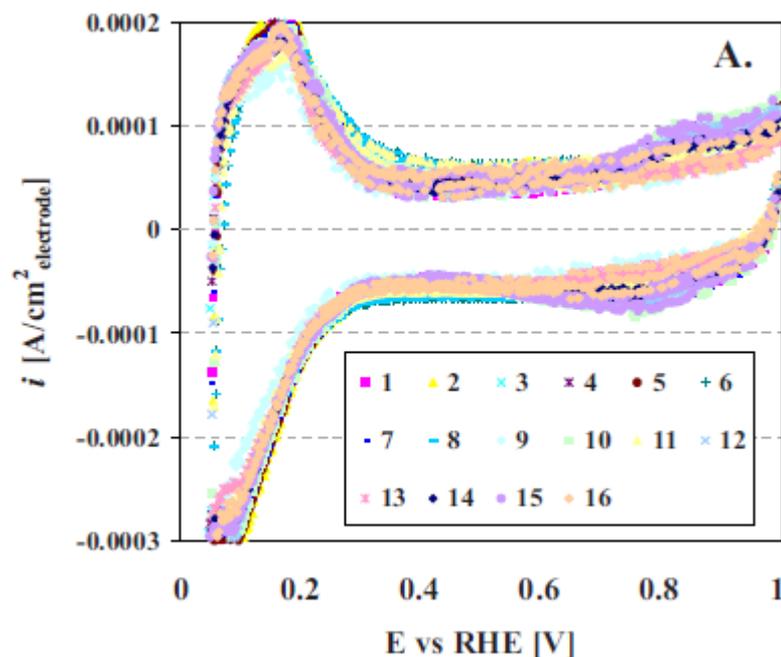


- Glassy Carbon Working Electrode
- Gold Spring Pin Connector

C. Side View -Electrochemical Cell

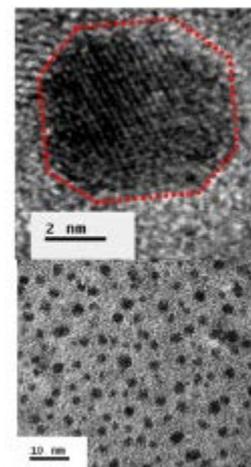
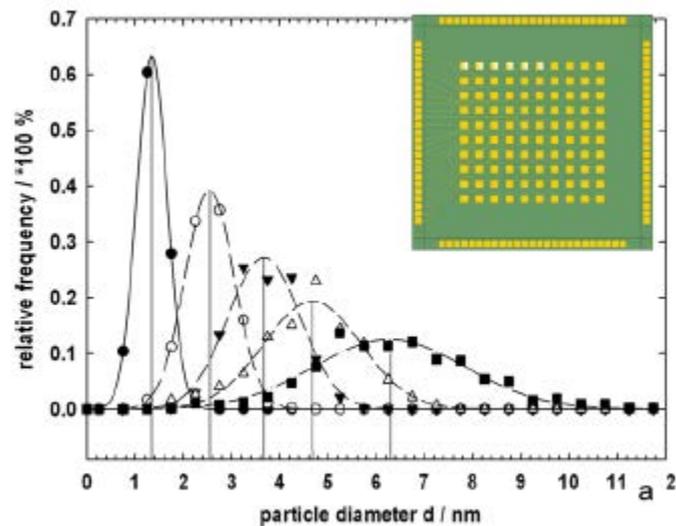
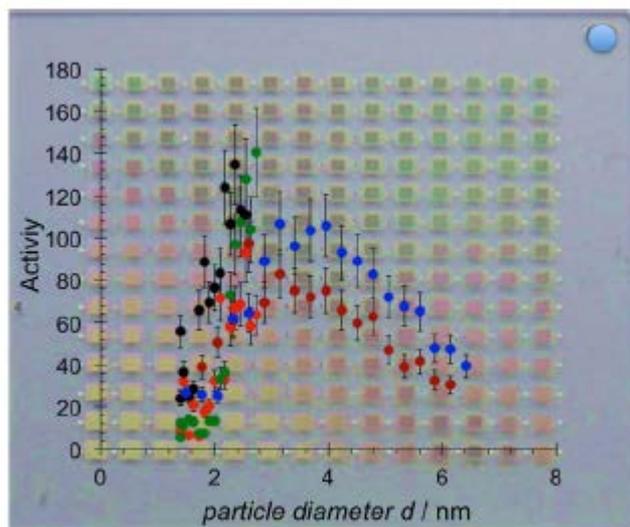


- Reference Electrode
- Counter Electrode (Pt)
- Circuit Board
- PVDF
- Electrolyte and Reactant



# Particle Size and Support Effects in Electrocatalysis

BRIAN E. HAYDEN



ACCOUNTS OF CHEMICAL RESEARCH ■ 1858–1866 ■ 2013 ■ Vol. 46, No. 8

# Combinatorial discovery of Ni-based binary and ternary catalysts for hydrazine electrooxidation for use in anion exchange membrane fuel cells

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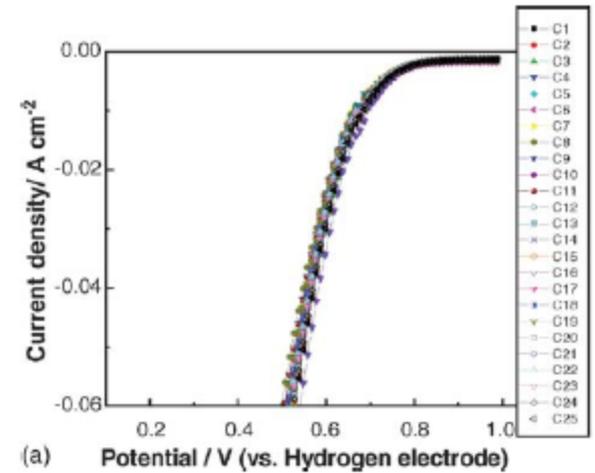
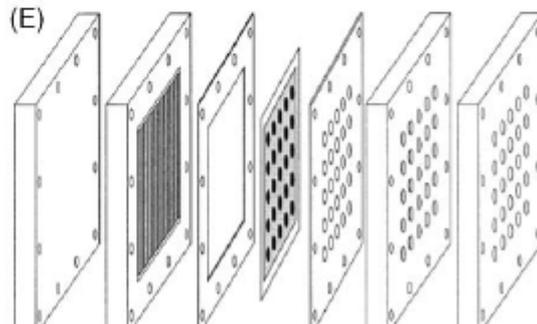
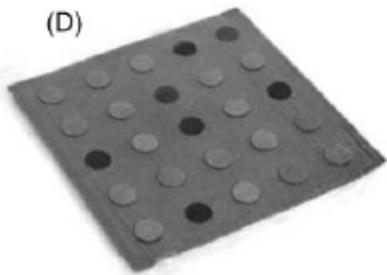
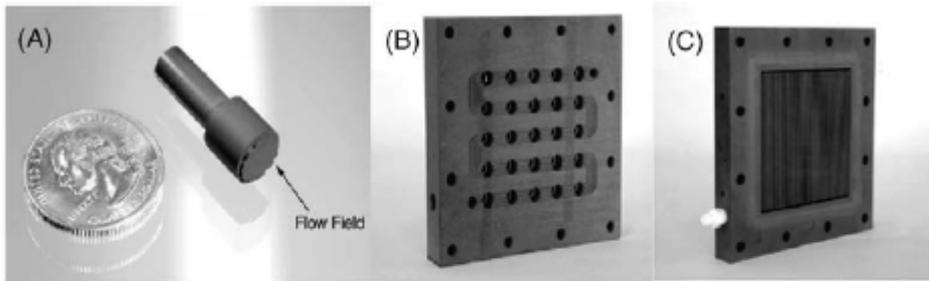
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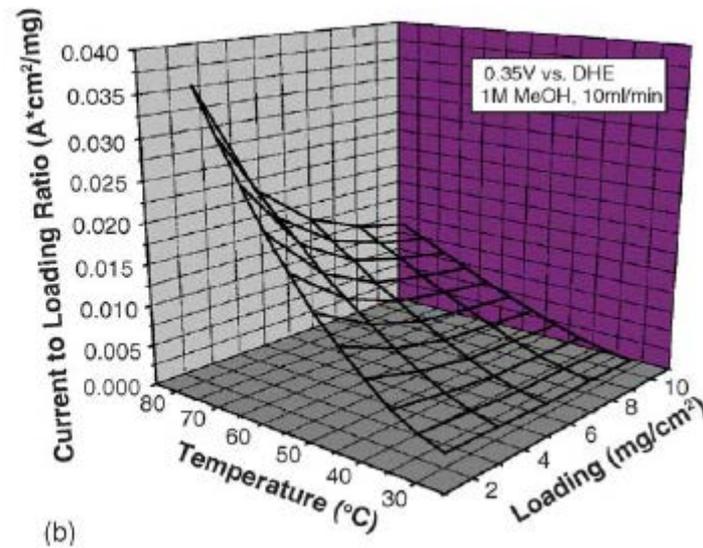
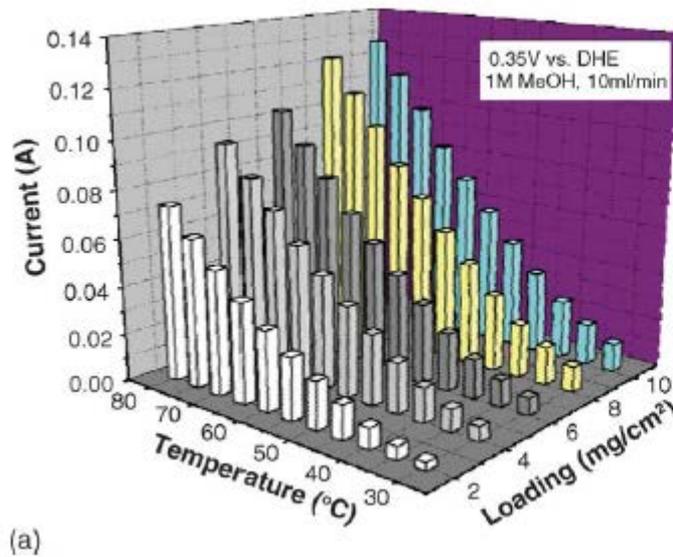
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*T. Sakamoto et al. / Journal of Power Sources 247 (2014) 605–611*





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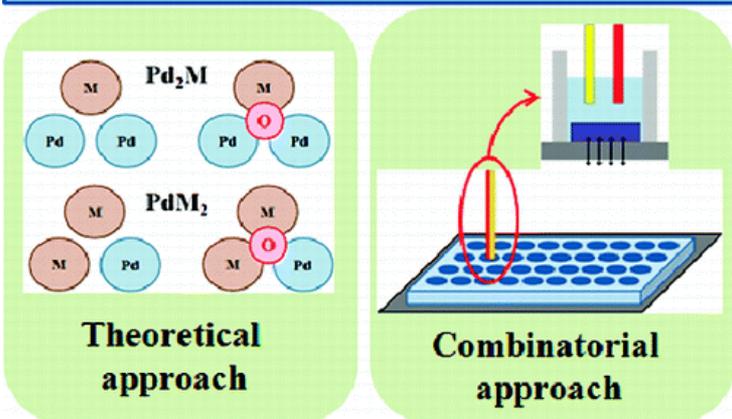
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### Development of new ORR catalysts



## Combinatorial Screening of Highly Active Pd Binary Catalysts for Electrochemical Oxygen Reduction

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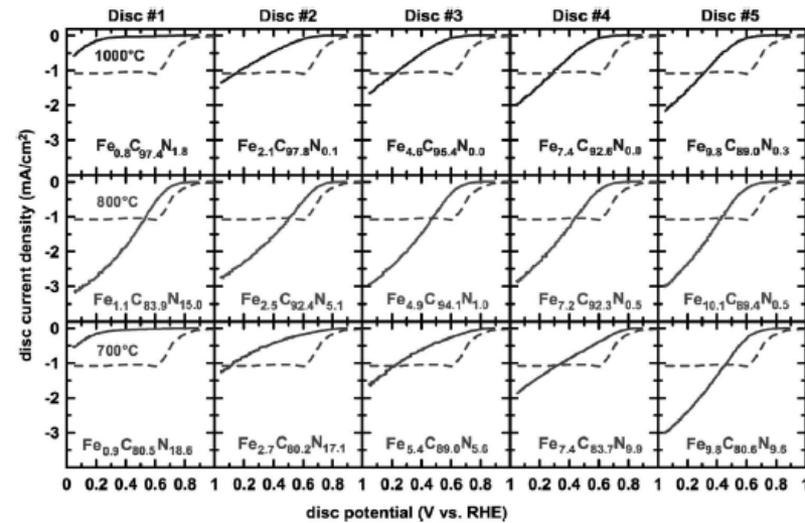
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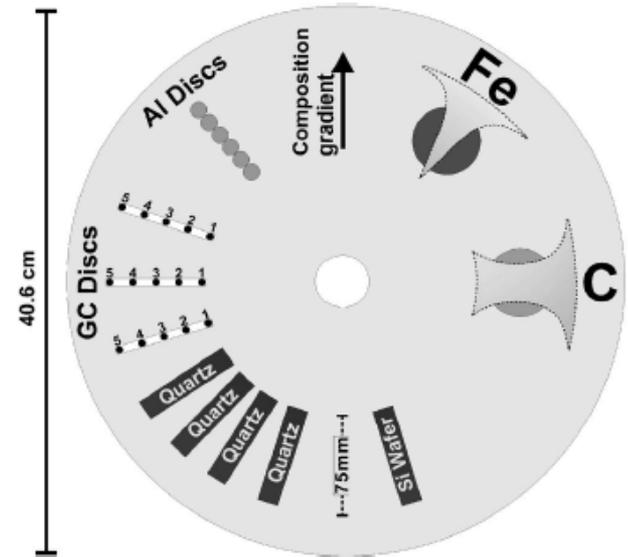


Review that the following figures were taken from.

**Fig. 12.** The ORR activity measurement results of the Fe–C–N arrays annealed at 700, 800, and 1000 °C. The testing was performed at a sweep rate of 5 mV s<sup>-1</sup> in 0.1 M HClO<sub>4</sub> electrolyte solution at room temperature. Composition of each disk was also shown in the figure. Dashed line is the activity of another Fe–C–N array. Reproduction of Fig. 3 of [49]. Reproduced by permission of The Electrochemical Society.)

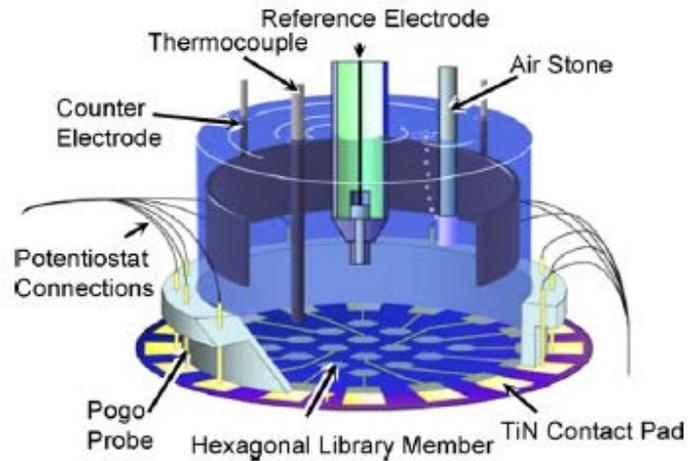


**Figure 3.** Disk current densities for sputtered libraries annealed at 700, 800, and 1000°C. Measurements were made at a sweep rate of 5 mV/s in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> at room temperature. The average composition on each disk is indicated on the plot. Also shown in each panel is the activity reported by Dodelet's group for  $\text{II}(0.2)\text{FeAc}(900)$  at 100 rpm (dashed line).<sup>18</sup>



**Figure 1.** Schematic diagram illustrating the layout of the rotating substrate table. Projections of the Fe and C targets and the masks that create the composition spread are also shown.

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## Combinatorial screening of thin film electrocatalysts for a direct methanol fuel cell anode

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Received 10 July 2006; received in revised form 18 August 2006; accepted 15 September 2006  
Available online 1 November 2006

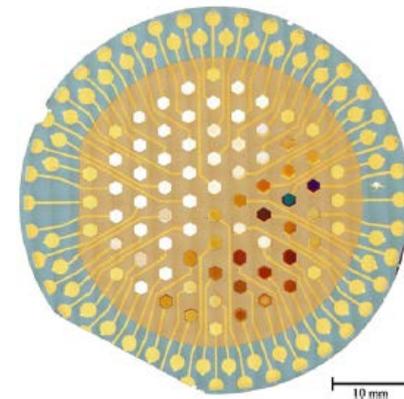


Fig. 7. A picture of combinatorial library fabricated on a silicon wafer. (Reproduction of Fig. 1 of [25].)

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