



# High Efficiency Electrolysis Materials Research

**Donald Pile**  
**David Ingersoll**

**Sandia National Laboratories**

**26 May 2004**

This presentation does not contain any proprietary or confidential information.



# *Objectives*

## **Improve the cell performance for electrolysis of water through improved catalysts and membranes**

- 1. Prepare structured polymer thin films as novel low resistance, hydroxyl conducting membranes and evaluate their electrochemical performance as electrolyte/separator**
- 2. Prepare and electrochemically evaluate transition metal (e.g., Mo) macrocycle complex-based electrocatalysts**
- 3. Develop combinatorial catalyst discovery using direct assessment of electrochemical activity**
- 4. Develop novel catalyst discovery through spatial correlation between localized electrochemical activity and catalyst composition/structure of more traditional electrocatalysts**



# ***Initial Objectives & Budget***

- **FY04 new start – *lab work initiated 4/04!***
- **Funding**
  - initially set at \$100k beginning mid-01/04
  - increased to \$188k (late-03/04)
- **Present Funding level limits technical activities to:**
  - 1. Hydroxyl-Conducting Membrane, and**
  - 2. Mo-Macrocycle Catalyst Development**
- **One month into lab work:**
  - initiated synthesis of catalyst material, prepared for evaluation and polymer film membrane development, performed additional literature search

# DOE Technical Barriers and Targets for Water Electrolysis

- **Barriers Addressed**

Q. Cost \_ through non-precious metal catalyst exhibiting improved performance

R. System Efficiency \_ seek to exceed present conversion efficiency

Z. Catalysts \_ improved electrodes for high conversion efficiency and durability

– Improved cell materials (stable, low-cost) & operation efficiency result in both lower capital costs and lower demand for electricity production

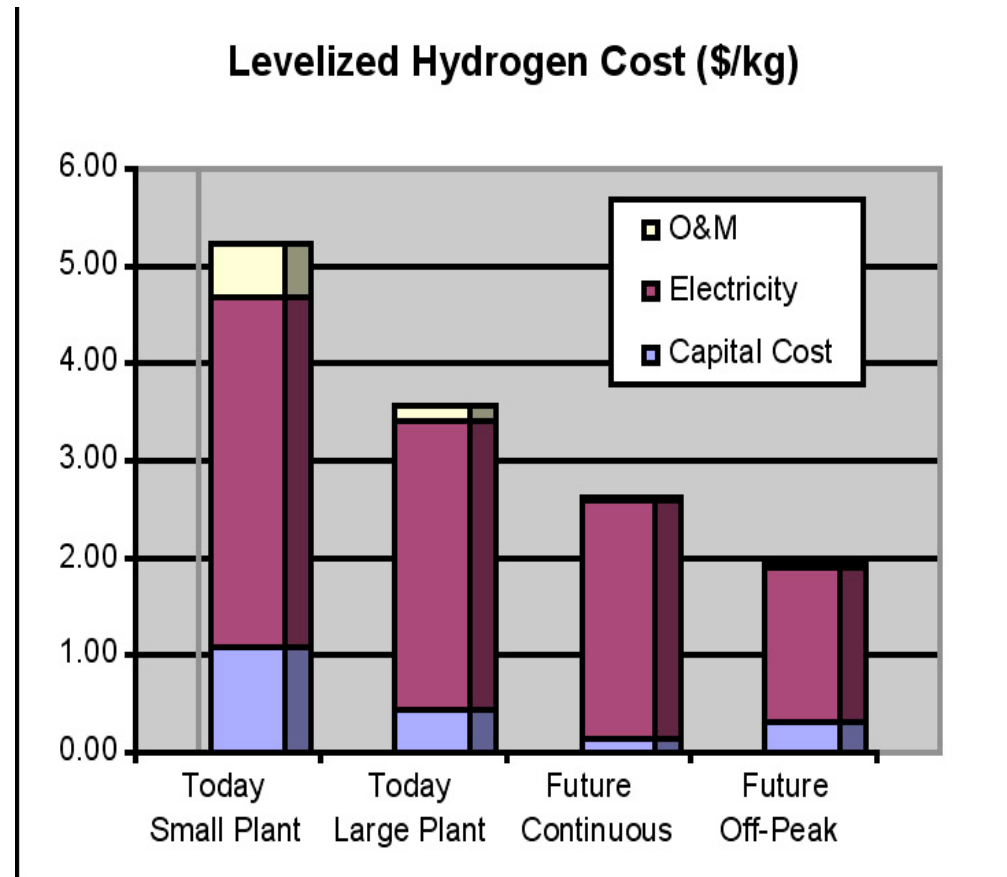
- **Targets for Project**

Cell Stack Technical Targets	2003 Status		2005 Target		2010 Target	
Cost / \$/kg	0.64	1.37	0.48	1.37	0.25	0.30
Energy Efficiency / %	72	65	76	70	81	79

250 kg/day Refueling Station / Small-Scale (2 kg/day) Refueling

# Hydrogen Production Through Electrolysis Cost Considerations

- Three principal cost aspects
  - Operation & Maintenance
  - Capital cost
  - Power (electricity)
- Relative cost breakdown dependant on plant characteristics
- Future projections based on anticipated improvements in stack design
- Single most important factor is cost of electrical energy



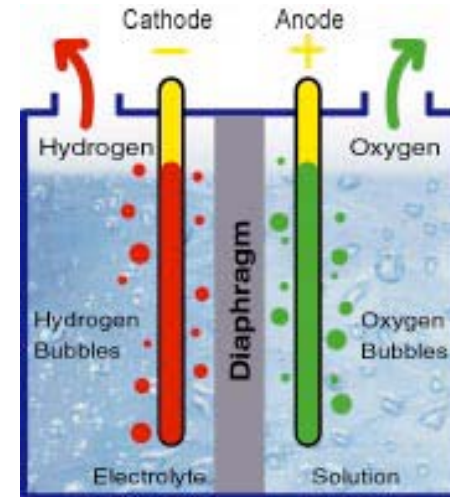
# Programmatic Needs vs Technical Approach Cost

LHC Parameter	% change in LHC
Capital Cost	0.16 %
Efficiency	0.83 %
O&M Cost	0.05 %

Levelized Hydrogen Cost (LHC) Parameter Sensitivity Study  
 - each parameter changed by 1% -

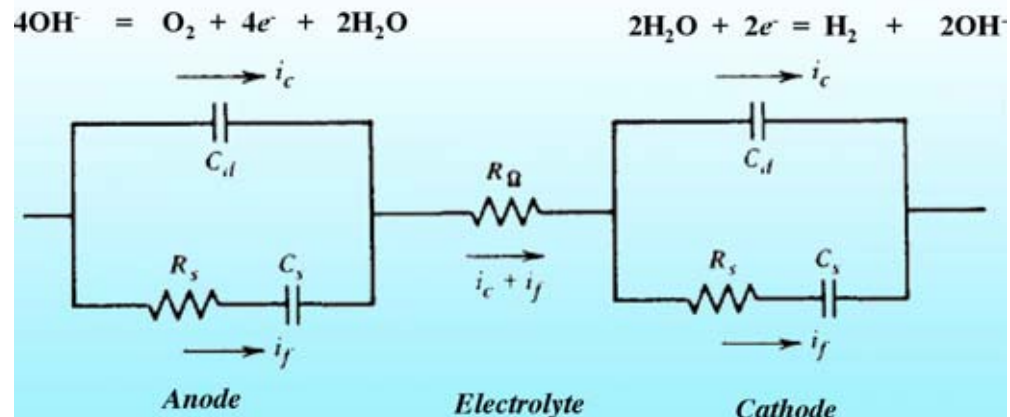
## Programmatic Motivation

- Meeting LHC cost objectives
  - Sensitivity study clearly indicates that improving cell efficiency provides the highest return.
  - Current cell efficiencies are in the range of 70-80%.
- Technical focus is on increasing cell efficiencies.
- Three possible focus areas:
  - Anode
  - Cathode
  - Electrolyte/separator
- Two programmatic time frames
  - Near term
  - Long term



From Stuart Energy

## Simplified Equivalent Circuit



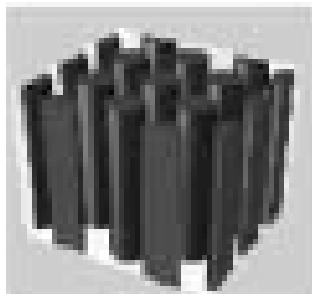


# ***Alkaline Versus Proton Exchange Membrane (PEM) Technology for Water Electrolysis***

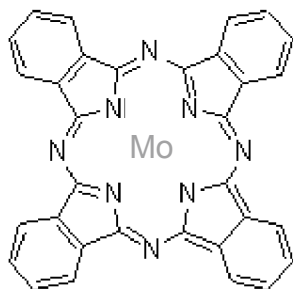
- **Long history of alkaline use in large industrial plants**
- **Advantages of alkaline cell environment**
  - **Enables use of non-noble metal catalysts**
    - **Relatively inexpensive & abundant**
    - **Relatively resistant to poisoning**
  - **Inherently better oxygen evolution kinetics**
  - **Inherently inexpensive electrolyte & cell separator**
  - **Enables use of inexpensive materials of construction**
  - **Less sensitive than PEM to cation impurities**

# Approach

- **Hydroxyl Exchange Membrane (HEM) Development**
  - Cast di-block copolymers (of various composition and processing conditions) to form channels having functionalized anionic exchange sites (e.g., quaternary amines) for hydroxyl ion transport
  - Test electrochemical impedance in alkaline electrolytes and various electrochemical conditions



- **Mo-Macrocycle Catalyst Development**
  - Pyrolyze molybdenum phthalocyanine (or porphyrin) mixed in polystyrene bead-formed template or in carbon black (various loadings and heat treatments) to form porous polymer catalyst
  - Evaluate catalysts' overpotentials and currents for hydrogen evolution reaction in alkaline media







# *Project Safety*

- **Primary Hazard Screenings (PHSs) in place for all laboratories and workers have previous experimental experience with electrochemical cells.**
- **Safely vent hydrogen produced during water electrolysis and safeguard against electrical shock and hazards**
- **Employ good laboratory practices**

# Project Timeline

## Task/Milestone Schedule

Task Number	Project Milestones	Task Completion Date				Progress Notes
		Original Plan	Revised Planned	Actual	Percent Complete	
1	Funding Approval	10/1/03	---	1/15/04	complete	Funding receipt dictates schedule
2	Post Doc Staffing	03/31/04		3/15/04	100%	On-Track.
3	Furnace/cell Set -up	04/15/04		04/1/04	100%	On-Track
4	Macrocyclic synthesis – 1 <sup>st</sup> prep	5/15/04			5%	Precursors ordered
5	1 <sup>st</sup> Polymer thin film prep.	05/30/04			3%	Precursors ordered and received
6	Electrochemical evaluation of 1 <sup>st</sup> macrocycle	06/30/04			-	Not yet started
7	Electrochemical evaluation of 1 <sup>st</sup> film	6/30/04				Not yet started
8	Porous electrode prep using macrocycle	7/30/04				Not yet started

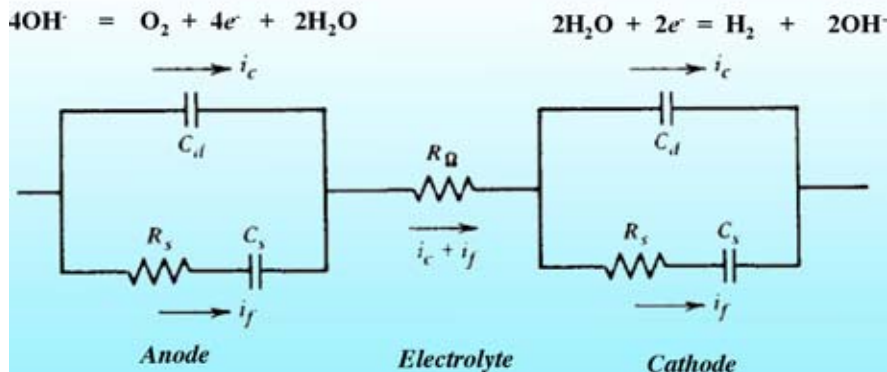


# ***Technical Accomplishments/Progress***

- **New start - Laboratory work commenced 4/04**
- **Program staffing completed in 3/04**
- **Conducted literature search for routes to pyrolyzing or polymerizing phthalocyanine and porphyrin macrocycle complexes**
- **Obtained initial materials for catalyst preparation and membrane synthesis**
- **Laboratory equipment/hardware in place and operational**

# Membrane Development Activity

Simplified Equivalent Circuit



## Problem Description:

- Increasing hydrolysis efficiency is required for meeting cost objectives
- A membrane provides physical separation between the electrodes.
- The issue is mobility/transport of species through the membrane
- The membrane characteristics, e.g., porosity, tortuosity, thickness, wetting characteristic, adds to the overall cell impedance, which can lead to  $iR$  losses (lower efficiencies) in the cell.
- The binder typically used in electrodes also increases cell resistance.

## Technical Approach:

- Develop and evaluate novel polymer for use as ion exchange membrane/binder for membrane electrode assembly (MEA) in alkaline media.
- Aliphatic and aromatic amine polymers to be evaluated.
- Di-block copolymers as well as cross-linking for stability in aqueous solutions.
- Quaternization of amine with haloalkane to form exchange sites.
- Ion Exchange to form mobile hydroxyl.

## Applications:

MEA for hydrolysis cells

Battery applications (alkaline cell, Zinc/air, nickel-metal hydride, etc.)

Alkaline fuel cell

# Membrane Development Activity controlling the architecture

- Transport of species through organized assemblies.
- Self-organizing assemblies can be prepared using di-block copolymers e.g., poly(vinylpyridine-co-styrene)
- Quaternization allows for formation of anion exchange sites
- Assembly can be controlled through control of:
  - Formulation
  - Solvent used in film formation
  - pH
  - Additives

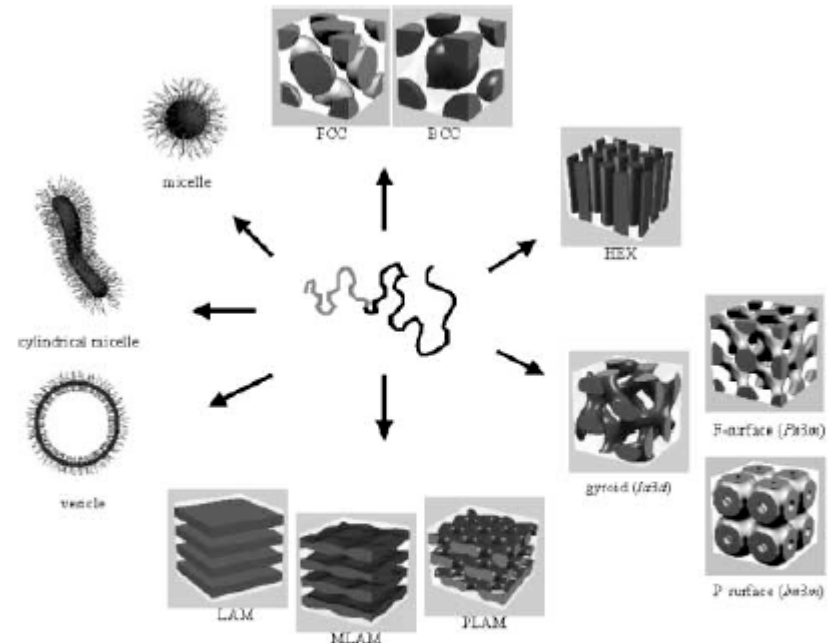


Figure 13. Self-organization structures of block copolymers and surfactants: spherical micelles, cylindrical micelles, vesicles, *fcc*- and *bcc*-packed spheres (FCC, BCC), hexagonally packed cylinders (HEX), various minimal surfaces (gyroid, F surface, P surface), simple lamellae (LAM), as well as modulated and perforated lamellae (MLAM, PLAM).

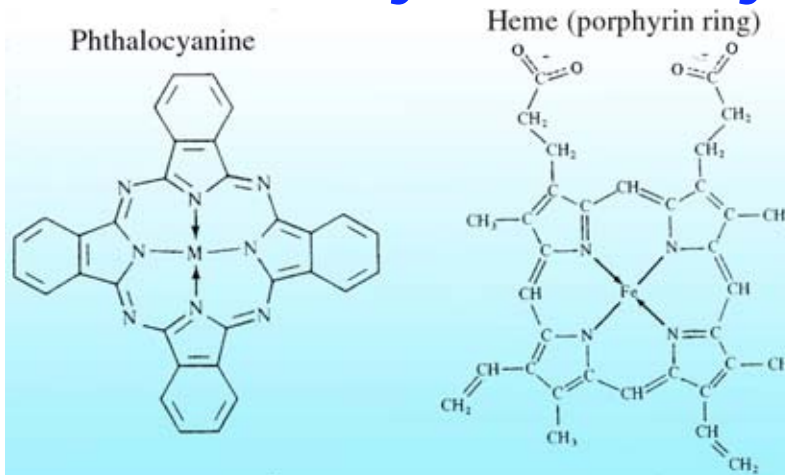
Förster and Plantenberg (2002) *Angew. Chem. Int. Ed.* 41(5) 688-714



## ***Goal - Membrane***

- **Development of a structurally organized and stable membrane selective for anion transport**
  - **Hydroxyl exchange membrane having room temperature conductivity  $> 80 \text{ mS/cm}$  %**
  - **Transport number  $\sim 1$  %**
  - **Chemically stable \$**
  - **Electrochemically stable \$**
  
- \$ lower maintenance costs**
- % lower operation costs**

# Mo-based Macrocyclic Catalyst Development



## Reduction reaction



## Oxidation reaction



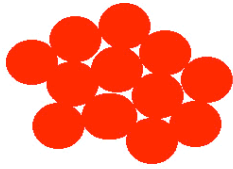
## Problem Description:

Increasing hydrolysis efficiency is required for meeting cost goals, and improved catalysts are one means for achieving this improved efficiency. Mo-based catalysts have been found to be very active catalysts for the hydrolysis reactions. However, the Mo catalyst is not stable under alkaline conditions, therefore has limited use.

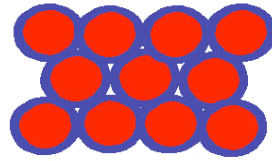
## Technical Approach:

- Develop and evaluate stable Mo-based catalyst - Mo metal shows excellent activity for HER but is not stable in base.
- Mo-based metal macrocycle. (Stable at high pH.)
- High surface area through self-assembly on spherical template array. (Increased surface area leads to increased reaction rates.)
- Macrocyclic complex is crosslinked and conjugated. (Crosslinking improves stability (i.e., insolubility) and conjugation increases electronic conductivity (decreases  $iR$  drop in the film).)
- Evaluate synergistic electrocatalytic affect with precious metals.

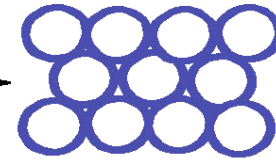
# Pictorial Representation of Template Synthesis Scheme



Template Formation

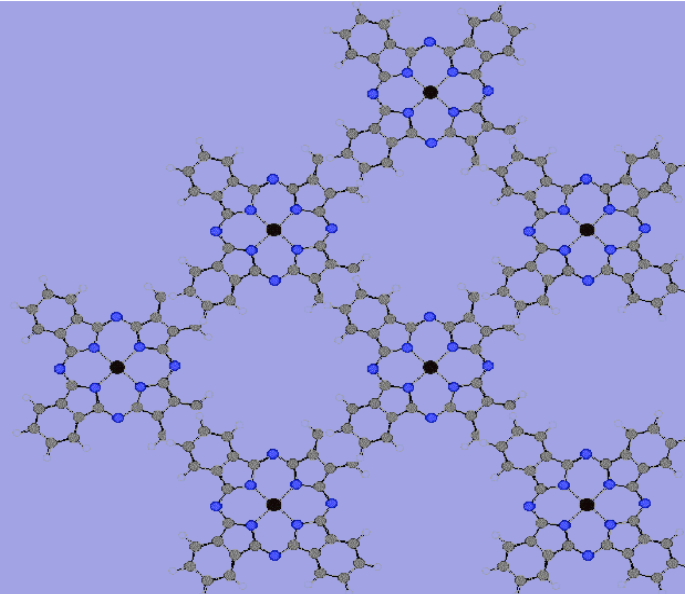
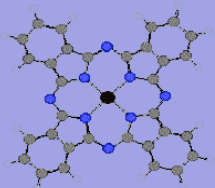


Coating and Conjugation



Template Removal

Monomeric Unit



Polymerized Macrocycle





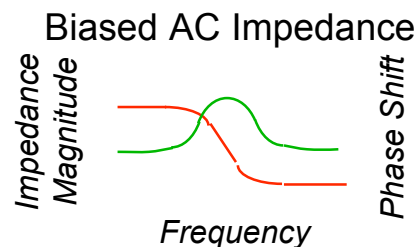
## ***Goal - Electrocatalyst***

- **Development of a stable non-precious metal Mo-based macrocyclic catalyst**
  - **Long-term stability during operation in KOH \$**
  - **Reduced overpotential for hydrogen evolution %**
  - **Decreased iR drop in cell due to improved electronic conductivity of immobilized catalyst %**
- \$ lower maintenance costs**
- % lower operation costs**

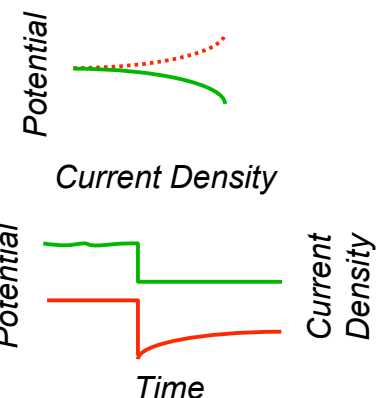
# Electrochemical Approach to Catalyst Discovery

## Identify electrochemical signatures

- Determine which electrochemical indicators of catalytic efficiency are applicable to screening techniques.
- Assess ability to make direct measurement of hydrogen generation.

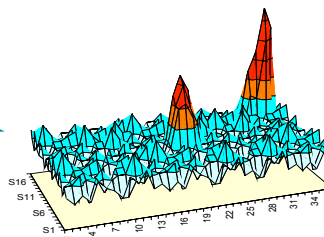


## Tafel behavior



## Screen materials and operating conditions

- Local electrochemical measurements for identifying 'hot spots' on state-of-the-art catalyst materials.
- Parallel & scanning techniques for combinatorial assessment of proprietary materials (Stuart Energy).



## Characterize structure & chemistry

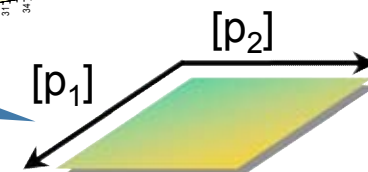
- Surface analytical techniques to identify the characteristics (chemical, microstructural, morphological) responsible for improved efficiency.
- Feed information back into production for scale build-up.

SEM

SECM

SIMS

AUGER



Technical challenges: high-throughput methods & localized measurements



# TOWARD IMPROVED CATALYSTS

## *PROPOSED CATALYST DEVELOPMENT ACTIVITIES*

- **COMBINATORIAL CATALYST DEVELOPMENT**
  - Combinatorial screening is an effective means for evaluating large numbers of potential candidates
- **General Approach**
  - Initial performance screening done spectroscopically
  - Electrochemical evaluation of selected candidates
- **Our approach**
  - Direct electrochemical screening of all candidates



# Toward Improved Catalysts

## Focused combinatorial approach

- This approach is predicated on the existence of good catalysts, e.g., Stuart Energy catalyst for hydrolysis, Pt/Ru for DMFC, Pt-black for PEM.
- These electrode structures are typically precious metals dispersed on a support.
- Although striving for uniformity, not all catalyst particles making up the electrode are identical -
  - variability in cluster size, composition, structure, etc.
- This variability undoubtedly extends to catalyst activity!
- In a device, we see only the ensemble response of all of these different species.
- We proposed to start with the best catalysts and electrode structures available, and perform small spot size characterization to identify the areas/clusters/species of high activity.
- These species would then be the targets for new material prep procedures.

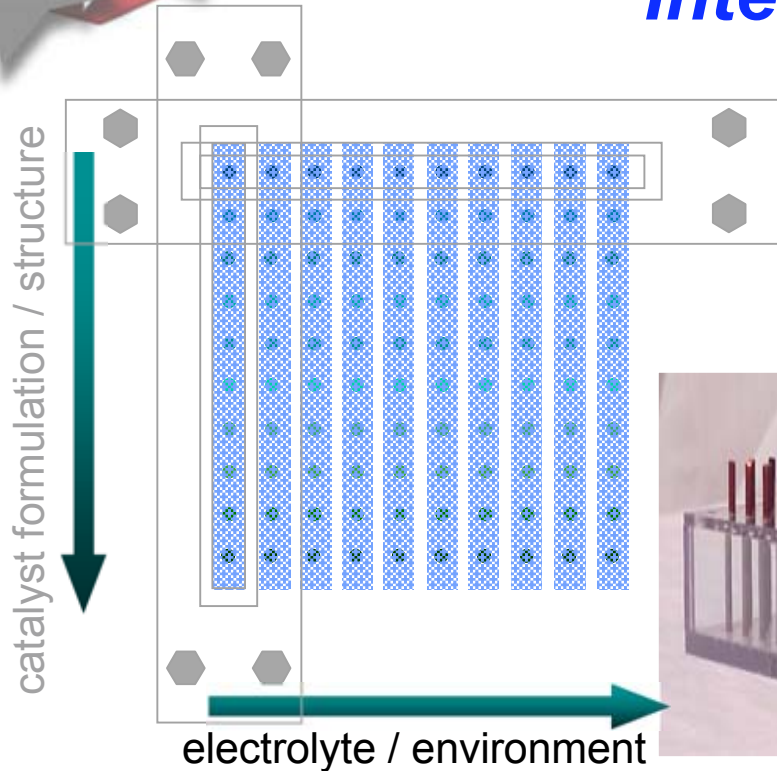


# *Interactions and Collaborations*

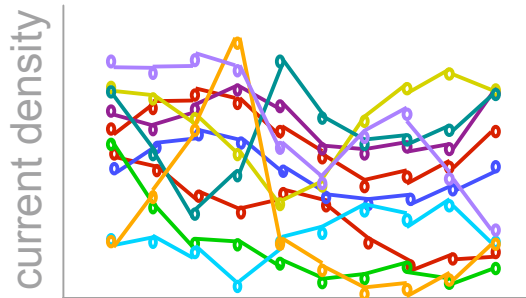
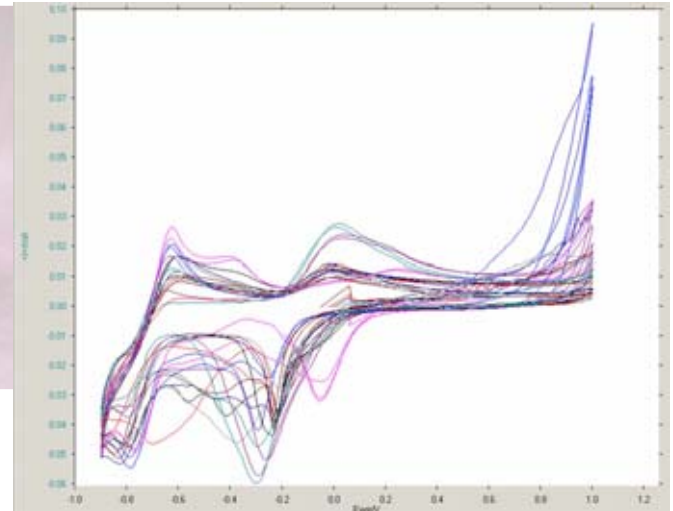
- **Leveraged Collaboration**
  - SNL: D. Wall, electrochemist – Biomicro Fuel Cell project
- **Potential Collaborators**
  - Stuart Energy – hydrogen infrastructure products
  - Teledyne Energy Systems – fuel cells and hydrolysis systems

# Interactions and Collaborations

SNL: D. Wall



Instrument development for combinatorial catalyst synthesis and direct electrochemical evaluation to screen large numbers of candidate systems  
→ Biomicro Fuel Cell Project



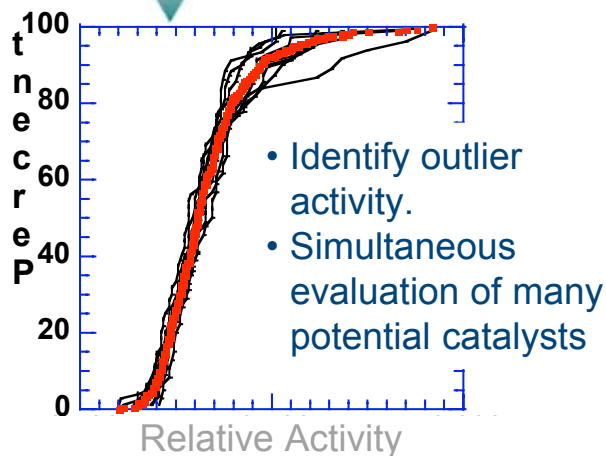
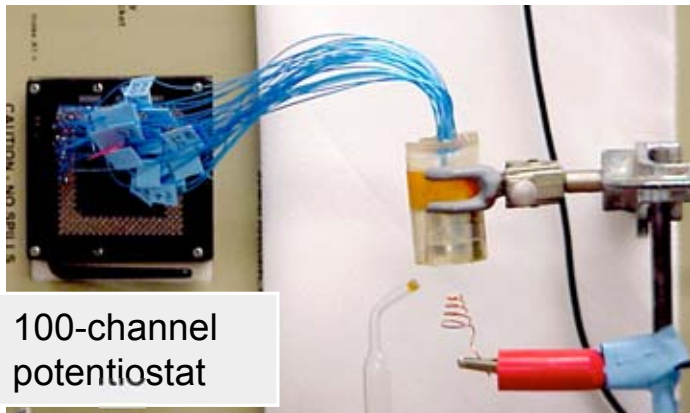
10 voltammograms obtained by a single parallel cyclic voltammetry experiment for 10 of the catalyst-electrolyte combinations in the 10X10 array

**Issues: Method generates a vast amount of information.  
How should best catalyst candidates be identified?**

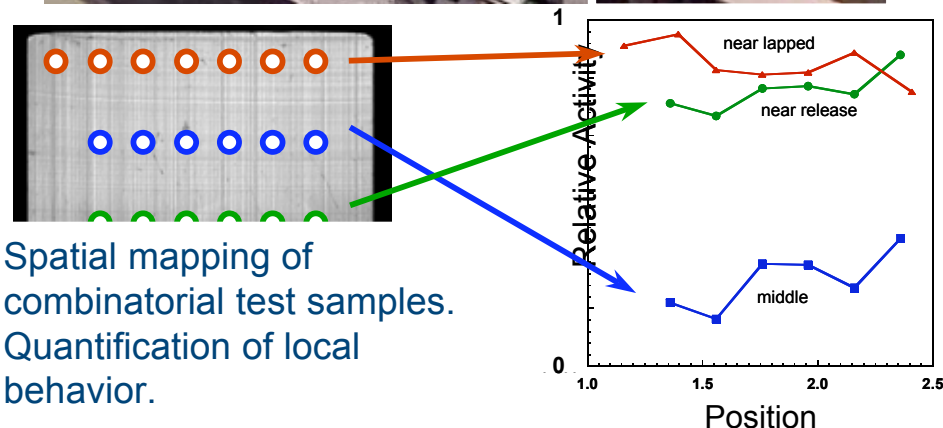
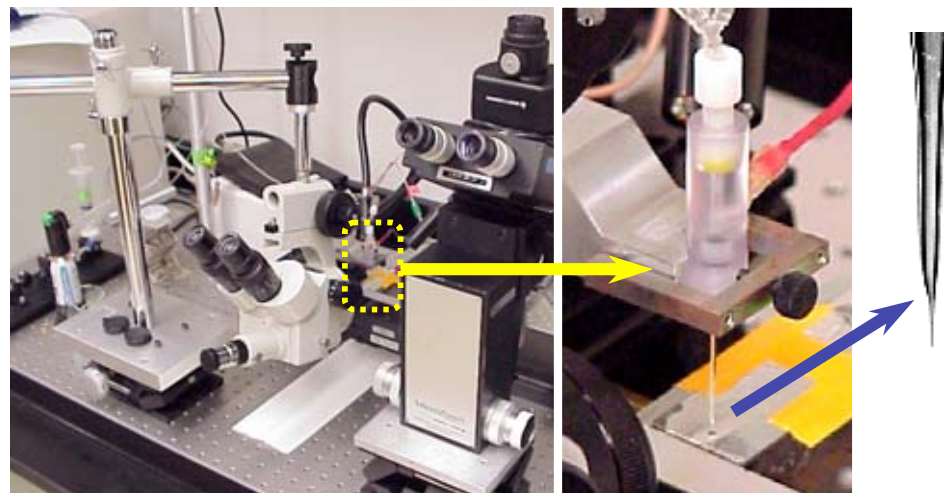
# Interactions and Collaborations

SNL: D. Wall (cont.)

## Parallel micro-electrodes



## Micro-capillary electrochemistry



## Impact

- Enables high-throughput catalyst/electrocatalyst discovery
- Applicable to Fuel cell development (e.g., precious metal alternatives).
- Benefits and leverages other programs: LIGA (A&E), Materials Aging (RF) and fundamental research (BES).



# *Future Work*

- **Remainder FY04**

- Evaluate electrochemical behavior of catalysts including structure/activity relationships under alkaline conditions and optimize synthesis conditions (e.g., pyrolysis vs. polymerization, processing variables, etc)
- Prepare structured polymer membranes and evaluate conductivity and transport characteristics as a function of structure.

- **FY05**

- Continue catalyst and membrane developments concurrent with hydrolysis cell performance evaluations
- Pending additional funding, expand catalyst discovery work