FY16 SBIR II Release 1: Regenerative Fuel Cell System

Paul Matter (Primary Contact), Minette Ocampo, Michael Beachy, Chris Holt, Nora Shaheen, Monica Chan, and Jimmy Gaydos
pH Matter, LLC
6655 Singletree Dr.
Columbus, OH 43229
Phone: (614) 396-7820
Email: info@phmatter.com

DOE Manager: Donna Ho
Phone: (202) 586-8000
Email: Donna.Ho@ee.doe.gov

Contract No: DE-SC0013111 (SBIR Phase II Release 1)

Subcontractors:
- Giner, Inc., Newton, MA
- National Renewable Energy Laboratory, Golden, CO

Project Start Date: April 12, 2016
Project End Date: April 11, 2018

Overall Objectives

- Demonstrate a reversible 25-cm^2 anion exchange membrane fuel cell (AEMFC) for 1,000 cycles (42% round-trip efficiency; >250 mA/cm^2 power generation; >50 mA/cm^2 energy storage).
- Incorporate membrane electrode assemblies (MEAs) into a regenerative stack.
- Perform economic analysis on reversible AEMFC system following DOE guidelines for candidate grid load-leveling technologies.

Fiscal Year (FY) 2018 Objectives

- Demonstrate a reversible 25-cm^2 AEMFC for 1,000 cycles (42% round-trip efficiency; >250 mA/cm^2 power generation; >50 mA/cm^2 energy storage).
- Incorporate MEAs into a regenerative stack.
- Perform economic analysis on reversible AEMFC system following DOE guidelines for candidate grid load-leveling technologies.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cell section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan,[1] with respect to alkaline fuel cells for energy storage:

(A) Durability: Increase the durability of reversible fuel cell electrodes for stationary load cycles

(B) Cost: Develop low-platinum group metal (PGM) and PGM-free catalysts and electrodes for reversible anion-exchange membrane fuel cells (oxygen and hydrogen electrodes)

(C) Performance: Optimize reversible anion-exchange membrane fuel cell and stack performance while maintaining cost and durability.

Technical Targets

This Phase II Small Business Innovation Research (SBIR) project is developing new catalyst materials and MEAs for a regenerative alkaline fuel cell stack. The materials being developed address the following technical targets for energy storage applications:

- 1,000 cycles at target current density and above the efficiency targets
- 42% efficiency; >250 mA/cm^2 power generation; >50 mA/cm^2 energy storage.

FY 2018 Accomplishments

The following work related to the technical objectives has been accomplished on this SBIR Phase II project:

- In 25-cm^2 reversible cell testing, demonstrated 360 cycles between target fuel cell and electrolysis current density at 50°C with cell that achieves performance and economic model cost and efficiency targets; demonstrated >1,000 cycles of stable performance (below

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

efficiency target); demonstrated 250 hours of simulated load cycle operation.

- Demonstrated 3-cell 25-cm^2 stack that simultaneously achieves performance and the economic model cost targets using low-cost platinum-free hydrogen and oxygen electrode catalysts; demonstrated 200 cycles.
- Further refined an economic model based on the assumptions developed by Steward et al. [1] and the Phase II targets. The model includes a sensitivity analysis for key cell parameters being developed (i.e., current density, efficiency, lifetime, and fuel cell cost).

INTRODUCTION

Low-temperature fuel cells, such as proton exchange membrane (PEM) and alkaline fuel cells, offer an efficient and clean means of energy conversion of hydrogen to electricity. However, PEM fuel cells typically require platinum (Pt) in the cathode to operate at high power density and high efficiency, which hurts the economics for this technology. Pt is used as an electrocatalyst for the oxygen reduction reaction (ORR); the cathode side half reaction is shown below for acidic and alkaline electrolytes, respectively:

(1) Oxygen reduction reaction (acid) $O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$

(2) Oxygen reduction reaction (alkaline) $O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

The slow kinetics in the cathode is one of the largest sources of inefficiency in fuel cells, thus high platinum catalyst loadings are needed to prevent even more voltage losses (or overpotential). At commercial scale, precious metals in the cathodes of PEM fuel cells would comprise a significant portion of the entire stack cost [1, 2]. Additionally, Pt-based ORR catalysts can degrade quickly under fuel cell operating conditions, such as frequent load cycling.

More recently, there has been renewed interest in alkaline fuel cells for stationary applications as development of commercial anion exchange membranes (AEMs) is helping to alleviate system-level problems with alkaline fuel cells, such as pressure balance. Further, recent published results at Los Alamos National Laboratory have shown that alkaline fuel cells could potentially operate at high efficiency with PGM-free ORR catalysts [3]. Alkaline fuel cells are of particular interest for energy storage applications that do not have volume limitations, such as grid load leveling. In an alkaline fuel cell, oxygen is reduced by reaction (2) above, and hydrogen is oxidized by reaction (3) below.

(3) Hydrogen oxidation reaction (alkaline) $H_2 + 2\ OH^- \rightarrow 2\ H_2O + 2\ e^-$

Alkaline fuel cells could potentially be operated in a reversible manner, allowing renewable energy to be stored in the form of hydrogen. This would be particularly valuable when coupled with renewable energy generation (wind or solar) to provide energy storage and load leveling. However, when operating in regeneration mode, cathode degradation is even more pronounced for conventional ORR catalysts because of the high voltages required for the oxygen evolution reaction (OER), the reverse of reaction (2) above. Consequently, in existing reversible systems, separate cell stacks for fuel cell and electrolysis operation are used, adding to the already high system cost. If a low-cost regenerative stack could be developed, it would be a key breakthrough in the commercial viability of energy storage systems [4]. In this project, pH Matter, LLC, is partnering with Giner, Inc., and the National Renewable Energy Laboratory (NREL) to develop and demonstrate a low-cost regenerative alkaline fuel cell.

APPROACH

The overall objective of the project is to develop and demonstrate a regenerative fuel cell stack technology that is economically viable in stationary energy storage. Researchers at pH Matter synthesized a matrix of PGM-free hydrogen oxidation reaction (HOR) / hydrogen evolution reaction (HER) catalysts, and gas diffusion electrodes based on these materials. Researchers as NREL synthesized a matrix of low-PGM hydrogen electrode materials. The HOR/HER materials and gas diffusion electrodes were characterized and tested under cycling conditions to determine performance and stability. Additionally, pH Matter optimized ORR/OER electrodes previously developed in Phase I for improved performance and durability at higher temperatures and pressures. The hydrogen and oxygen electrodes were then demonstrated in 25-cm^2 single cells for up to 1,000 cycles using a novel unitized reversible cell design at pH Matter. Materials that degraded during cycling were characterized by pH Matter and NREL to determine degradation mechanisms. Engineers at Giner tested cells in parallel using a commercial electrolyzer design. Down-selected cells were then incorporated into fuel cell and/or electrolyzer stacks and demonstrated in simulated application testing at pH Matter and Giner. The project establishes a foundation for future work, where the technology will be incorporated into a prototype

regenerative fuel cell system. Additionally, a design and economic model of the regenerative fuel cell system were built to verify advantages of the approach compared to available energy storage technologies.

RESULTS

In previous work, the team developed novel PGM-free oxygen electrode and low-PGM (Pt-free) hydrogen electrode catalysts, and optimized electrodes for regenerative cell operation. Regenerative cells showed excellent stability for cycling for up to 360 cycles above the target performance. This year, work was expanded to longer cycle numbers, simulated operation, and stack testing. After initial degradation and break-in at 60°C, 25-cm^2 cells were shown to be stable for more than 1,000 cycles. Although the performance fell below the project targets during the break-in period, the long-term stability at 60°C and 70°C was found to be exceptional. Figure 1 shows the stability of a cell cycling between 150 mA/cm^2 and 50 mA/cm^2 over 1,000 times in accelerated degradation tests. Cells were also operated for up to 250 hours under simulated load cycling. The load cycle tests were designed to simulate operation of the cells within an energy storage device, such as seasonal solar storage. In these tests, the cells operated for 15 hours under electrolysis operation at 50 mA/cm^2, followed by 5 hours of fuel cell operation at 150 mA/cm^2. An example of the load cycling is shown in Figure 2. Finally, cells were loaded into a 3-cell stack at pH Matter. The stack was based on pH Matter's unique patent-pending reversible unitized cell design. The initial current-density performance in the stack matched the project targets, and the stack was cycled 200 times, as shown in Figure 3.

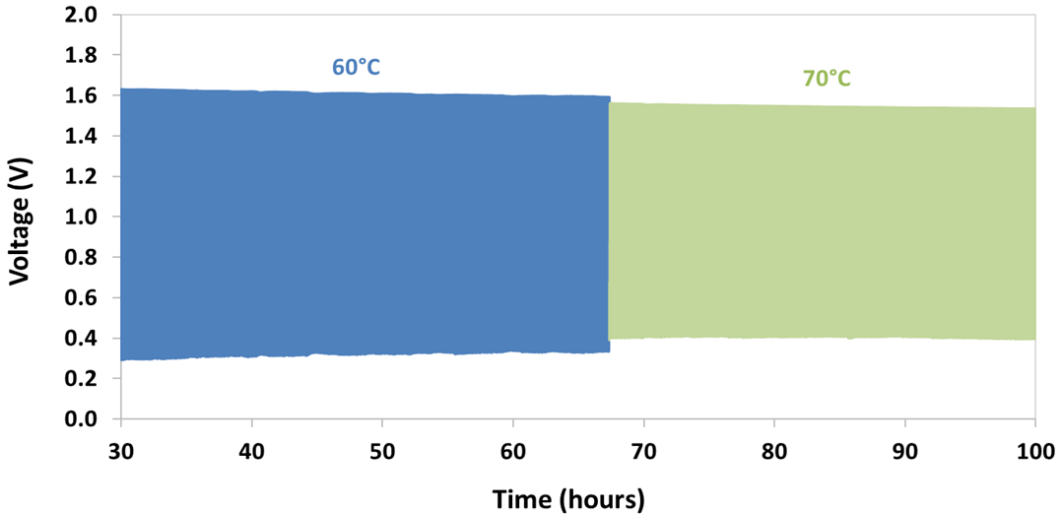

Figure 1. Accelerated degradation testing of 25-cm^2 unitized reversible cell containing down-selected low-PGM hydrogen electrode and PGM-free oxygen electrode showing stability for >1,000 cycles

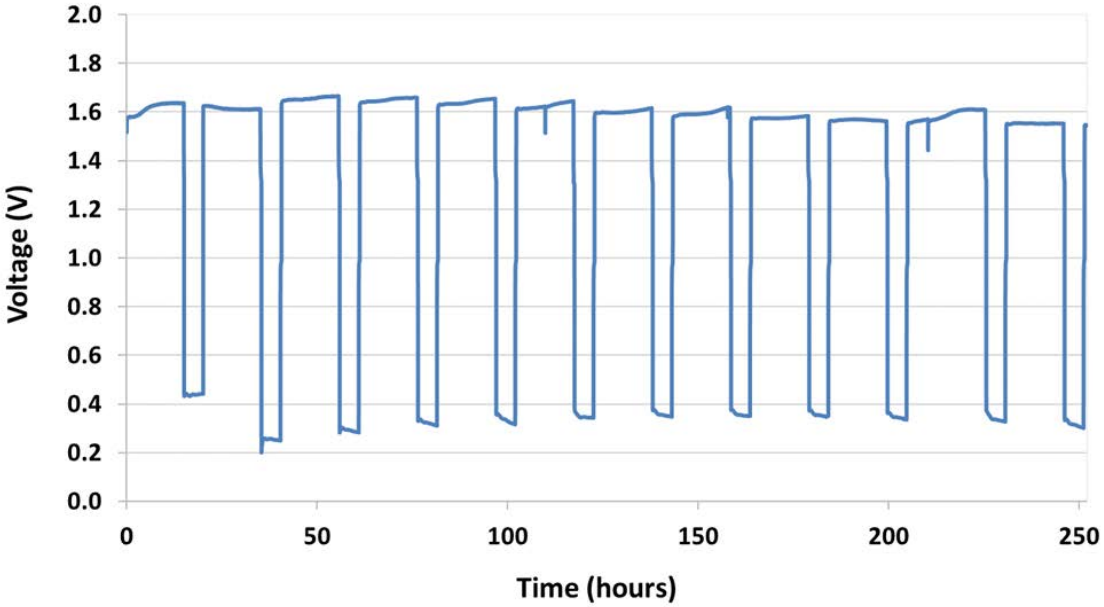

Figure 2. Simulated load cycling at 60°C of 25-cm² unitized reversible cell containing down-selected low-PGM hydrogen electrode and PGM-free oxygen electrode showing stability for >250 hours

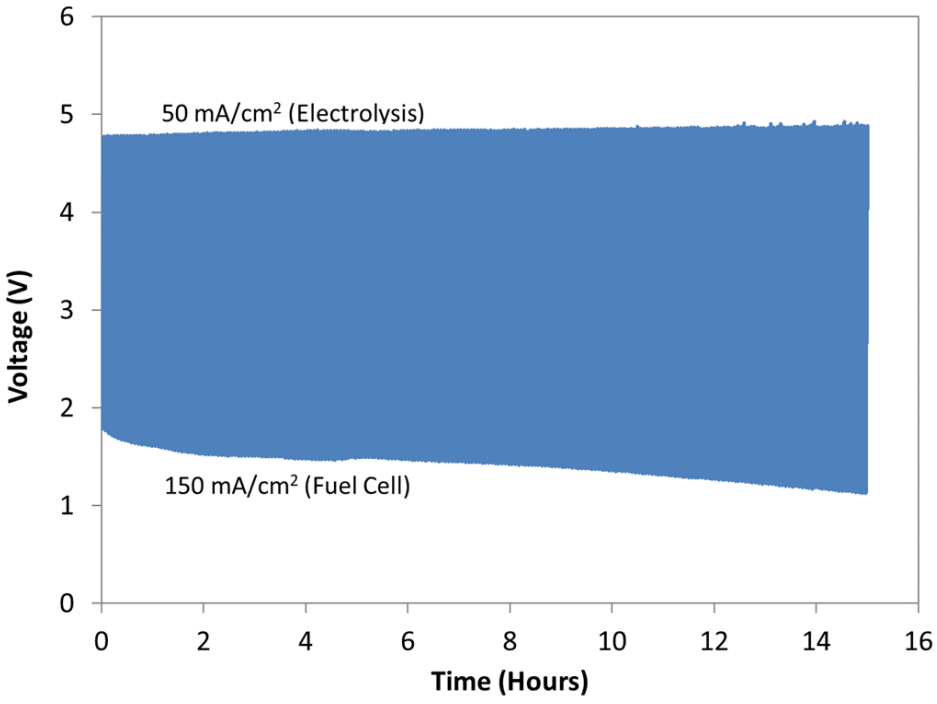

Figure 3. Accelerated degradation testing at 50°C of 25-cm² unitized reversible 3-cell stack containing down-selected low-PGM hydrogen electrode and PGM-free oxygen electrode showing stability for >200 cycles

In fiscal year 2018, NREL supported testing and characterization on the project by examining the degradation of components. In general, degradation was found to occur during electrolysis operation of the oxygen electrode. NREL examined long-term oxygen-side degradation for 3 days each at progressively higher voltages (1.6, 1.7, and 1.8 V). Recoverable degradation was found to occur from carbonation of the electrolyte. After 9

days of operation minimal electrolysis performance degradation occurred, although a small increase in high frequency resistance and catalyst resistance was detected. These results were reported in this year's Annual Merit Review presentation. Giner supported the project by testing 50-cm^2 cells and a 4-cell stack in a commercial electrolyzer design. Cells with pH Matter's down-selected electrodes showed stable performance for electrolysis in the single cells for >100 hours. A 4-cell stack was demonstrated for 700 hours under simulated load operation with the down-selected electrode materials in the commercial design. These results were also reported in the Annual Merit Review presentation. Additionally, Giner provided input for economic modeling.

The economic model was updated this year to project electricity costs for energy stored with a reversible alkaline fuel cell system. The guidelines for the model and assumptions generally followed those used by Steward et al. [1] and assumed a unitized reversible alkaline fuel cell system operating at up to 2,000 psi storage pressure for 4 years. The delivered electricity cost for this scenario was determined to be $0.175/kWh. The system was compared to a discrete storage system with a PEM fuel cell stack and an alkaline membrane electrolyzer. The discrete electrolyzer was the same cost and performance as the unitized reversible stack while the PEM stack cost and performance were based on DOE estimates [5]. The discrete system required only hydrogen storage, as the PEM stacks were assumed to operate with air. For the discrete case, the delivered electricity cost was determined to be $0.223/kWh. Table 1 breaks down the economic comparison. However, the discrete system may have advantages with longevity, customizable sizing for load cycles, and lower PEM fuel cell cost with future automotive adoption. Likewise, the unitized system may have unaccounted size/weight advantages for certain applications. Consequently, the advantages of a discrete versus unitized reversible fuel cell system will ultimately depend on the application.

Table 1. Economic Comparison of a Discrete versus a Unitized Fuel Cell Storage System

	Discrete	Unitized
Upfront Power Cost ($/kW)	Fuel Cell + Electrolyzer	Reversible Cell Stack
Storage Capacity Cost ($/kWh)	$23	$35
Round-Trip Efficiency	43%	43%
Delivered Energy ($/kWh)	0.223	0.175

CONCLUSIONS AND UPCOMING ACTIVITIES

The following conclusions can be drawn from work completed on this project:

- The novel PGM-free oxygen electrode developed on this project shows performance comparable to precious metal catalysts, good stability during cycling from ORR to OER voltages, and excellent stability during long-term electrolysis or fuel cell operation.
- PGM-free electrodes developed on this project show higher over-potential than commercial Pt/Ru but excellent stability. The novel low-PGM hydrogen electrodes developed on this project show similar over-potential as commercial Pt/Ru and excellent stability but require further optimization for high current density operation.
- Full 25-cm^2 cells that meet the project cost and performance targets have been demonstrated for 360 cycles above the go/no-go operating conditions.
- Full 25-cm^2 cells that meet the project cost targets, but are below the performance targets after initial break-in at 60°C, have been demonstrated for >1,000 cycles with exceptional stability.
- Performance results measured in 25-cm^2 accelerated degradation tests were demonstrated in long-term simulated load cycling for more than 250 hours.

- The performance results in 25-cm^2 cells were replicated in a 3-cell stack, and durability for 200 cycles was demonstrated.
- NREL confirmed the stability of the oxygen-side electrodes in electrolysis testing and found electrolyte carbonation to be the main source of electrolysis degradation. This degradation was mostly recoverable with replacement of liquid electrolyte.
- Giner demonstrated operation of the hydrogen and oxygen electrodes in a 50-cm^2 4-cell alkaline membrane electrolyzer stack for more than 500 hours.
- Economic modeling suggests that the reversible AEMFC concept would be an excellent energy storage option for grid load leveling if performance targets can be achieved at the system level. The unitized system has potential cost and size advantages versus a discrete system.

Although the project was completed in 2018, future planned work on the reversible cell technology will include:

- Further improve economics with further optimization of electrodes for higher power and improvement of catalysts for lower over-potential.
- Incorporate novel membranes into the cells to increase cell lifetime.
- Improve mechanical integrity of the cells to enable demonstration of higher-pressure operation at the cell and stack levels.
- Demonstrate long-term operation over thousands of hours and under various load cycle conditions.
- Demonstrate the stack at the kW scale.
- Integrate the stack into a system with energy storage in gas cylinders.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. S.M. Alia, C. Ngo, S. Shulda, S. Pylypenko, B.S. Pivovar, "Platinum-Nickel Nanowires as Electrocatalysts in Alkaline Hydrogen Oxidation and Evolution," 230th ECS Meeting (Honolulu, HI, 2016) 2787.
2. S.M. Alia, C. Ngo, S. Shulda, S. Pylypenko, B.S. Pivovar, "Platinum-Nickel Nanowires as Electrocatalysts in Alkaline Hydrogen Oxidation and Evolution," AIChE Annual Meeting (San Francisco, CA, 2016) 474452.
3. P. Matter, M. Ocampo, C. Holt, M. Beachy, N. Shaheen, M. Chan, and J. Gaydos, "Reversible Fuel Cell System for Energy Storage," Hydrogen Symposium at the 2017 TechConnect World Innovation Conference (May 2017).
4. P. Matter, "Reversible Fuel Cell System for Energy Storage and Hydrogen Production," Solar Power International (Las Vegas, NV, September 2017).
5. P. Matter, M. Ocampo, C. Holt, M. Beachy, N. Shaheen, M. Chan, M. Galliger, J. Gaydos, H. Xu, S. Zhao, S. Alia, A. Park, and B. Pivovar, "Low-Cost Reversible Alkaline Fuel Cell," Fuel Cell Seminar (Long Beach, CA, November 2017).

REFERENCES

1. D. Steward, G. Saur, M. Penev, and T. Ramsden, *Lifecycle Cost Analysis of Hydrogen Versus Other Technologies for Electrical Energy Storage*. NREL Report NREL/TP-560-46719 (2009). Accessed July 23, 2015. http://www.nrel.gov/docs/fy10osti/46719.pdf.

2. Brian D. James, Jennie M. Moton, and Whitney G. Colella, *Mass Production Cost Estimation of Direct H_2 PEM Fuel Cell Systems for Transportation Applications: 2013 Update*. Accessed July 23, 2015. http://energy.gov/sites/prod/files/2014/11/f19/fcto_sa_2013_pemfc_transportation_cost_analysis.pdf.

3. H.T. Chung, J.H. Won, and P. Zelenay, "Active and stable carbon nanotube/nanoparticle composite electrocatalyst for oxygen reduction." *Nature Communications* 4 (2013). Accessed July 23, 2015. doi: 10.1038/ncomms2944.

4. R.J. Remick and D. Wheeler, *Reversible Fuel Cells Workshop Summary Report*. Accessed July 23, 2015. http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/rev_fc_wkshp_report.pdf

5. A. Wilson, G. Kleen, and D. Papageorgopoulos, "Fuel Cell System Cost – 2017," DOE Hydrogen and Fuel Cells Program Record 17007. Accessed at https://www.hydrogen.energy.gov/pdfs/17007_fuel_cell_system_cost_2017.pdf.