High Efficiency Electrolysis Materials Research

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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

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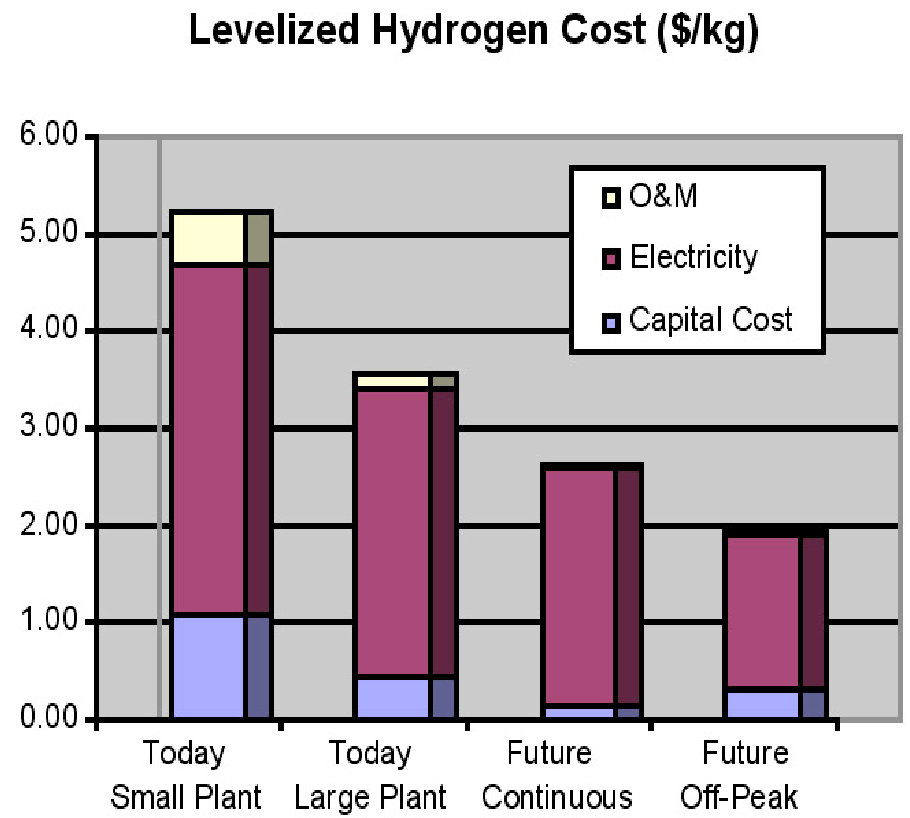
Hydrogen Production Through Electrolysis Cost Considerations

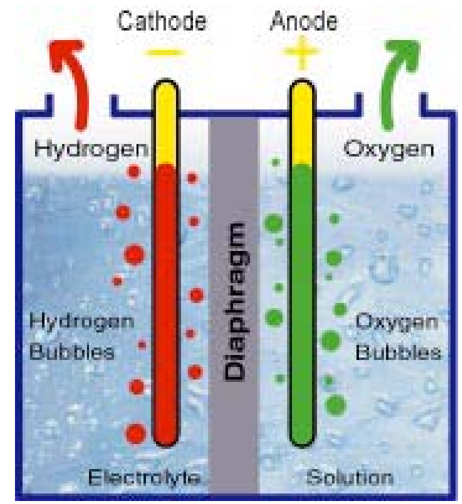
- Three principal cost aspects
  - Operation & Maintenance
  - Capital cost
  - Power (electricity)
- Relative cost breakdown dependant on plant characteristics
- Future projections based on anticipated improvements in stack design
- Single most important factor is cost of electrical energy



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% -

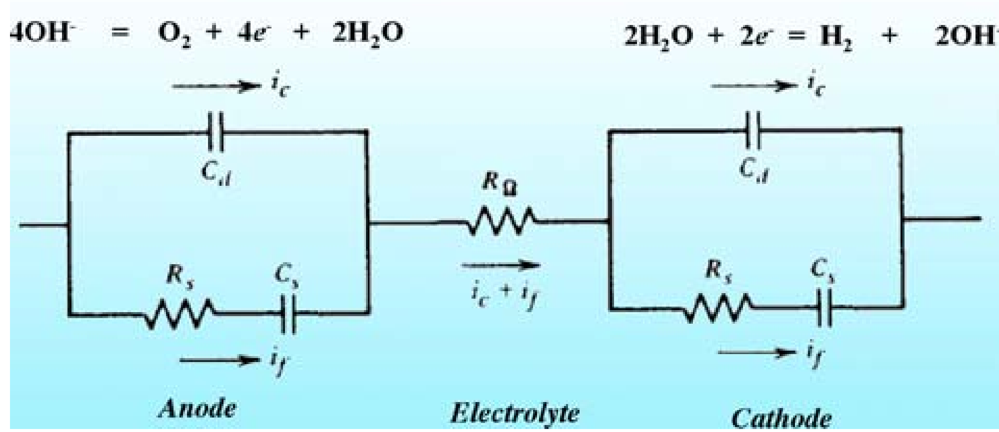


From Stuart Energy

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

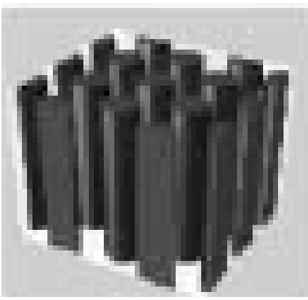
Simplified Equivalent Circuit



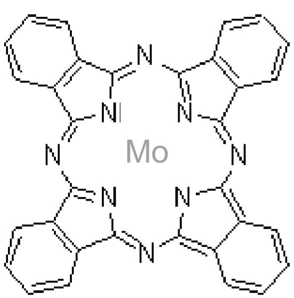
Alkaline Versus Proton Exchange Membrane (PEM) Technology for Water Electrolysis

- 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 – 1st prep	5/15/04			5%	Precursors ordered
5	1st Polymer thin film prep.	05/30/04			3%	Precursors ordered and received
6	Electrochemical evaluation of 1st macrocycle	06/30/04			-	Not yet started
7	Electrochemical evaluation of 1st film	6/30/04				Not yet started
8	Porous electrode prep using macrocycle	7/30/04				Not yet started

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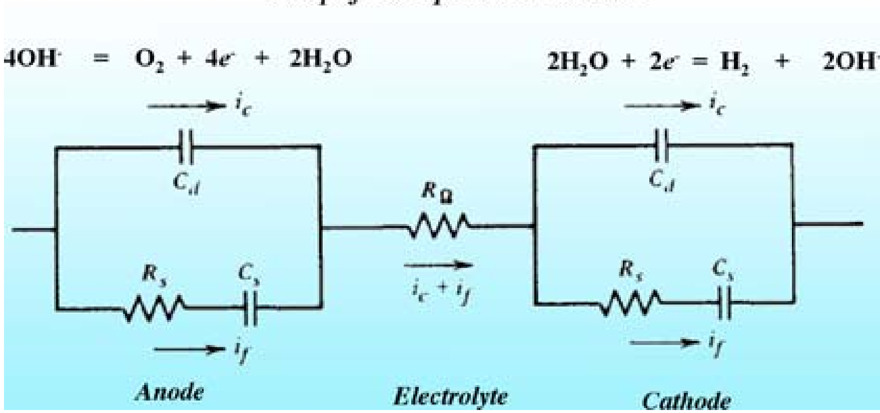
Technical Accomplishments/Progress

- 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 *i*R 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

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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**

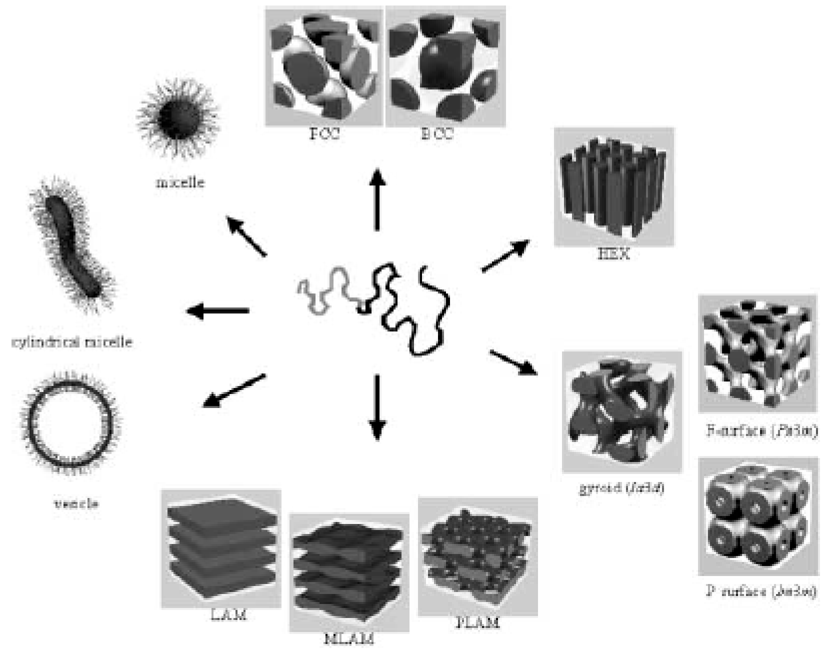

Figure 13. Self-organization structures of block copolymers and surfactants: spherical micelles, cylindrical micelles, vesicles, *fcc*- and *bcc*-packed spheres (FCC, BCC), hexagonally packed cylinders (HEX), various minimal surfaces (gyroid, F surface, P surface), simple lamellae (LAM), as well as modulated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

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

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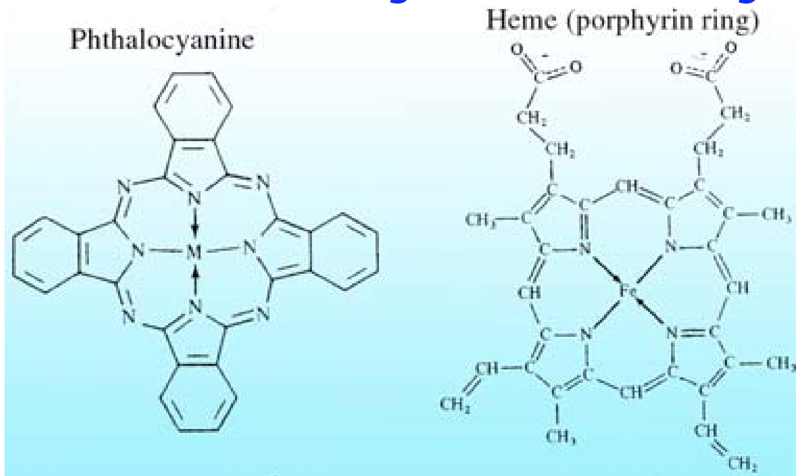
Goal - Membrane

- Development of a structurally organized and stable membrane selective for anion transport
  - Hydroxyl exchange membrane having room temperature conductivity > 80 mS/cm %
  - Transport number ~ 1 %
  - Chemically stable $
  - Electrochemically stable $

$ lower maintenance costs

% lower operation costs

Mo-based Macrocycle Catalyst Development



Reduction reaction

$2H_2O + 2e^- = H_2 + 2OH^-$ E' = -0.8277 V

Oxidation reaction

$4OH^- = O_2 + 4e^- + 2H_2O$ E' = 0.401 V

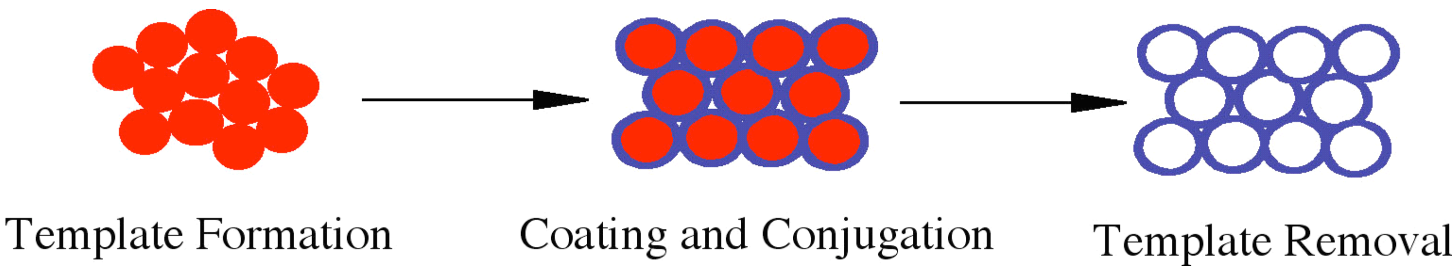
Problem Description:

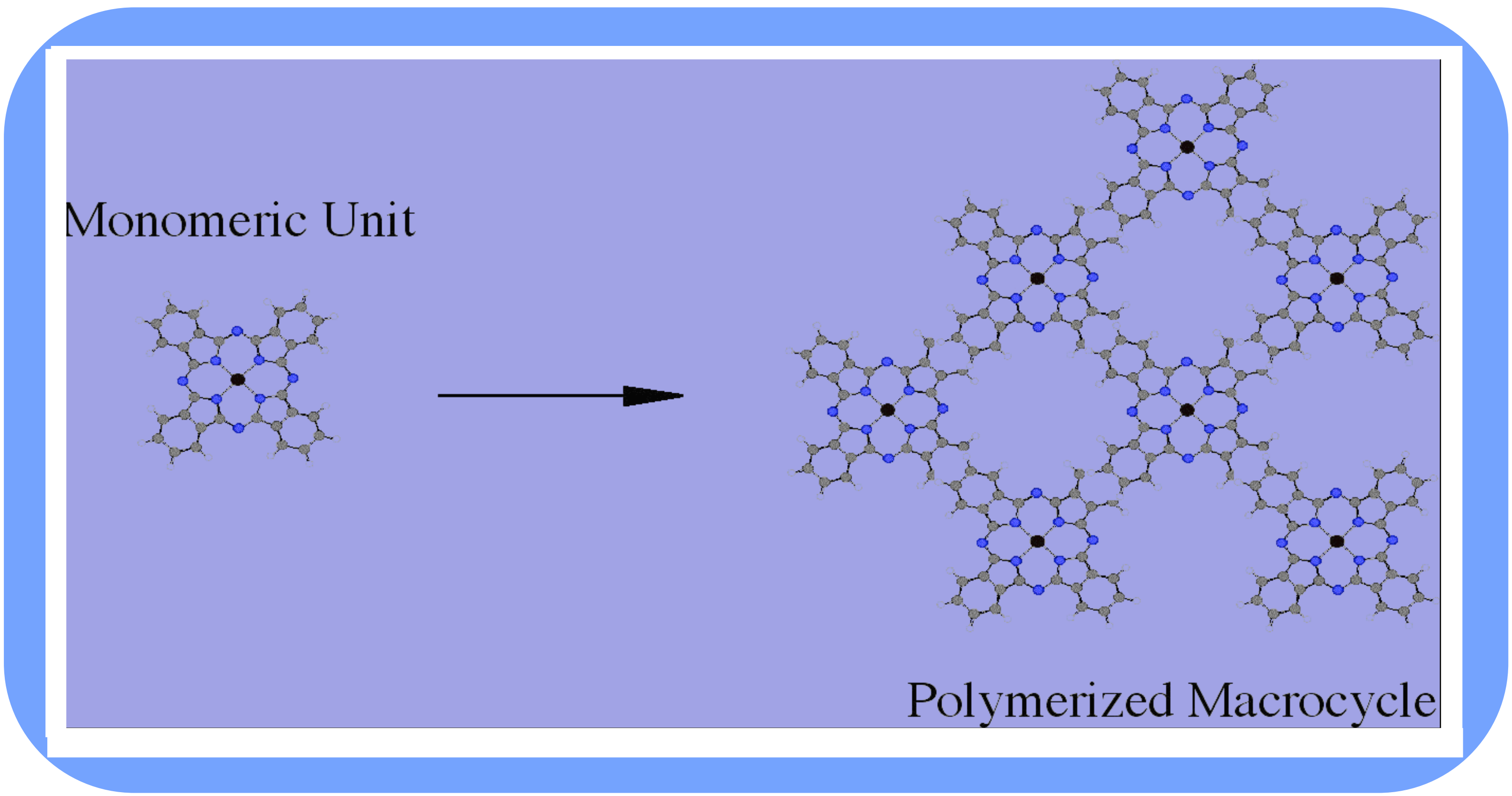
Increasing hydrolysis efficiency is required for meeting cost goals, and improved catalysts are one means for achieving this improved efficiency. Mo-based catalysts have been found to be very active catalysts for the hydrolysis reactions. However, the Mo catalyst is not stable under alkaline conditions, 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 *i*R drop in the film).**
- **Evaluate synergistic electrocatalytic affect with precious metals.**

Pictorial Representation of Template Synthesis Scheme





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

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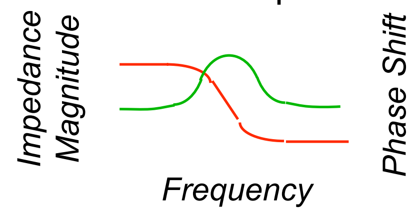
Electrochemical Approach to Catalyst Discovery

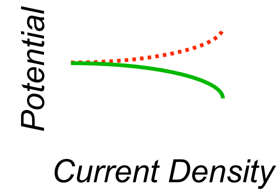
Identify electrochemical signatures

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

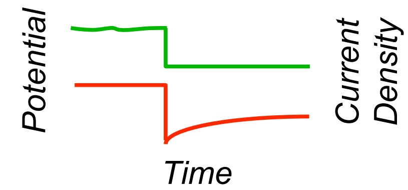
Biased AC Impedance



Tafel behavior

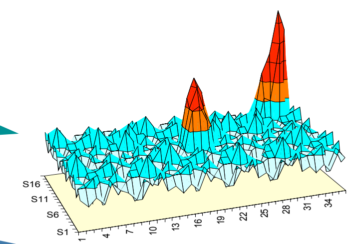


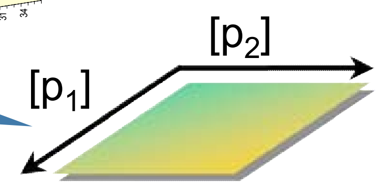
Potential step (current decay)



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

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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

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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.

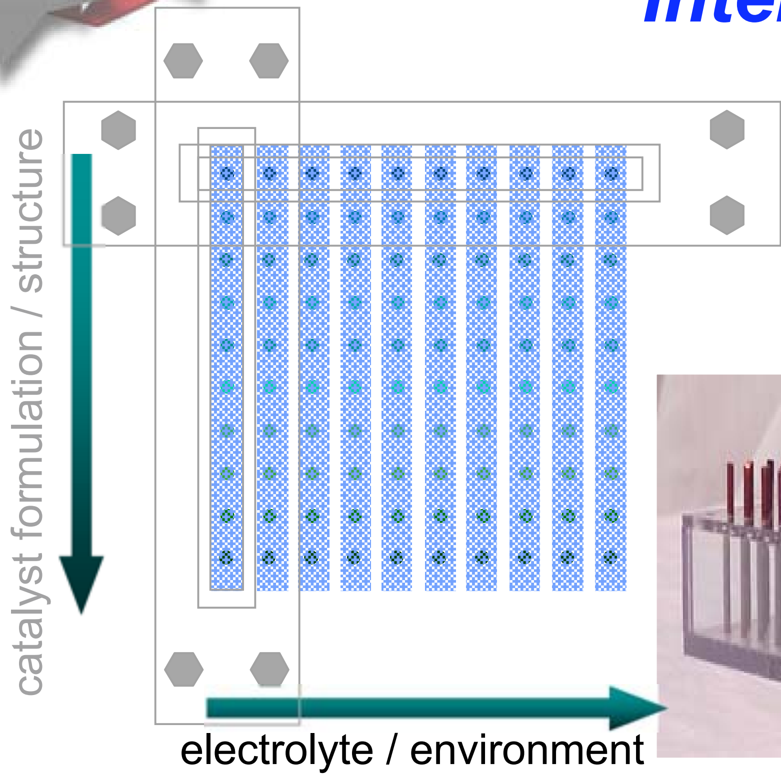
- These species would then be the targets for new material prep procedures.

Interactions and Collaborations

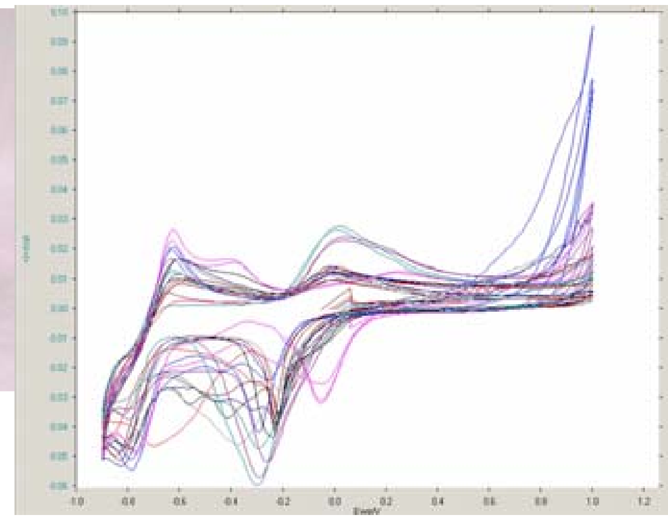
- Leveraged Collaboration
  - SNL: D. Wall, electrochemist – Biomicro Fuel Cell project
- Potential Collaborators
  - Stuart Energy – hydrogen infrastructure products
  - Teledyne Energy Systems – fuel cells and hydrolysis systems

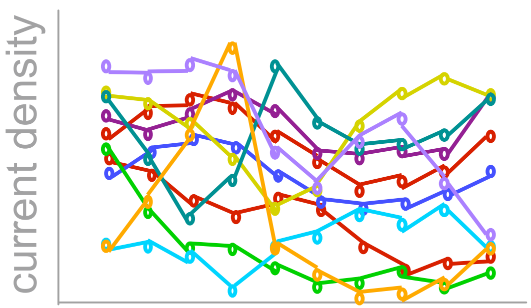
Interactions and Collaborations

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?

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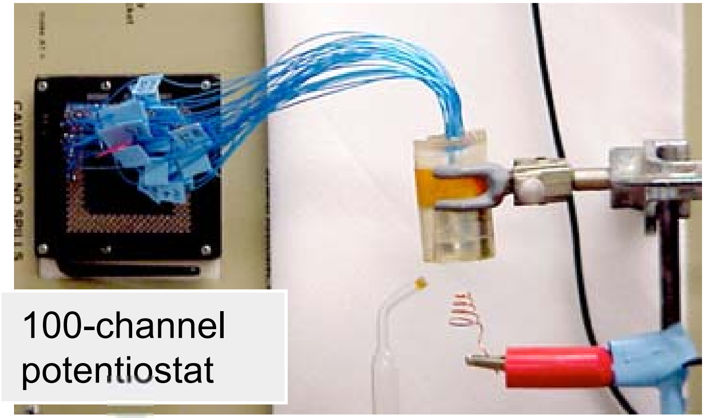
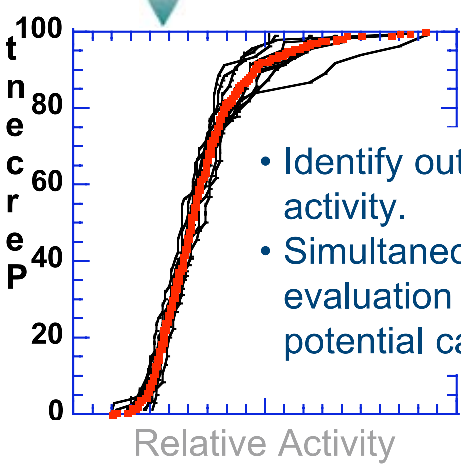
Interactions and Collaborations

SNL: D. Wall (cont.)

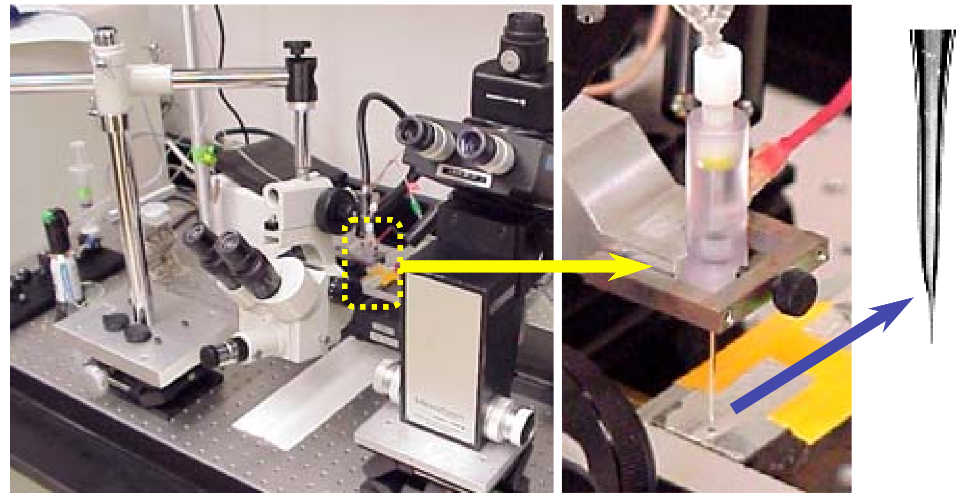
Parallel micro-electrodes

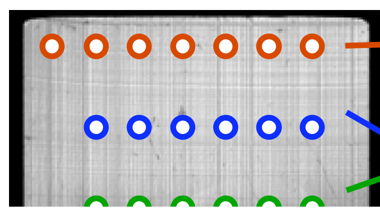


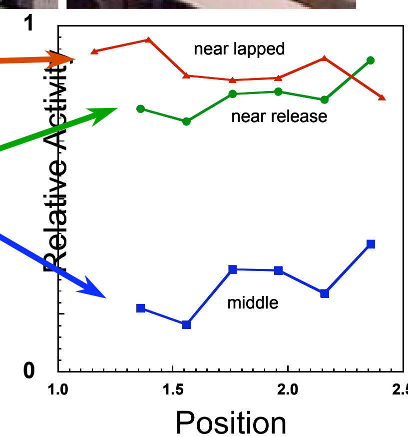


- Identify outlier activity.
- Simultaneous evaluation of many potential catalysts

Micro-capillary electrochemistry







- Spatial mapping of combinatorial test samples.
- Quantification of local behavior.

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).

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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**