

## IV.H.6 Increasing the Efficiency of the Water Electrolysis Cell

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*Projected End Date: Project continuation and direction determined annually by DOE*

### Objectives

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

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- G. Capital Cost
- H. System Efficiency

### Technical Targets

This project is conducting fundamental studies of hydroxyl ion-conducting cell separator membranes and non-precious metal-based electrocatalysts. Insights gained from these studies will be applied toward the design and synthesis of electrolysis cell materials for meeting the following DOE 2010 water electrolysis cell stack targets:

- Cost: \$0.39/kg (\$0.39/gge) H<sub>2</sub>
- Total Cell Efficiency: 76%

### Approach

- Synthesize quaternary ammonium-based polymers in membrane form
- Evaluate ion conductivity and materials properties of membrane
- Synthesize catalysts from transition metal phthalocyanines
- Characterize electrochemical behavior of electrocatalysts with respect to water reduction and oxidation, and hydrogen and oxygen evolution reactions, respectively

## Accomplishments

- Prepared quaternized and crosslinked poly(4-vinylpyridine) possessing ion conductivity on the order of benchmark proton exchange membrane room temperature conductivity (80 mS/cm), but suffering mechanical and chemical instability
- Prepared chemically and mechanically robust amine-containing biopolymer possessing ion conductivity two orders of magnitude lower than target, but having potential for additional processing and quaternization for further gains
- Prepared catalysts by pyrolysis of cobalt, copper, iron, and molybdenum phthalocyanines by free-powder and templated routes
- Measured electrocatalytic activity of catalysts by cyclic voltammetry in alkaline solution (25% potassium hydroxide, KOH)

## Future Directions

- Improve physical and chemical properties of polymer films
- Measure ionic conductivity of further developed membranes and commercial membranes employed in alkaline water electrolysis
- Measure transference number for the hydroxyl ion
- Evaluate long-term performance and stability of membranes in alkaline solutions
- Evaluate other transition metal macrocycle complexes
- Further develop templated preparation of catalysts, e.g., microparticle fumed silica
- Prepare polymeric catalysts directly from precursors
- Assess properties of catalysts prepared by new routes

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## Introduction

Hydrogen can be produced by water electrolysis, a process that uses electricity to dissociate water into hydrogen and oxygen. Since electricity costs factor heavily in this method, improving electrolysis cell efficiencies can lead to decreased hydrogen production costs. Typical water electrolyzers are operated using alkaline solutions. The alkaline cell environment enables the use of non-noble metal catalysts which are relatively inexpensive, abundant, and resistant to poisoning. Oxygen evolution – the necessary other electrochemical reaction in the cell – is inherently faster in alkaline solutions. Two areas that significantly impact cell efficiency are cell membranes and electrocatalysts. We have been preparing and evaluating (a) an alkaline exchange membrane that primarily conducts hydroxyl ions in the cell electrolyte and (b) electrocatalysts based on molybdenum and other non-precious, transition metal macrocycles. The hydroxyl ion exchange membrane is the alkaline analog to the proton exchange membrane (PEM).

## Approach

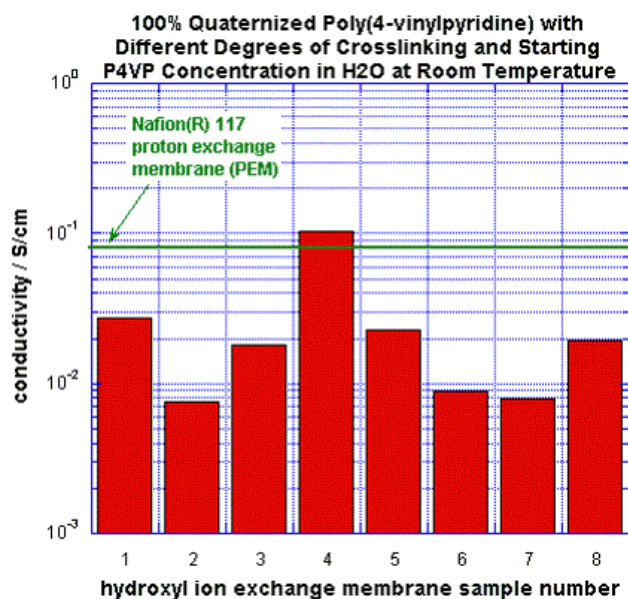
To decrease the electrolyte resistance which contributes to  $i \cdot R$  (current-resistance) potential drop between the electrodes, we are making a thermally, mechanically, and chemically stable solid polymer electrolyte consisting of highly mobile hydroxyl ions that are the only ions that migrate in the potential field between cathode and anode, thereby decreasing cell resistance. Thin film membranes will enable the close spacing of cathode and anode, thereby lowering resistance and decreasing volume. To favor anions as the mobile ion, amine-containing polymers are quaternized to form positive-charged sites on the immobile polymer. The anion from the quaternization step is exchanged out with hydroxyl ion from a base, such as potassium hydroxide.

To decrease the charge transfer resistance to hydrogen evolution, thereby increasing the potential-dependent rate, we are synthesizing electrocatalysts based on an open network of transition-metal macrocycle molecules that provide electronic

conduction between catalytic metallic ion sites. To date, transition metal phthalocyanines have been prepared by pyrolysis and evaluated. One method for creating an open structure is to use a template consisting of microparticles packed with the precursor compound during the heat treatment.

## Results

A few amine-containing polymers – poly(4-vinylpyridine), polyethyleneimine, and a biopolymer – have been quaternized and crosslinked to form membranes. The highest ionic conductivity is achieved by the quaternized poly(4-vinylpyridine) polymer membranes. Figure 1 shows the results for several samples and compares them with the target room temperature conductivity possessed by Nafion<sup>®</sup>, a proton exchange membrane. While the electrochemical properties of the quaternized poly(4-vinylpyridine) membranes are good, the mechanical and chemical properties are poor. The polymer film can be handled, but can be easily torn. Rehydrating dried films results in spallation of pieces from the dried polymer. Furthermore, the pyridinium group undergoes an irreversible oxidation in base, resulting in chemical degradation. The quaternized polyethyleneimine polymer is quite ionic as evidenced by the solubility of the polymer in water.



**Figure 1.** Chart of ion conductivities measured for variously prepared quaternized and crosslinked poly(4-vinylpyridine) polymer membranes.

This mechanical instability warrants further crosslinking and/or blending with another insoluble polymer. Another amine-containing polymer, a biopolymer (under patent consideration), exhibits greater mechanical and chemical stability, but to date has not been easily quaternized to yield sufficient ion conductivity. This polymer's ionic conductivity is approximately two orders of magnitude lower than the target. The summary of these membrane properties is given in Table 1.

**Table 1.** Summary of Properties for Three Types of Polymer Membranes Prepared

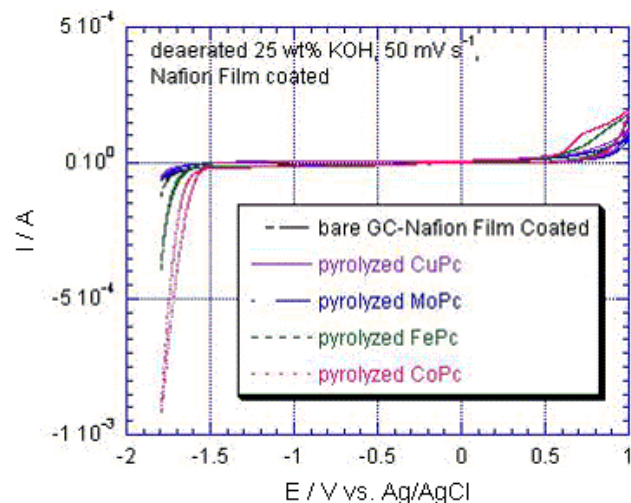
Property/Polymer	quaternized P4VP	quaternized PEI	CMSP
<b>Electrochemical</b> <sup>%</sup> Target ionic conductivity (room temperature) is $\geq 80 \text{ mS cm}^{-1}$	10-100 $\text{mS cm}^{-1}$	–	~2 orders of magnitude below target conductivity
<b>Mechanical</b> <sup>§</sup>	fragile; becomes brittle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

<sup>%</sup> lower operation costs,

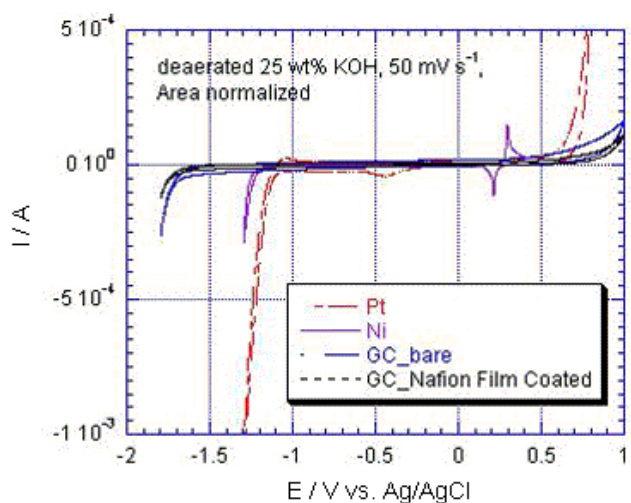
<sup>§</sup> lower maintenance costs

The transition-metal macrocycle catalysts were prepared from cobalt, copper, iron, and molybdenum phthalocyanines (Pc). These 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). These results are shown in Figure 2. The cathodic (negative) current between -1.6 V and -1.8 V (vs. Ag/AgCl reference electrode) results from water reduction to evolve hydrogen gas. These catalysts, while catalytic – compare with the glassy carbon (GC) electrode which is not catalytic – do not support the large currents at the relatively lower overpotentials (i.e., more positive on the potential scale) exhibited by metals. Figure 3 shows the water stability regions (potential window between water reduction and oxidation) for Pt, Ni, and GC in the low current portions of their cyclic voltammograms. By comparison, the macrocycle

catalysts require  $\sim 300$ - $500$  mV more overpotential to generate hydrogen at the same rate as by a solid metal surface. The larger overpotential for the phthalocyanine catalysts likely arises because of  $i \cdot R$



**Figure 2.** Cyclic Voltammograms of Prepared Electrocatalysts on Glassy Carbon (GC) and Coated by Nafion<sup>®</sup> Film in Deaerated 25 wt% KOH



**Figure 3.** Cyclic Voltammograms of Bare Metals and Glassy Carbon (GC) in Deaerated 25 wt% KOH

drop in the catalyst layer because of poor conjugation between the macrocycle ligands. Some preparations involved mixing the compound with microparticles serving as a template for creating an open network structure upon removal of the template. The template approaches tried have not given improved catalytic properties. A suitable template that withstands the preparation steps and is easily removed to create open structure is presently being sought.

These findings guide the direction of continued research, the plans and approaches of which are enumerated in the Future Directions section above.

### **Conclusions**

- Hydroxyl Ion Exchange Membranes
  - 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.
- Macrocycle Catalysts
  - Prepared phthalocyanines that were catalytic for water electrolysis, but the Mo species had lower activity than other transition metal species

### **Special Recognitions & Awards/Patents Issued**

1. U.S. Provisional Patent Application # 60/681,509 filed on May 16, 2005, titled “Hydroxyl Ion Exchange Membrane”

### **FY 2005 Publications/Presentations**

1. Quarterly reports
2. Internal seminar
3. Annual Program Review poster presentation
4. Manuscript in preparation