



Hydrogen Production - Increasing the Efficiency of Water Electrolysis

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Project ID #
PDP39



Overview

Timeline

- March 15, 2004 start
- September 30, 2007 end
- 30% complete

Budget

- Total project funding
 - \$241K (to date)
- FY04: \$156K
- FY05: \$85K (to date)

Partners

- Potential industry collaboration

Barriers

The relevant technical barriers (§3.1.4.2.2) and technical targets (Table 3.1.4) from the 2005 HFCIT Program Multi-Year Program Plan (www.eere.energy.gov/hydrogenandfuelcells/mypp)

- **G. Capital Cost** → through non-precious metal catalyst exhibiting improved performance
- **H. System Efficiency** → by exceeding present conversion efficiency
- Improved cell materials (stable, low-cost) & total cell efficiency result in both lower capital costs and lower demand for electricity production

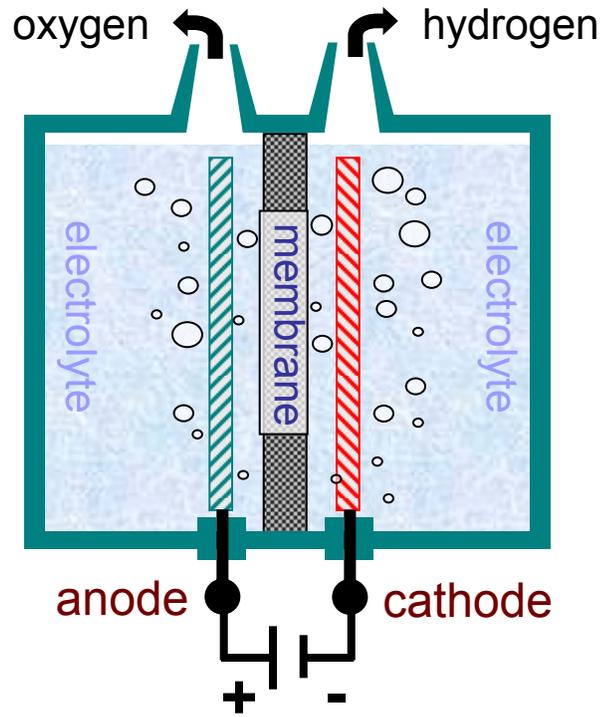


Objectives

Improve the efficiency – and consequently lower the cost – of the electrolytic production of hydrogen through (1) more conductive membranes and (2) higher activity catalysts

1. Prepare polymer thin films as low resistance, hydroxyl ion conducting membranes and evaluate their electrochemical performance as electrolyte/separator in alkaline-based water electrolysis cells
2. Prepare and electrochemically evaluate transition metal (e.g., molybdenum) macrocycle complex-based electrocatalysts as low-cost, high catalytic materials for hydrogen evolution

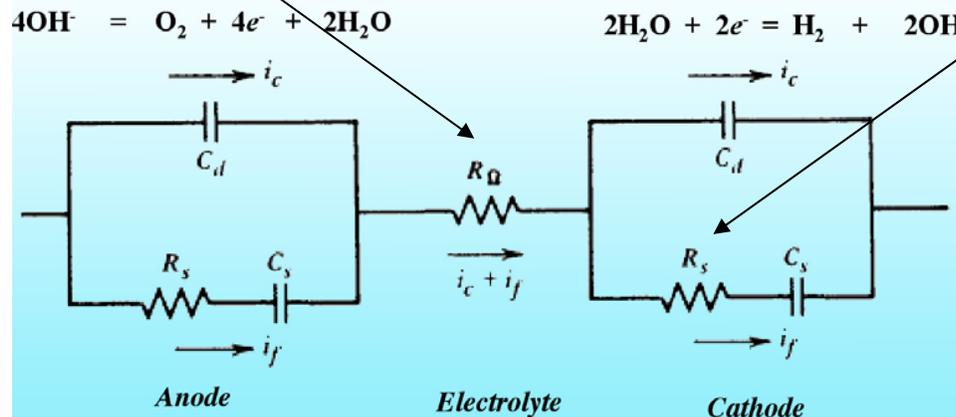
Water Electrolysis Cell



1. Decrease electrolyte resistance which contributes to $i \times R$ potential drop between the electrodes

2. Decrease charge transfer resistance to hydrogen evolution, thereby increasing potential-dependent rate

Simplified Equivalent Circuit





Alkaline vs. 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
- Disadvantage of alkaline cell environment
 - Carbon dioxide absorption leading to carbonate formation



Technical Accomplishments

1. Hydroxyl Ion Exchange Membranes (HEMs)
 - Obtained good properties in separate developed polymers, but not all combined in a single composition.
 - Achieved good ionic conductivity in the 10-100 mS/cm range.
2. Macrocycle Catalysts
 - Prepared phthalocyanines that were catalytic for water electrolysis, but the Mo species had lower activity than other transition metal species

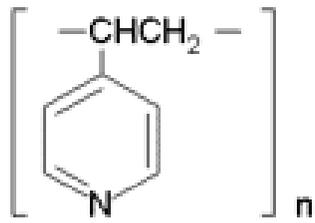


Approach – 1. Membrane

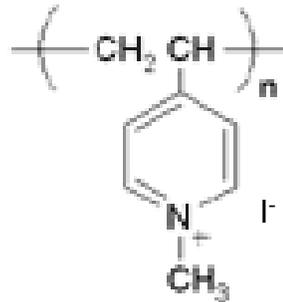
1. Make a thermally, mechanically, and chemically stable solid polymer electrolyte consisting of highly mobile hydroxyl ions that are the only ions that migrate in the potential field between cathode and anode, thereby decreasing cell resistance.
- **Develop and evaluate novel polymer for use as anion exchange membrane for membrane electrode assembly (MEA) in alkaline media.**
 - **Use polymers containing amines that can be**
 - quaternized with a haloalkane to form fixed positive-charge exchange sites,
 - cross-linked to provide increased stability in aqueous solutions, and
 - ion exchanged to form mobile hydroxyl ion.

Membrane Synthesis Method

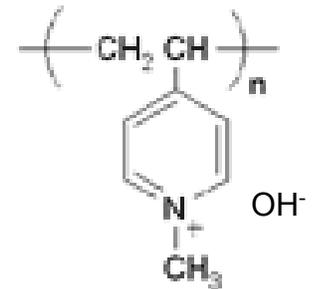
poly(4-vinylpyridine)
(P4VP)



react with
methyl iodide
→
(or dibromobutane
to also crosslink)



exchange
with base
→



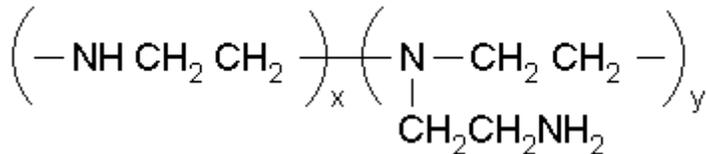
amine-containing polymer

quaternized
(and crosslinked)
polymer

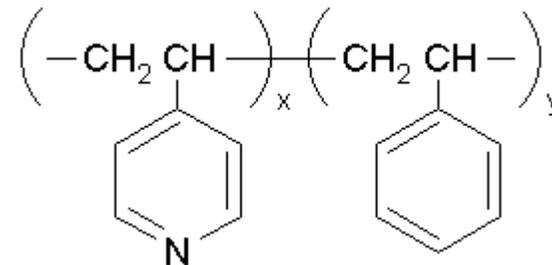
hydroxyl ion
exchange membrane
(HEM),
after casting

Other amine-containing polymers:

polyethylenimine (branched)
(PEI)



diblock copolymer
poly(4-vinylpyridine-*b*-styrene)



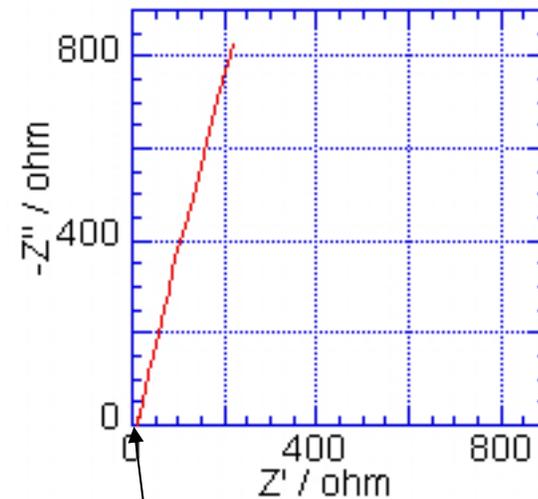
Membrane Characterization

Conductivity cell

quaternized P4VP film disk

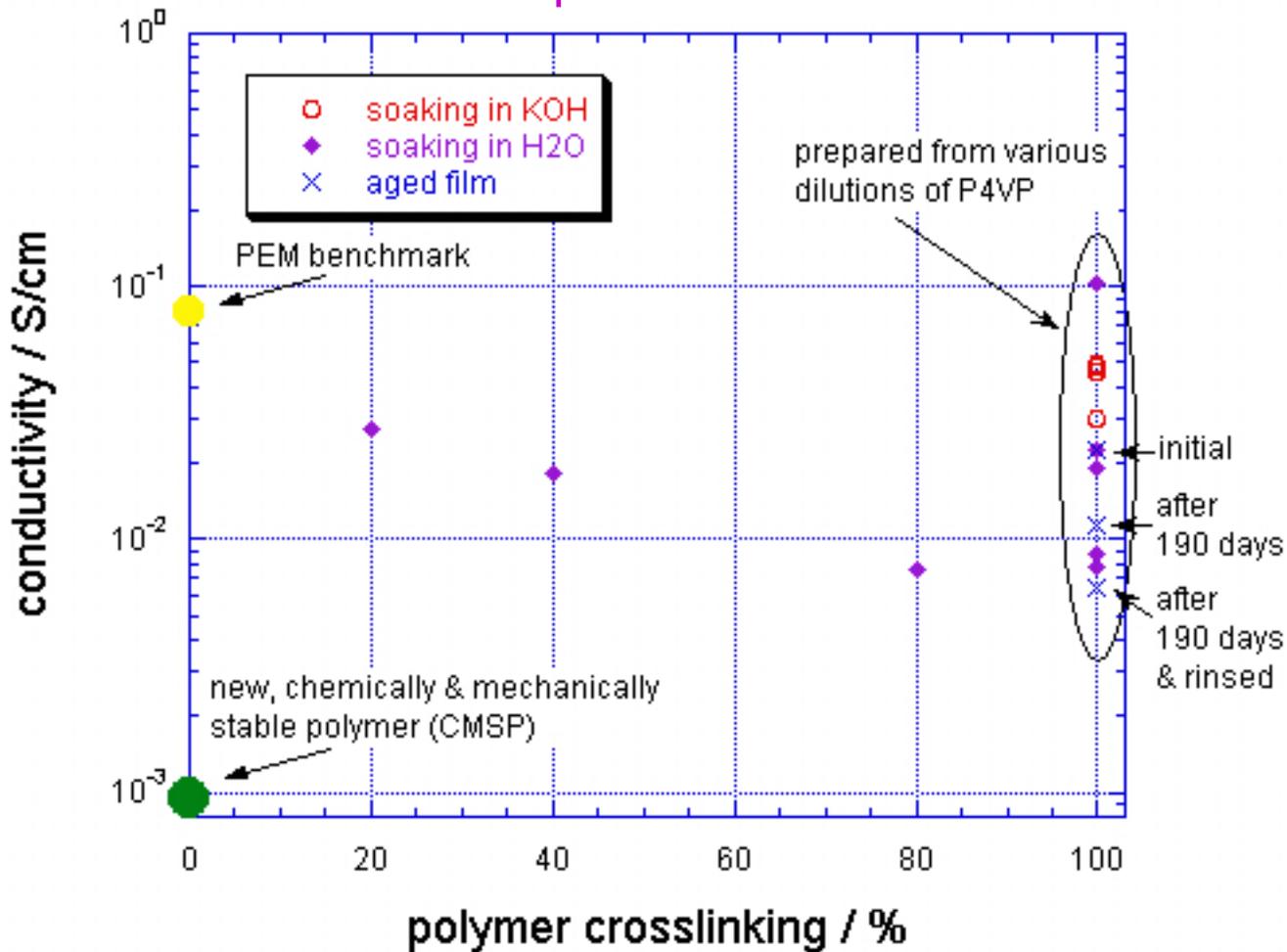


Electrochemical Impedance Spectroscopy (EIS)
(example curve: quaternized P4VP film with 100% crosslinking and OH⁻ ion, after rinsing in water)



Membrane Conductivity

Data for quaternized P4VP



Achievements:

- Quaternized P4VP shows comparable ion conductivity to that demonstrated by PEMs (compare with yellow dot)

Challenges:

- Quaternized P4VP is mechanically “brittle” and degrades over time (see “x” markers on plot)
- Without higher crosslinking, quaternized PEI is soluble in alkaline media

Note:

- A new polymer (CMSP) is being developed to include good non-electrochemical properties along with the desired ionic conductivity, which is presently low (see green dot on plot).

Membrane Summary

Property \ Polymer	quaternized P4VP	quaternized PEI	CMSP
Electrochemical [%] Target ionic conductivity (room temperature) is $\geq 80 \text{ mS cm}^{-1}$.	10-100 mS cm^{-1}	—	~2 orders of magnitude below target conductivity
Mechanical ^{\$}	fragile; becomes brittle when dried ¹	dissolves in water ²	solid both in water and base
Chemical ^{\$} Stable in base	No ³	Yes	Yes
Thermal ^{%, \$}	—	—	good to $\sim 100 \text{ }^\circ\text{C}$

[%] lower operation costs

^{\$} lower maintenance costs

Notes:

- 1: Polymer film can be handled, but can be easily torn. Rehydrating film results in spallation of pieces from dried film.
- 2: Solubility of polymer film can be counteracted by greater crosslinking and limited number of quaternized sites.
- 3: The pyridinium group undergoes an irreversible oxidation in base.



Future Work – 1. Membrane

- Improve physical and chemical properties
 - Increase film porosity, using strategies of forming pores (e.g., dibutyl phthalate incorporated during synthesis and later leached out)
 - Stabilize film through crosslinking
 - Control number of fixed positive-charge sites
- Measure ionic conductivity of commercial membranes for alkaline water electrolysis, in addition to developed membranes
- Measure transference number for the hydroxyl ion (in a full electrolysis cell)
- Evaluate long-term performance and stability of membranes in alkaline solutions

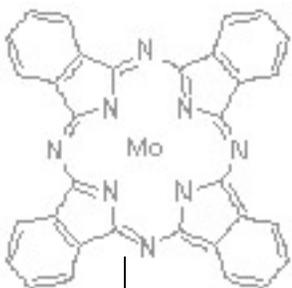


Approach – 2. Catalyst

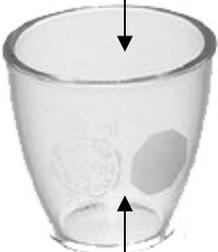
2. Synthesize water reduction (hydrogen evolution) electrocatalysts based on an open network of transition-metal macrocycle molecules that provide electronic conduction between catalytic metallic ion sites.
- **Develop and evaluate stable, polymeric transition metal macrocycle-based catalyst**
 - for example, molybdenum (Mo) metal shows excellent activity for hydrogen evolution but is not stable in alkaline conditions; however, the transition metal-based metal macrocycles are stable at high pH.
 - **Tailored physical and chemical properties:**
 - high surface area increases the number of reaction sites – can be achieved through self-assembly on spherical template array or incorporating rigid polymer bonds,
 - crosslinking improves stability (i.e., insolubility), and
 - conjugation increases electronic conductivity (decreases $I \times R$ potential drop in the film).

Macrocycle Catalyst Preparation

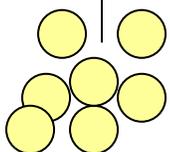
Transition metal macrocycle



e.g., molybdenum phthalocyanine (MoPc)



Heat treat/pyrolyze at 500 °C



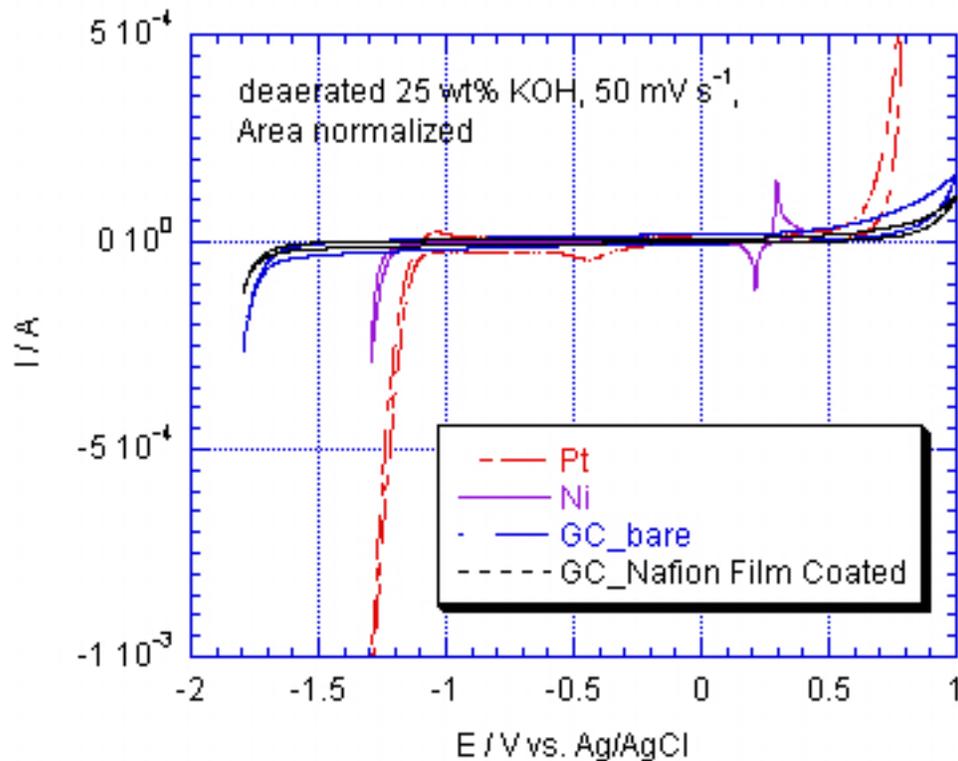
Template beads/particles can be added



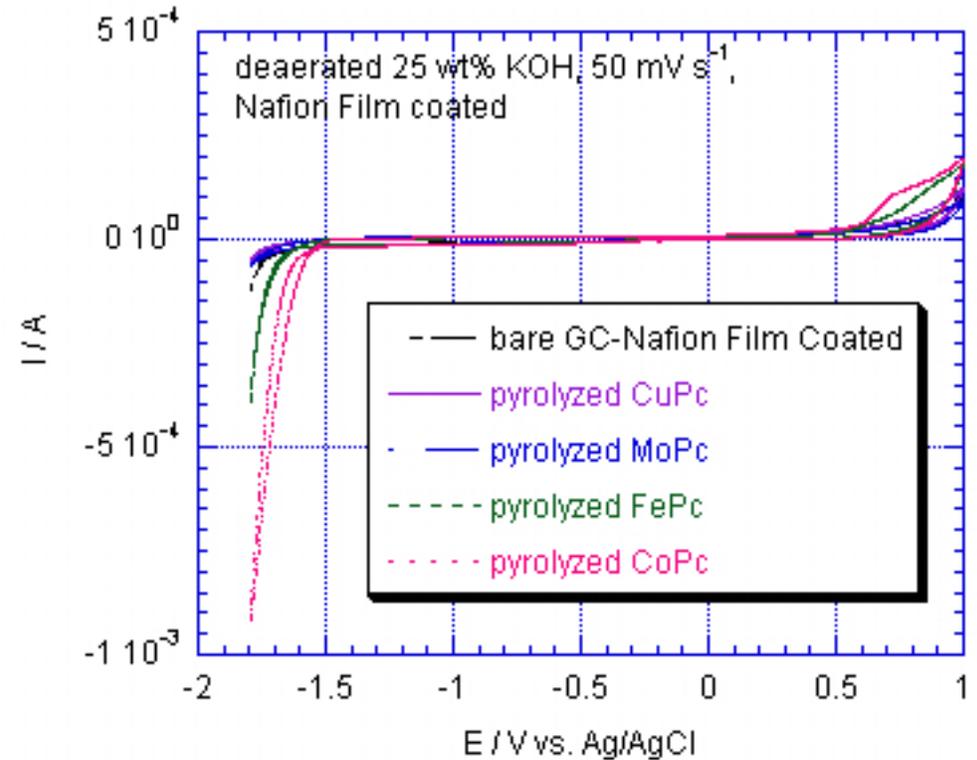
- Remove template (if added)
- Disperse material in water & deliver aliquot to glassy carbon (GC) electrode surface
- A Nafion film coating keeps catalyst particles on electrode

Cyclic voltammetry in 25 wt% KOH

Macrocycle Catalyst Results



- Various electrode surfaces: metals Pt and Ni compared with non-catalytic glassy carbon (GC).
- GC covered with Nafion film yields approximately half the current available from a bare surface.

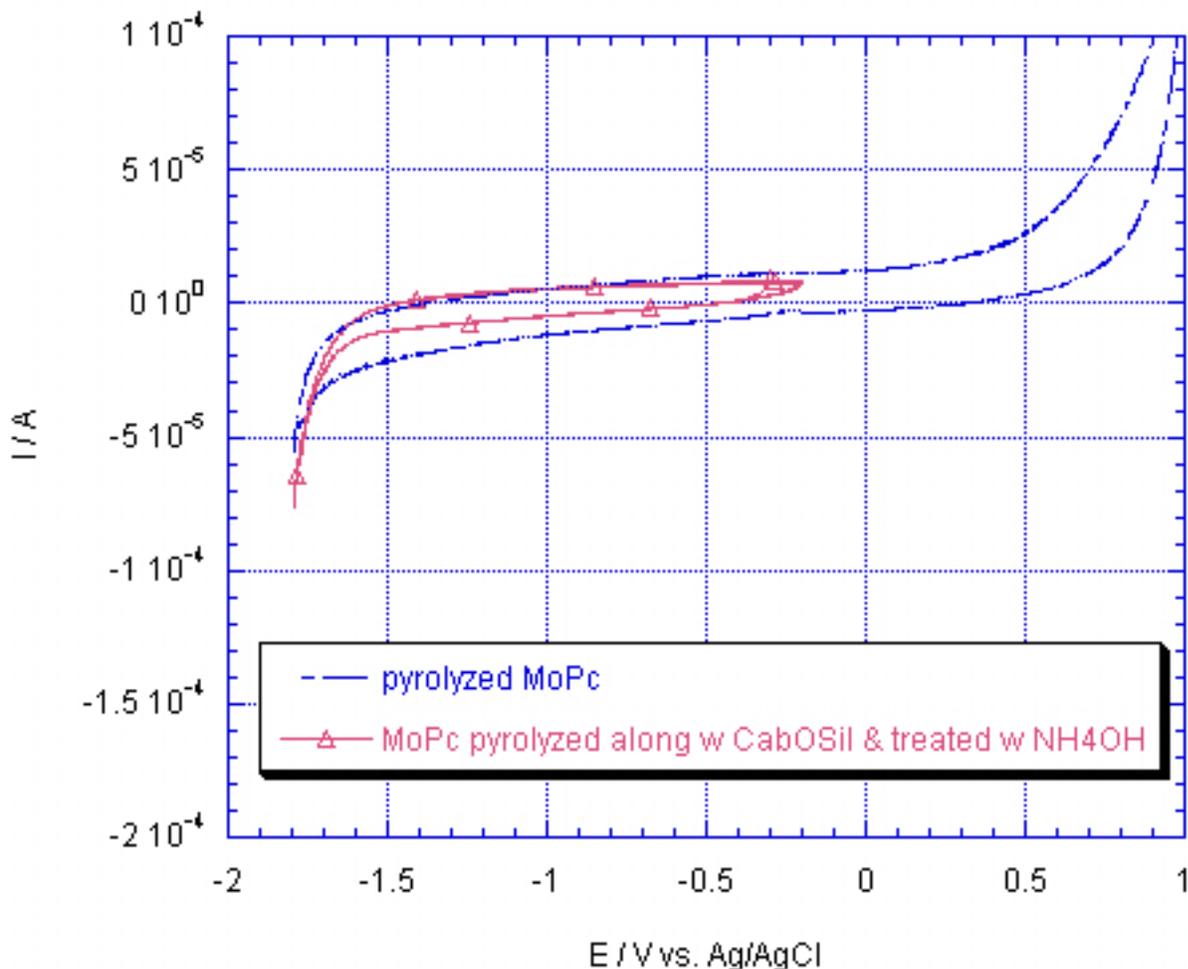


- Some pyrolyzed phthalocyanines (Pcs) are catalytic, but do not support the current magnitudes available from a metal electrode.

Macrocycle Catalyst Template

Catalysts prepared on templates yield similar reactivity to those prepared without template

- A mixture of Cab-O-Sil® fumed silica particles and MoPc was pyrolyzed
- NH_4OH was used to dissolve the silica
- Comparison of cyclic voltammograms revealed a slight increase in catalytic activity
- Similar results were observed for using PS beads, which had the problem of pyrolyzing and vaporizing during heat treatment





Macrocycle Catalyst Summary

- Challenges with present route
 - Finding a suitable template that withstands the preparation steps and is easily removed to create open structure
 - Obtaining sufficient conjugation between macrocycle ligands to achieve electron conduction in catalyst
- Transition metal macrocycle-based catalysts prepared by pyrolysis/heat treatment show some catalytic activity. FePc and CoPc exhibited greater rates of hydrogen evolution than that of other macrocycles tested (MoPc and CuPc).
- Phthalocyanine catalysts do not support the level of current (production rates) capable by metal electrodes for a given overpotential, likely because of $I \times R$ drop in catalyst layer.



Responses to Previous Year's Reviewers' Comments

- The synthetic pathway toward cross linking the monomer was not effectively described.
 - Heat treatment/pyrolysis at a low enough temperature was sought to form bonding between monomers. A direct polymerization route was later found in the literature, but it does not yield a fully conjugated polymer. See Catalyst Preparation and Future Work slides.
- It is not clear whether the PS template can be removed without destroying macrocyclic framework.
 - Polystyrene will dissolve in the appropriate solvent, but perhaps the catalyst's open structure might collapse upon drying. However, it was later learned that the PS pyrolyzes during processing. Another microparticle was tested. See Catalyst Template slide.



Future Work – 2. Catalyst

- Evaluate other transition metal macrocycle complexes
- Further develop fumed silica template preparation
- Prepare polymer catalysts by other routes
 - Poly(phthalocyanine) directly from precursors (e.g., 1,2,4,5-tetracyanobenzene or pyromellitic anhydride, along with a metal salt)
 - Network polymer containing phthalocyanine units (from reacting bis(phthalonitrile) monomers possessing spirobisindane linking groups)
- Assess properties of catalysts from new preparation routes
 - Processability
 - Insolubility
 - Conductivity
 - Electrochemical activity



Publications and Presentations

- No publication to date has been submitted.
- This work has not yet been presented at a conference due to funding uncertainties and intellectual property concerns.
- Two technical advances have been filed within Sandia and a patent application is in preparation.



Hydrogen Safety

The most significant hydrogen hazard associated with this project is accumulation of hydrogen gas generated in the electrochemical cell during electrolysis, which along with oxygen, produced by the water oxidation reaction or present in the air, can become flammable.



Hydrogen Safety

Our approach to deal with this hazard is purging the electrochemical cell with inert gas (e.g., argon) during electrolysis experiments, thus displacing any generated hydrogen from the system. Furthermore, these experiments are conducted in a fume hood.