

II.A.5 Economical Production of Hydrogen through Development of Novel, High Efficiency Electrocatalysts for Alkaline Membrane Electrolysis

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Illinois Institute of Technology (IIT), Chicago, IL

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Project End Date: April 21, 2015

Overall Objectives

- Understand and optimize activity of pyrochlore catalysts for oxygen evolution based on composition and microstructure
- Determine the impact of key anion exchange membrane properties (conductivity, water uptake, gas crossover) on performance
- Derivatize polymer backbones to form new anion exchange membranes (AEMs) and characterize said AEMs for mechanical and electrochemical properties
- Select the system circulating fluid based on performance and stability
- Process promising membrane and catalyst materials into electrodes and test
- Scale up downselected materials to a relevant stack active area and height and operate in a relevant environment
- Develop a prototype system package and perform testing of up to 500 hours
- Provide product cost analysis and H₂A modeling demonstrating the cost saving

Fiscal Year (FY) 2013 Objectives

- Demonstrate high activity of pyrochlore catalysts for oxygen evolution
- Optimize catalyst composition and microstructure
- Form and characterize new anion exchange membranes and demonstrate acceptable conductivity for electrolysis
- Process promising membrane and catalyst materials into MEAs
- Scale up to a relevant stack active area and height and operate in a relevant environment

Technical Barriers

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

(F) Capital Cost

Technical Targets

The technical targets for this project are presented in Table 1.

TABLE 1. Proton Energy Systems Progress Towards Meeting Technical Targets for Distributed Water Electrolysis Hydrogen Production

Characteristics	Units	2012 Target	2017 Target	Proton Status
Hydrogen Cost	\$/gge	<3.70	<3.00	3.51
Electrolyzer Capital Cost	\$/gge	0.70	0.30	0.57
Electrolyzer Energy Efficiency	% (LHV)	69	74	58

gge - gasoline gallon equivalent; LHV - lower heating value
Note: Estimates are based on H₂A v2.1, for electrolysis only (compression-storage-delivery not included). Model assumes \$0.05/kWh.
Electrolyzer cost based on 1,500 kg/day capacity, 500 units/year; efficiency based on system projections, and technology which could be implemented within five years.

Development of Alkaline Exchange Membrane Systems

This project is designed to significantly reduce the capital cost of hydrogen generation through elimination of the most expensive materials in the cell stack. It is likely that the AEM cells will not achieve the same efficiency as proton exchange membrane (PEM) technology for similar current densities, but not all markets will be as sensitive to electrical

cost. Proton has developed the following targets for AEM technology based on current technology status:

- Demonstrate cell voltages of 1.8 V at 500 mA/cm² or greater
- Increase stack durability to greater than 1,000 hours
- Reduce stack contribution to the overall system at MW scale by \$100K (\$100/kW)

FY 2013 Accomplishments

- Synthesized desired pyrochlores and proved structure with X-ray diffraction
- Demonstrated up to order of magnitude increase in mass activity for the oxygen evolution reaction (OER)
- Completed process trials for improved electrode adhesion and stability
- Tested cells for up to 200 hours
- Demonstrated modeling results consistent with experimental trends to give direction in Phase 2 composition refinement



INTRODUCTION

There are currently two primary commercial electrolyzer options: systems based on liquid potassium hydroxide electrolyte and systems based on solid PEM electrolytes. While the PEM systems allow higher current densities and safety advantages such as lack of corrosive electrolyte and ability to run at low pressure oxygen, the materials of construction are expensive. Primary contributors to the cell cost are catalysts, membranes and flow fields. Moving to a hybrid system which uses an AEM enables the attractive operating parameters of the PEM case, while allowing use of less expensive materials. For example, flow fields can be made of stainless steel, while a larger variety of catalyst materials are stable in basic media. While AEM materials are still less stable and efficient than PEM materials, Proton has made significant progress in increasing the performance of AEMs for electrolysis. This technology has the long-term potential of reducing the stack cost by up to 75%. In the current project, work is being performed on catalyst materials to reduce the amount of noble metal needed in the baseline catalyst composition, and define the operating requirements of the system. While these catalysts still contain some PGM content, the conversion to stainless steel flow fields is still the major opportunity for AEM electrolysis in terms of cost contribution.

APPROACH

Electrolysis using anion exchange membranes introduces some new considerations to cell operating conditions. The schematic for acid-based systems vs. basic systems is shown in Figure 1. Because the water is actually consumed on the hydrogen side of the cell in the basic system, water management becomes a key consideration. Phase separation is more straightforward in an anode feed cell, because only the water transported through the separator has to be removed from the hydrogen, which becomes a smaller fraction of the total flow as the hydrogen pressure is increased. However, cathode feed would potentially enable higher current densities, by reducing any mass transfer limitations due to the rate of water transport across the membrane. Proton's past work under Advanced Research Projects Agency–Energy (ARPA-E) funding has shown that AEM electrolysis at greater than 500 mA/cm² is achievable with no evidence of mass transfer. Proton has therefore chosen to continue to leverage existing cell designs and balance of plant configurations established for our anode feed commercial products. A second consideration is the electrolyte. Anion exchange membranes are not at the same level of maturity as PEM materials, and tend to be less stable in strongly alkaline environments. In addition, they rapidly carbonate in air, blocking hydroxide conducting sites. While deionized water is the preferred fluid for the electrolyzer, using a buffered solution such as carbonate may provide stability enhancements without significantly impacting performance.

In the Phase 1 project, the pyrochlore class of catalysts (A₂B₂O₆₋₇) were investigated in AEM cells for improved activity at the oxygen electrode vs. noble metal oxide baseline catalysts. This approach leverages several advantages of the pyrochlores. First, these materials have good kinetics for oxygen evolution, as supported by density functional theory calculations performed in this project. Also, these materials are stable in basic media, such as the polymer electrolyte. Finally, it has been demonstrated that these structures can be made into nanoparticles. This characteristic is especially important, as several reports of oxygen evolution catalysts

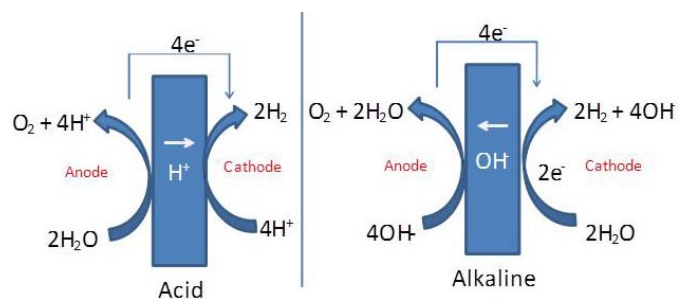


FIGURE 1. Acidic vs. Basic Membrane-Based Electrolysis Cell Schematic

exist in the literature which claim very high activity as normalized by surface area, but have not been successfully made at relevant surface areas. In the Phase 1 project, compounds using Bi or Pb for the A metal and B metals including Ru and Ir were investigated.

RESULTS

As shown in Figure 2, the desired catalyst compositions were successfully synthesized in the Phase 1 project. While some of the formulations were lower than desired in surface area, the ruthenates were acceptable, and electronic conductivities for all the samples measured were good. Even at the lower than desired surface areas for some catalysts, mass activity measurements using rotating disk electrodes (RDE) showed promise, as shown in Figure 3. While iridium oxide is not the most active known oxygen evolution catalyst in basic media, it serves as the baseline in this study. Nickel alloys and nickel-based oxides are well known for catalytic activity in the alkaline liquid systems. However, Proton's ARPA-E project has demonstrated that iridium oxide performance translates very well from RDE testing to a practical electrode configuration, while the nickel systems still require understanding around the ionomer-catalyst-

membrane interface. IrO_2 is therefore still an appropriate baseline for comparison. Platinum is also included for reference, as platinum is not a very good oxygen evolution catalyst. Typical cell voltages are 300 mV higher for platinum than IrO_2 .

Proton has spent considerable effort to develop AEM electrolysis electrode configurations, in collaboration with our ARPA-E project partners especially at Penn State. The AEM membranes are much less stable at high temperature vs. PEM materials and cannot withstand many of the processing conditions of traditional electrolysis MEA manufacturing. Using a gas diffusion electrode approach in which the electrodes can be directly sprayed on the gas diffusion material mitigates this stress on the membrane and results in more stable, reproducible results. Proton has also translated this technique to PEM systems and demonstrated very close to equivalent performance. In addition, the AEM materials tend to be significantly stiffer than the PEM materials, and are thinner than standard PEM electrolysis membranes. The thinner membrane is required due to the slower diffusion of hydroxide vs. protons. While the improved stiffness results in the membranes being easier to handle, these characteristics require adjustments to the cell design, particularly in the seal area, to effectively operate the stack and avoid overboard leaks while not overloading the membrane. Proton made some of these adjustments on the ARPA-E project and has continued to improve the cell on this project. Based on this background work, Proton was able to rapidly test new material candidates from IIT and compare to established performance baselines for the AEM cell.

Stack testing demonstrated good translation of the RDE results as shown in Figure 4. The lead ruthenates showed the most promise, consistent with the higher surface area of these materials. Figure 4a shows the initial performance

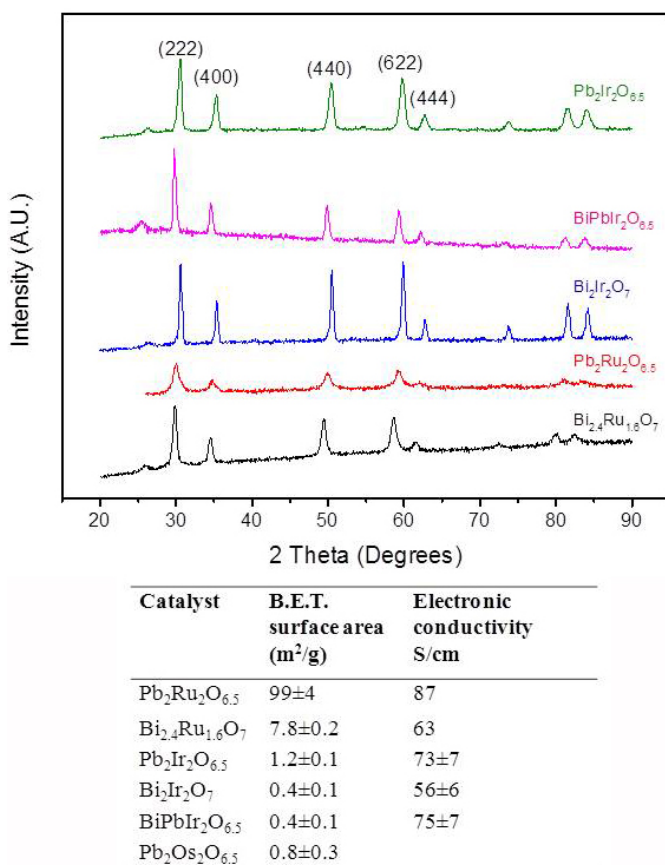


FIGURE 2. X-Ray Diffraction Analysis, Synthesized Pyrochlore Catalysts

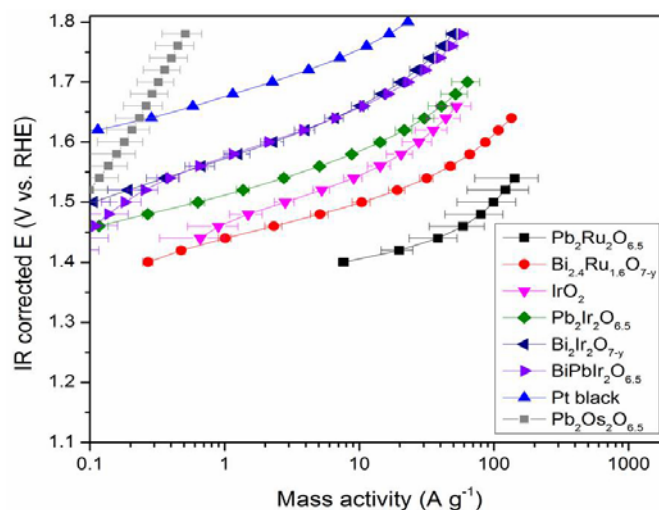


FIGURE 3. Mass Activity for OER, RDE Analysis

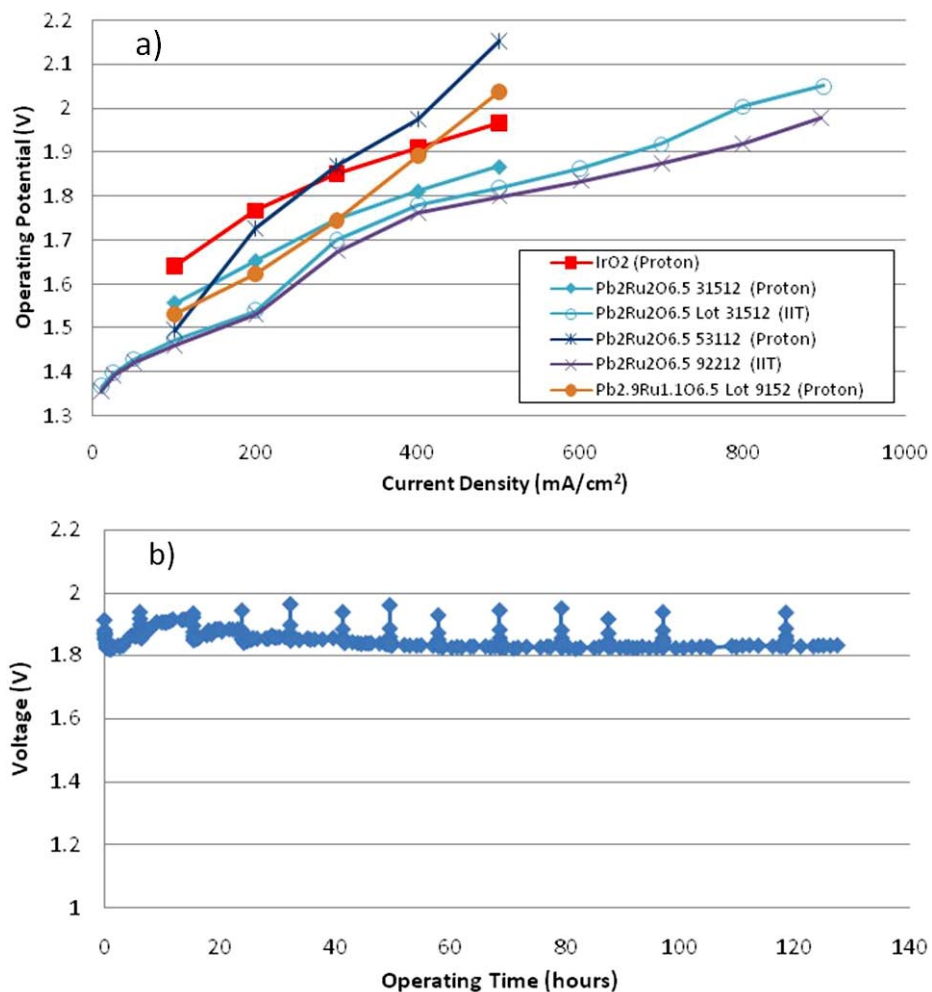


FIGURE 4. Cell Stack Performance, Lead Ruthenate Catalysts: a) Polarization Curve; b) Durability Performance at 500 mA/cm² in Carbonate Electrolyte

data, while Figure 4b shows stable voltage performance at good efficiencies in a carbonate electrolyte. While carbonate conductivity should be lower than hydroxide conductivity, it is believed that the performance does not significantly decline because of the increased ionic conductivity of the liquid phase and high water content of the membranes under electrolysis conditions. In addition, there was good agreement between results obtained at IIT vs. Proton in similar test hardware, demonstrating consistent electrode fabrication and test protocol. Initial performance with IIT membranes and ionomers also showed high efficiency, although durability needs to be improved.

Finally, density functional theory and d-band orbital theory were applied to the catalyst compositions tested. A four-step mechanism was proposed for the oxygen evolution reaction, with the ruthenium compounds showing higher predicted performance, as demonstrated in the cell testing. Generally good agreement was obtained between modeling and theory, particularly when corrected for surface

area. Larger metal-adsorbate repulsion for the hydroxide absorption leads to lower OER activity, mainly dictated by the B cation. However, the modeling also predicts that there may be further room for improvement beyond the highest performing Phase 1 materials, if the surface area can be corrected on the bismuth materials.

CONCLUSIONS AND FUTURE DIRECTIONS

- In the Phase 1 project, improvements over past AEM electrolysis cells were demonstrated. High OER activity was achieved with lead ruthenate materials, reducing noble metal content. Future work includes determining the influence of composition on pyrochlore microstructure, physical properties, and activity.
- Initial IIT membrane performance met efficiency targets. In Phase 2, focus will be on improving durability through investigation of key AEM properties

(conductivity, ion exchange capacity, water uptake, gas crossover) and modification of membrane characteristics.

- Carbonate in the electrolyte served as a stabilizer for the AEM electrolyzer, without negatively impacting efficiency. A system trade study of electrolyte type vs. cost and stability will be performed in the next phase and a prototype lab system will be developed.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Final Report, Phase 1 Small Business Innovation Research.
2. “Bridging the Infrastructure Gap: Cost Effective Generation of Hydrogen from Water”, Department Seminar, Colorado School of Mines, November 2012.
3. “Material Advancements for Cost Effective Hydrogen Energy Storage: Megawatt Electrolysis Development”, Spring ACS Meeting, Esther Takeuchi Award Symposium, New Orleans, April 2013.