

V.A.10 Regenerative Fuel Cell System (SBIR Phase II)

Paul Matter (Primary Contact), Minette Ocampo, Michael Beachy, Chris Holt, Nora Shaheen, Monica Chan, and Jimmy Gaydos
pH Matter LLC
1275 Kinnear Rd.
Columbus, OH 43212
Phone: (614) 396-7820
Email: info@phmatter.com

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

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Subcontractors:

- Hui Xu and Shuai Zhao, Giner, Inc., Newton, MA
- Bryan Pivovar, Shaun Alia, and Andrew Park, National Renewable Energy Laboratory (NREL), Golden, CO

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Demonstration Plan, 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-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 SBIR project is developing new catalyst materials and membrane electrode assemblies 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/cm² power generation; >50 mA/cm² energy storage

Overall Objectives

- Demonstrate a reversible 25-cm² anion exchange membrane fuel cell (AEMFC) for 1,000 cycles (42% round-trip efficiency; >250 mA/cm² power generation; >50 mA/cm² energy storage).
- Incorporate membrane electrode assemblies into a regenerative stack.
- Perform economic analysis on reversible AEMFC system following established DOE guidelines for candidate grid load leveling technologies.

Fiscal Year (FY) 2017 Objectives

- Demonstrate a reversible 25-cm² AEMFC that achieves performance targets (42% round-trip efficiency; >250 mA/cm² power generation; >50 mA/cm² energy storage) with <10% degradation over 200 cycles.
- Perform economic analysis on the AEMFC system following a previous DOE analysis [1] for candidate grid energy storage 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

FY 2017 Accomplishments

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

- Developed low-cost Pt-free hydrogen electrode catalyst; demonstrated 25-cm² cell that simultaneously achieves performance and the economic model cost targets.
- In 25-cm² 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 targets.
- 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 in the cathode to operate at high power density

and high efficiency, which hurts the economics for this technology. Platinum 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)

$$\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}$$
- (2) Oxygen Reduction Reaction (alkaline)

$$\text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^-$$

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. 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 non-platinum 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, and hydrogen is oxidized by Reaction 3.

- (3) Hydrogen Oxidation Reaction (alkaline)

$$\text{H}_2 + 2 \text{OH}^- \rightarrow 2 \text{H}_2\text{O} + 2 \text{e}^-$$

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. 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 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 will synthesize a matrix of platinum group metal (PGM)-free hydrogen oxidation reaction–hydrogen evolution reaction catalysts, and gas diffusion electrodes (GDEs) based on these materials. Researchers at NREL will synthesize a matrix of low-PGM hydrogen electrode materials. The hydrogen oxidation reaction–hydrogen evolution reaction materials and GDEs will be fully characterized and tested under cycling conditions to determine performance and stability. Additionally, pH Matter will further optimize ORR/OER electrodes previously developed in Phase I for improved performance and durability at higher temperatures and pressures. The hydrogen and oxygen electrodes will then be demonstrated in 25-cm² single cells for over 1,000 cycles. Cells that degrade during cycling will be characterized by pH Matter and NREL to determine degradation mechanisms. This information will be used to iteratively prepare more optimized cells. Engineers at Giner will test cells in conjunction with Giner’s water-management membrane technology. Down-selected cells will then be incorporated into a regenerative fuel cell stack and demonstrated in simulated application testing at Giner. The project will establish 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 will be built to verify advantages of the approach compared to available energy storage technologies. The successful result of this Phase II work will demonstrate the feasibility of a regenerative fuel cell system with economic advantages compared to existing technologies.

RESULTS

In Phase I of this project, PGM-free catalysts for ORR and OER based on nitrogen- and phosphorus-doped graphitic carbon (CN_xP_y) were synthesized and tested in a half-cell GDE test stand. GDEs were made using a screen-printing method. Various catalyst formulations, catalyst loadings, ionomers and/or binders, ink compositions, and electrode substrates were examined. Testing was conducted with commercial AEMs in an in-house constructed stainless steel half-cell set-up. This testing demonstrated the durability of the down-selected CN_xP_y catalyst for over 100 h in either fuel cell or electrolysis operation and for over 300 cycles between fuel cell and electrolysis operation.

In the most recent year, work has focused on development of novel PGM-free and low-PGM hydrogen electrode catalysts, and optimization of the electrodes for regenerative cell operation. Fuel cell I-V curves for down-selected hydrogen electrode catalysts are shown in Figure 1. NREL has

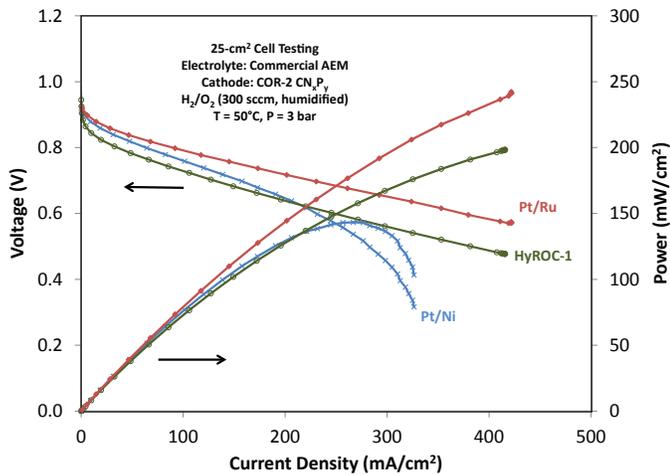


FIGURE 1. 25-cm² fuel cell performance curves at 50°C for cells containing down-selected hydrogen electrodes and optimized PGM-free oxygen-electrode; Pt/Ru is the commercial standard catalyst with 3.2 mg/cm² Pt loading, Pt/Ni is NREL's down-selected nano-wire catalyst with 1.0 mg/cm² Pt loading, and HyROC-1 is pH Matter's down-selected proprietary catalyst with no Pt.

developed Pt/Ni nano-wires with low-Pt loading that show kinetic activity that matches the commercial Pt/Ru standard; however, further electrode optimization is required to match performance at high current density. pH Matter developed a low-cost Pt-free composition (HyROC-1) that has slightly higher overpotential, but performs well at high current density. Further, pH Matter and Giner optimized the oxygen electrode composition and membrane/electrolyte interface. All of the cells in Figure 1 were tested with the same optimized PGM-free oxygen electrode in a 25-cm² test stand.

For the grid load-leveling application, it is expected that current density will be highest (by a factor of 5–6) during periodic cell discharges (ORR operation) compared to OER operation. Cell testing examined cycling between fuel cell and electrolysis conditions. For these tests at 50°C and 3 bar, cycles were conducted at 50 mA/cm² for electrolysis, and 200 mA/cm² for ORR with the direction of the current being reversed every 2 min (1 min of current, 1 min of rest). The regenerative cell showed excellent stability for cycling during these tests in up to 360 cycles above the go/no-go target performance. Figure 2 shows the cycle test for pH Matter's Pt-free cell with a commercial AEM, and operating in pure hydrogen and oxygen. The results demonstrate the ability of this cell technology to undergo a number of cycles without rapid degradation.

Finally, an economic model was updated to project electricity costs for energy stored with a reversible alkaline fuel cell system based on the recent test results. The guidelines for the model and assumptions generally followed those used by Steward et al. [1], but assumed a reversible alkaline fuel cell stack that could operate for 1,000 cycles

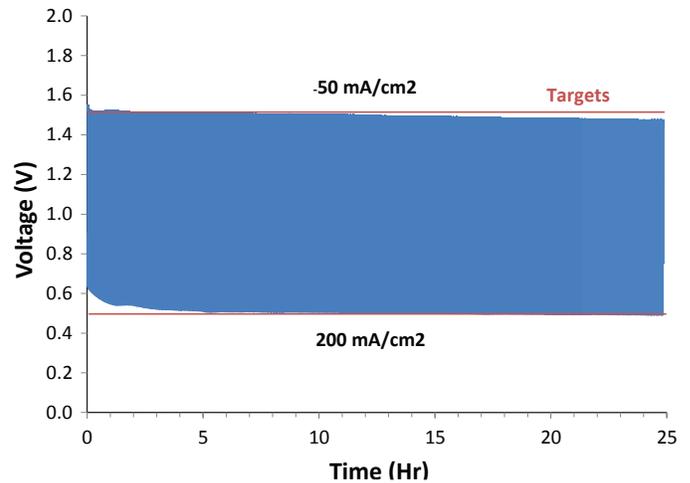


FIGURE 2. 25-cm² fuel cell/electrolysis cycling at 50°C with CN_xP_y oxygen electrode and Pt-free hydrogen electrode; cycles were run for 1 min in fuel cell operation at 200 mA/cm² and 1 min electrolysis operation at 50 mA/cm², with 1 min relaxation at open circuit voltage (OCV); go/no-go targets for end of life are 1.5 V (~82% efficiency) for electrolysis and 0.5 V (~41% efficiency) for fuel cell operation.

at the demonstrated performance. The projected delivered electricity would cost less than \$0.18/kWh if technical targets can be achieved at the stack scale. At this cost a reversible alkaline membrane fuel cell would be cost-competitive with compressed air energy storage and pumped hydro energy storage approaches; however, unlike these approaches, a fuel cell system is not subject to geologic restrictions. The model was also used to run sensitivity of the electricity cost to a number of factors. The sensitivity analysis found that competitive economic performance will be dependent on stack life-time greater than four years.

CONCLUSIONS AND UPCOMING ACTIVITIES

The following conclusions can be drawn from work completed to this point:

- 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.
- The novel PGM-free hydrogen electrodes developed on this project shows 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-cm² cells that meet the project cost and performance targets have been demonstrated for 360 cycles above the go/no-go operating conditions.
- 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.

Future work in the remainder of the Phase II project will include:

- Further optimization of hydrogen electrodes for improved performance.
- Characterization of the electrodes before and after cycling to better understand any degradation mechanisms.
- Demonstration of single cell durability over 1,000 cycles.
- Demonstration of a regenerative stack.
- Design of a prototype energy storage system that incorporates the stack.
- Update economic analysis of a reversible AEMFC system for a specific energy storage application.

FY 2017 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 2016 (Honolulu, HI) 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 2016 (San Francisco, CA) 474452.
3. P. Matter, M. Ocampo, C. Holt, M. Beachy, N. Shaheen, M. Chan, and J. Gaydos, *Reversible Fuel Cell System for Energy Storage*, 2017 TechConnect World Innovation Conference, May 17, 2017, Washington, D.C.
4. P. Matter, M. Ocampo, M. Beachy, C. Holt, N. Shaheen, M. Chan, and J. Gaydos, *Regenerative Fuel Cell System*, 2017 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation, June 8, 2017, Washington, DC.

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1. Steward, D., 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>
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