

V.A.9 Non-Platinum Group Metal OER/ORR Catalysts for Alkaline Membrane Fuel Cells and Electrolyzers

Nemanja Danilovic (Primary Contact),
Katherine Ayers

Proton Energy Systems d/b/a Proton OnSite
10 Technology Drive
Wallingford, CT 06492
Phone: (203) 678-2154
E-mail: ndanilovic@protononsite.com

DOE Manager
Jacob Spendelow
Email: Spendelow@lanl.gov

Contract Number: DE-SC0013179

Subcontractor
Professor Charles Dismukes, Rutgers University,
New Brunswick, NJ

Project Start Date: February 17, 2015
Project End Date: November 16, 2015

Technical Targets

See Table 1.

FY 2015 Accomplishments

- Synthesis, performance and reproducibility at 5 grams verified for LiCoO_2
- Synthesized and characterized multiple A and B-site doped ABCoO_2 (A=Mg, Zn; B=Mn) by rotating disk electrode studies
- Defined flowfield geometry, fabricated hardware and optimized wet proofing for oxygen electrode
- Obtained baseline performance in fuel cell and electrolysis mode for anion exchange membrane (AEM)-based unitized regenerative fuel cells (URFCs)
- Obtained preliminary fuel cell and electrolysis data for LiCoO_2 with 1,300-hour stability test completed in electrolysis mode



Overall and Fiscal Year (FY) 2015 Objectives

- Produce 2–10 gram quantities of the cubic phase of lithium cobalt oxide (LiCoO_2) and A site derivatives of LiCoO_2 (A = Li^+ , Mg^{2+} , Zn^{2+}) while preserving particle size, composition purity, and surface structural integrity
- Synthesize O site imide (NH) derivatives of the cubic phase of LiCoO_2 , $\text{LiCoO}_x(\text{NH})_{2-x}$ and screen for enhanced oxygen reduction reaction (ORR) activity
- Optimize ionic and electronic conductivity as well as water transport through modification of flow field geometries and degree of hydrophobicity
- Develop manufacturing methods to combine catalysts and ionomers with an alkaline exchange membrane
- Benchmark oxygen evolution reaction (OER) catalysts in membrane electrode configurations as single cell stacks

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Production and Fuel Cells sections of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration (MYRDD) Plan:

(G) Capital Cost (Electrolyzer + Fuel Cell)

INTRODUCTION

Two key cost issues represent barriers to implementation of regenerative fuel cells for energy applications. First, the platinum group metal (PGM) catalysts typically used for polymer electrolyte membrane based systems are scarce and expensive. Second, the stack is still a significant cost component of both the electrolyzer and fuel cell subsystems, as discussed at a 2011 Department of Energy workshop on reversible fuel cells. AEMs and ionomers have been gaining stability through significant research and development by multiple groups, and have shown enough feasibility to generate interest in integrating them into devices. At the same time, the alkaline chemistry opens up a wider range of stable materials, including non-noble metals. The end goal of this work is to enable a PGM-free reversible fuel cell, also known as a URFC, based on AEM materials.

The URFC configuration combines the functionality of an electrolyzer and fuel cell stack in one integrated unit. As fuel cell developments have been leveraged in electrolysis cells, there now exists a pathway to design of efficient, durable URFCs compatible with both modes of operation. In addition to enabling catalysts containing nickel, iron, and cobalt that have activity for water splitting and stability in alkaline environments, the AEM cell also eliminates the need for expensive flow field materials such as titanium for

TABLE 1. Technical Targets - Portable Power Fuel Cell Systems and Distributed Forecourt Water Electrolysis Hydrogen Production from the 2012 MYRRD Plan

Table 3.4.7.a Technical Targets: Portable Power Fuel Cell Systems (<2 Watt) ^a				
Characteristic	Units	2011 Status	2013 Targets	2015 Targets
Specific power ^b	W/kg	5	8	10
Power density ^b	W/L	7	10	13
Specific energy ^{b,c}	Wh/kg	110	200	230
Energy density ^{b,c}	Wh/L	150	250	300
Cost ^d	\$/system	150	130	70
Durability ^{e,f}	hours	1,500	3,000	5,000
Mean time between failures ^{f,g}	hours	500	1,500	5,000

Table 3.1.4 Technical Targets: Distributed Forecourt Water Electrolysis Hydrogen Production ^{a, b, c, l}				
Characteristics	Units	2011 Status	2015 Target	2020 Target
Hydrogen Levelized Cost ^d (Production Only)	\$/kg	4.20 ^d	3.90 ^d	2.30 ^d
Electrolyzer System Capital Cost	\$/kg	0.70	0.50	0.50
	\$/kW	430 ^{e, f}	300 ^f	300 ^f
System Energy Efficiency ^g	% (LHV)	67	72	75
	kWh/kg	50	46	44
Stack Energy Efficiency ^h	% (LHV)	74	76	77
	kWh/kg	45	44	43
Electricity Price	\$/kWh	From AEO 2009 ⁱ	From AEO 2009 ⁱ	0.037 ^j

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 1500 kg/day capacity, 500 units/year. Efficiency based on system projections and demonstrated stack efficiency of 74% LHV efficiency.

the high potential oxygen electrode, allowing substitution with stainless steel or nickel. Proton Energy Systems d/b/a Proton OnSite (Proton) will leverage experience in water management and URFC design, with catalyst synthesis and characterization expertise at Rutgers University, to focus on a bifunctional oxygen electrode in Phase I, to demonstrate a catalyst and flow field configuration that enable efficient operation for both OER and ORR.

APPROACH

In this project, Proton is focusing on cell design and electrode testing while Rutgers develops a new class of bifunctional OER-ORR catalysts based on modified cubic-LiCoO₂. The project focuses on three developments: (1) modification of catalysts that have been shown to provide good OER activity in AEM systems for application to ORR, (2) processing and assembly to stabilize the electrode structure, and (3) changes in cell design to improve water transport in the cell. Rutgers will tune the activity and

stability of the catalyst through metal substitution, and doping of the oxide with nitrides or imides. Proton will leverage recent developments in ink deposition and gas diffusion layer formulation to improve overall cell stability. Treating the oxygen electrode to wick the water away from the electrode is likely to improve stability, while making the hydrogen electrode more hydrophilic may be beneficial to fuel cell performance based on our previous Advanced Research Projects Agency-Energy program.

RESULTS

Rutgers synthesized well-defined non-PGM catalysts based on LiCoO₂ and lithium manganese oxide (LiMn₂O₄) families using sol gel methods. This synthetic approach yielded high phase purity and high surface area as verified by X-ray diffraction and scanning electron microscopy. The ORR and OER activity was tuned by substitution of the cobalt sites with manganese, making compounds with the general formula LiMn_{2-x}Co_xO₄ (0 < x < 1.5). Cyclic

voltammetry showed that adding manganese enhanced ORR activity, but pure LiMn_2O_4 loses OER activity. A reasonable balance could be obtained by partial substitution (Figure 1).

Promising compounds were then delivered to Proton for testing. Electrolysis screening was performed first, using either deionized water or potassium carbonate. Improved performance was demonstrated for the Rutgers catalyst vs. previously tested catalysts. A durability test was then performed, using stainless steel flow fields and gas diffusion layers on the oxygen side and carbon on the hydrogen side. Potassium carbonate was used and electrolyte was fed to the anode. Over 1,200 hours of operation were demonstrated as shown in Figure 2.

Fuel cell testing was then performed using platinum-platinum cells to examine the impact of the flow field geometry. The anode was underhumidified to prevent flooding while the cathode was overhumidified to lessen dryout. Serpentine and straight channel configurations with and without wetproofing on the hydrogen electrode were compared, with serpentine channels on both electrodes demonstrating the best performance (Figure 3).

Cyclic voltammetry data demonstrated that the LiCoO_2 meets technical targets for OER and ORR. However, OER performance was more affected by testing in fuel cell mode first than ORR performance was impacted by testing first in electrolysis mode. Full cell data also showed better OER performance before fuel cell testing, but the difference was not nearly as large, only resulting in about 50 mV loss at 0.4 A/cm^2 (Figure 4). Fuel cell performance was significantly lower than the optimized platinum data in Figure 3 and slightly lower than the worst platinum data. Additional optimization of the water transport is expected to significantly improve the fuel cell performance, based on the Rutgers data.

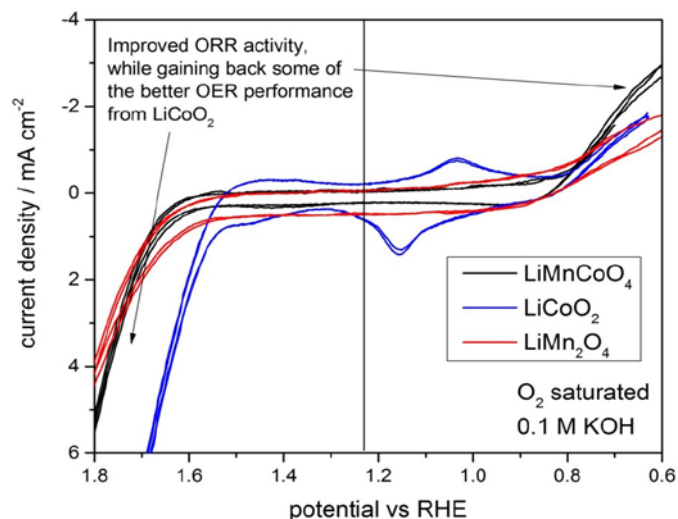


FIGURE 1. Cyclic voltammetry of lithium cobalt manganese oxide compounds

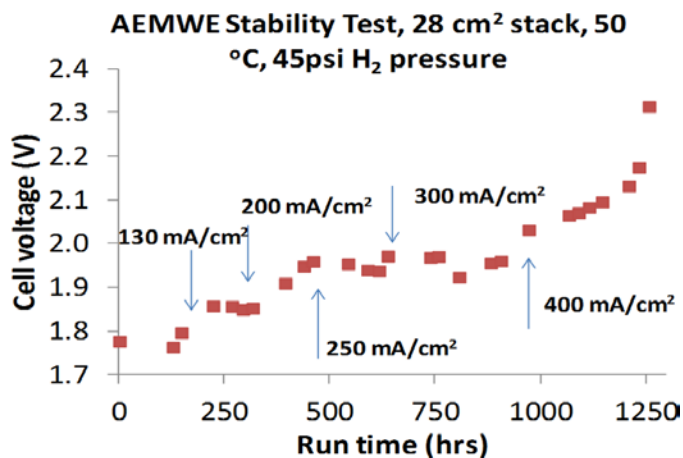


FIGURE 2. Durability and rate capability testing for lithium cobalt oxide (AEMWE = anion exchange membrane water electrolysis)

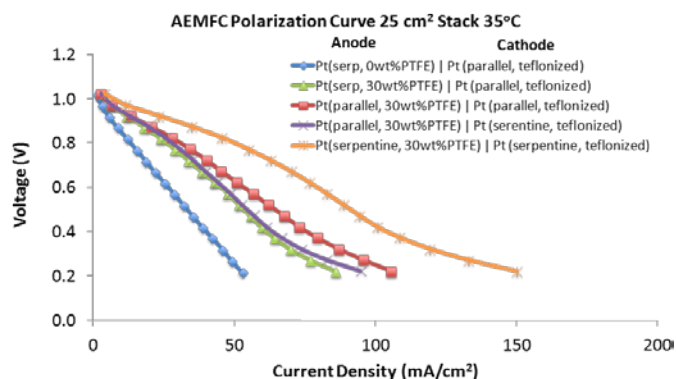


FIGURE 3. Fuel cell performance vs. flow field and gas diffusion layer configuration (AEMFC = anion exchange membrane fuel cell; PTFE = polytetrafluoroethylene)

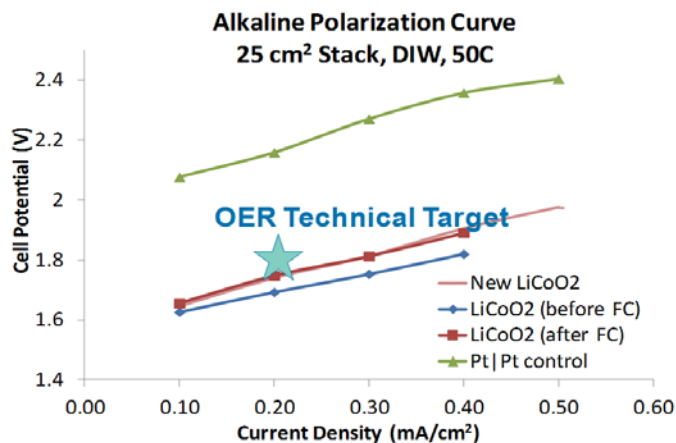


FIGURE 4. Electrolysis testing before and after fuel cell testing (DIW = deionized water)

CONCLUSIONS AND FUTURE DIRECTIONS

- Concluded that LiCoO_2 shows good promise for OER/ORR in bench screening, but in cell water management may not be ideal
- Evaluate impact of improved hydrogen catalyst structure and water transport improvements on ORR performance
- Promote configuration to 28 cm^2 retest with LiCoO_2 anode
- Conduct 10 cycles using new cathode, LiCoO_2 anode
- Continue to evaluate anion and cation dopants on ORR/OER activity