

## V.A.10 Non-Precious Metal Bi-Functional Catalysts

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### Overall Objectives

- Prepare and characterize a matrix of catalysts and membrane electrode assemblies (MEAs) for use in reversible anion exchange membrane (AEM) fuel cell systems
- Demonstrate a bi-functional gas diffusion electrode (GDE) that meets project targets ( $350 \text{ mW/cm}^2$ , <10% degradation over hundreds of cycles)
- Perform economic analysis on reversible AEM fuel cell system following published guidelines for candidate grid load leveling technologies [1]

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### Technical Barriers

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

- (A) Durability: increase the durability/stability of catalysts

- (B) Cost: development of low-cost non-precious group metal (PGM) catalysts for reversible anion-exchange membrane fuel cells (oxygen reduction and oxygen evolution)
- (C) Performance: integrate catalysts with membranes and GDLs into MEAs that operate at high power and efficiency

### Technical Targets

This Phase I small business innovation research (SBIR) project is developing new catalyst materials for reversible alkaline fuel cells. The materials being developed address the following technical requirements for regenerative energy storage applications:

- Hundreds of cycles with less than 10% voltage loss
- Power density competitive with PGM catalysts ( $>350 \text{ mW/cm}^2$  at 0.8 V vs. reversible hydrogen electrode [RHE])

### FY 2015 Accomplishments

By the midpoint of this nine-month Phase I SBIR, the following work related to the technical objectives has been accomplished:

- Used rotating disk electrode (RDE) set-up to test an array of catalysts for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), and durability for cycling between the two reactions. Identified several compositions with excellent stability (<10 mV potential loss after 100 cycles), and with over-potentials competitive with state-of-the-art precious metal catalysts.
- Prepared a matrix of gas diffusion electrodes that incorporated down-selected catalysts. In half-cell testing, demonstrated stable current density exceeding  $450 \text{ mA/cm}^2$  at 0.8 V vs. RHE when operating in pure oxygen at 70°C.
- In half-cell testing, demonstrated GDE with no degradation after 50 cycles between projected ORR and OER voltages at room temperature, and current density of  $40 \text{ mA/cm}^2$ .
- Built an economic model demonstrating that if technical targets can be achieved at the stack scale, then a reversible alkaline membrane fuel cell would be cost-competitive with compressed air energy storage and pumped hydro energy storage approaches. Unlike these low cost energy storage approaches, the fuel cell system would not be subject to geological restrictions. The projected delivered electricity would

cost <\$0.14/kWh using the assumptions developed by Steward et al. [1].



## 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 electro-catalyst for ORR; the cathode side half reaction is shown below for acidic and alkaline electrolytes, respectively:



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 over-potential). 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 AEMs is helping to alleviate system-level problems with alkaline fuel cells, such as pressure balance and carbonate precipitation. Further, recent published results at Los Alamos National Laboratory have shown that alkaline fuel cells could potentially operate at high efficiency with non-platinum catalysts [3]. Alkaline fuel cells are of particular interest for energy storage applications that do not have size constraints, such as grid load leveling. The 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 catalysts because of the high voltages required for OER, the reverse of Reactions 1 or 2 above. Consequently, in existing reversible systems, a separate precious metal electrode is typically used for oxygen evolution, adding to the already high system cost. If a low-cost bi-functional cathode could be developed for reversible fuel cells, it would be a key breakthrough in the commercial viability of such systems [5]. In this project, pH Matter, LLC, is developing and demonstrating a low cost, non-precious

metal, bi-functional cathode for use in reversible alkaline fuel cell systems.

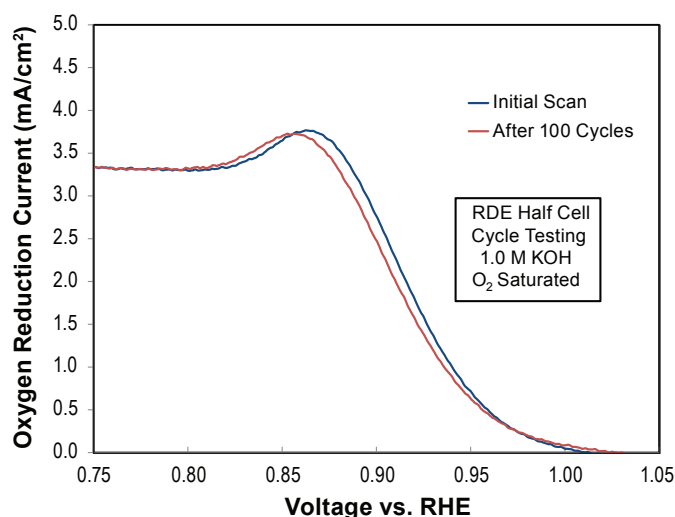
## APPROACH

The overall objective of the proposed project is to develop and demonstrate a bi-functional cathode that meets DOE targets for reversible fuel cells for use in stationary energy storage. In the project, researchers at pH Matter will synthesize several variations of novel catalysts, and a matrix of GDEs based on these materials. The materials and GDEs will be fully characterized and tested under bi-functional conditions to determine what properties are important for performance and stability. This information will be used to prepare a second iteration of more optimized GDEs, which will be incorporated into MEAs. The materials in the MEAs will be subjected to longer-term tests in order to demonstrate their capacities to function as next generation non-precious-metal catalysts for reversible fuel cell cathodes. The project will establish a foundation for future work, where larger reversible fuel cells based on the novel cathodes will be further optimized and demonstrated over longer times and in fuel cell stacks. Additionally, an economic model of the reversible fuel cell system is being built to provide input to design and operating condition decisions, and to verify advantages of the system approach compared to available technologies. The proposed Phase I work is intended to demonstrate the feasibility of the novel catalysts to enable a reversible fuel cell system with economic advantages compared to existing technologies.

## RESULTS

The Phase I project first began with synthesis of a matrix of novel non-precious metal catalysts. The materials were tested for ORR and OER cycling in a conventional thin-film RDE set-up operating in 1.0 M KOH. The test cell was jacketed with an oil bath for temperature control. Samples were subjected to 100 cycles, typically from 1.2 V to 0.75 V and 1.2 V to 1.5 V vs RHE at room temperature, 50°C, and 70°C. Differences were observed in initial activity and stability. The least stable samples degraded more rapidly at 70°C. Figure 1 shows the ORR current for a carbon-based catalyst doped with nitrogen and phosphorus that demonstrated high performance (exceeded the take-off current of commercial 20 wt% platinum on VULCAN<sup>®</sup> carbon), and was stable over 100 cycles. This result is significant with respect to the objectives because it demonstrates catalyst stability when cycled to OER voltages, and intrinsic performance that is competitive with state-of-the-art precious metal catalysts. The particular sample shown in Figure 1 was down-selected for most of the GDE testing.

GDEs were made using a screen-printing method. Various catalysts, catalyst loadings, ionomers and/or binders, ink compositions, and electrode substrates were examined.

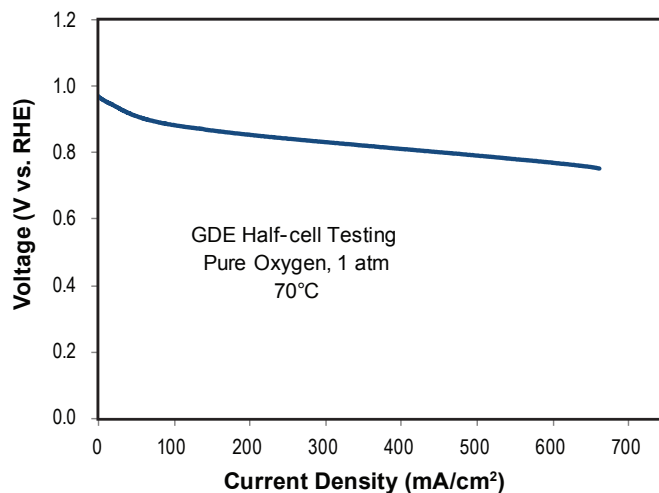


**FIGURE 1.** Oxygen reduction current of non-precious metal catalyst before and after 100 cycles during RDE testing in oxygen saturated 1 M KOH at room temperature from 0.75 V to 1.45 V vs. RHE

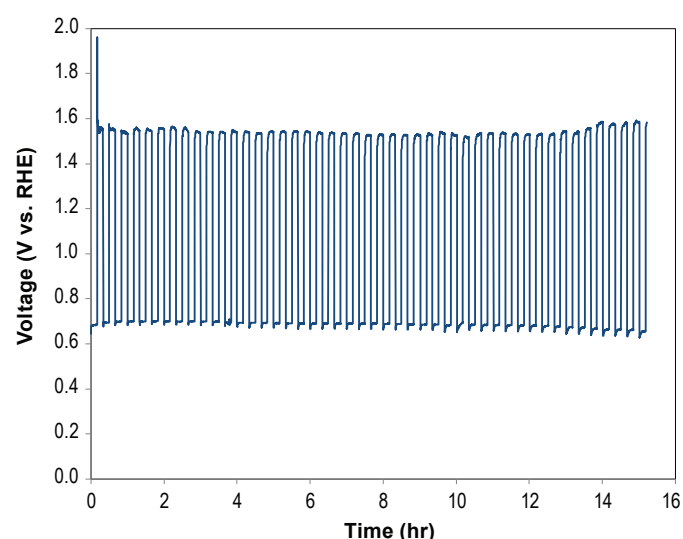
Testing was conducted with both aqueous electrolyte, and AEMs in an in-house constructed stainless steel half-cell set-up. Initial tests focused on ORR performance. For the grid load-leveling application, it is expected that current density will be highest (by a factor of 5–6) during periodic cell discharges (ORR operation) compared to OER operation. Testing for the ORR performance demonstrated that optimal GDEs could produce high current density at 70°C in pure oxygen, as shown in Figure 2. Over 450 mA/cm<sup>2</sup> was obtained at 0.8 V vs RHE. This result is significant, as it demonstrates the novel catalyst can produce sufficient current at low enough over-potential to meet operating targets.

Half-cell GDE testing also examined cycling between ORR and OER conditions. For these tests at room temperature, cycles were conducted at 40 mA/cm<sup>2</sup>, with the direction of the current being reversed every 10 minutes. Some GDE configurations showed excellent stability for ORR and OER during these tests in up to 50 cycles. Figure 3 shows the half-cell cycle test for the standard material using an ionomer and AEM, and operating in pure oxygen (note that four of the cycles were removed due to data collection errors). Work remains in the second half of Phase I to demonstrate stability under conditions that are optimal for ORR performance (i.e., optimized GDE composition and higher temperatures) and in full-cell configurations.

In the first half of the project, an economic model was built to project electricity costs for energy stored with a regenerative alkaline fuel cell system. 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 at Phase I targets. The model demonstrated that if technical targets can be achieved at the stack scale, then a reversible alkaline membrane fuel



**FIGURE 2.** Current-voltage curve obtained in half-cell GDE testing of non-precious metal catalyst at 70°C in pure oxygen; aqueous 5 M KOH fed to the counter electrode chamber



**FIGURE 3.** Cycle testing obtained in half-cell GDE testing at room temperature for non-precious metal catalyst in pure oxygen; aqueous 2 M KOH fed to the counter electrode chamber

cell would be cost-competitive with compressed air energy storage and pumped hydro energy storage approaches. However, unlike these approaches, fuel cell systems would not be subject to geologic restrictions. The projected delivered electricity would cost less than \$0.14/kWh. The model was also used to run sensitivity of the electricity cost to a number of factors, particularly those that have yet to be demonstrated. The sensitivity analysis found that competitive economic performance will be dependent on stack lifetime greater than four years, and achieving roundtrip efficiency higher than 42%.

## CONCLUSIONS AND FUTURE DIRECTIONS

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

- The novel non-precious metal catalysts being developed on this project show performance comparable to precious metal ORR catalysts, and good stability during cycling from ORR to OER voltages.
- The performance of GDEs optimized for ORR performance would enable DOE targets to be achieved for power density and efficiency for AEM fuel cells.
- The cycling stability for 50 cycles has been demonstrated with GDEs that are not optimized for ORR performance.
- The economic modeling suggests that the reversible AEM fuel cell concept would be an excellent energy storage option for grid load leveling if performance targets can be achieved at the stack and system level.

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

- Demonstration of cycling stability at higher ORR performance conditions.
- Demonstration of bi-functional electrode performance in full cell configurations.
- Update of economic model based on demonstrated performance.
- Demonstration of the technology is a prototype energy storage system.

## FY 2015 PUBLICATIONS/PRESENTATIONS

1. Matter, Paul H., Minette Ocampo, Michael Beachy, and Chris Holt, "Non-Precious Metal Bi-Functional Catalysts." *DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation* (2015), June 8, 2015, Arlington, VA.

## REFERENCES

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>
2. James, Brian D., Jennie M. Moton, and Whitney G. Colella, "Mass Production Cost Estimation of Direct H<sub>2</sub> 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](http://energy.gov/sites/prod/files/2014/11/f19/fcto_sa_2013_pemfc_transportation_cost_analysis.pdf)
3. Chung, H.T., 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. Remick, R.J., 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](http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/rev_fc_wkshp_report.pdf)