HydroGEN Seedling: Developing Novel Platinum-Group-Metal-Free Catalysts for Alkaline Hydrogen and Oxygen Evolution Reactions

Sanjeev Mukerjee
Northeastern University
360 Huntington Ave
Boston, MA 02115
Phone: 617-373-2382
Email: s.mukerjee@northeastern.edu

DOE Manager: David Peterson
Phone: 240-562-1747
Email: David.Peterson@ee.doe.gov

Subcontractors:
- University of Delaware, Newark, DE
- Advent North America, Cambridge, MA

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Project End Date: December 31, 2020

Overall Objectives

- Evaluate various transition metal moieties as hydrogen evolution reaction (HER) and/or oxygen evolution reaction (OER) catalysts for anion exchange membrane electrolyzers (AEMEls).
- Optimize the support material for AEMEl OER catalysts.
- Develop, optimize, and characterize novel anion exchange membrane (AEM) and ionomer materials for high-temperature operation.
- Develop methods for AEMEl electrode preparation that supports high current density, efficient gas evolution, and low resistance.
- Elucidate the influence of the electrode/electrolyte interface on the kinetics of the hydrogen evolution and oxygen evolution reactions.

Fiscal Year (FY) 2019 Objectives

- Determine the HER activity of transition metal catalysts. Appropriate catalysts must demonstrate an overpotential of 200 mV at 500 mA/cm^2.
- Establish a requisite baseline overpotential of 125 mV at 500 mA/cm^2 for a supported metal/metal-oxide OER catalyst.
- Introduce a support matrix or cross-linking to the multi-ammonium-cation side-chain-based poly(aryl piperidinium) polymer (PAP-MQN) anion exchange polymer to reduce swelling from water and increase tensile strength. The resulting membranes must achieve an area-specific resistance (ASR) of 0.08 Ωcm^2 and demonstrate a loss of <10% of its ion-exchange capacity after a 1000-hour treatment in 1M KOH at 90°C.
- Initiate collaboration with Energy Materials Network (EMN) partners for subsequent determination of the physical properties of anion exchange materials and theoretical characterization of the electrode/electrolyte interface.

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[1]:

- System Efficiency and Electricity Cost.

Technical Targets

The overall project goal is a cell-level performance of 1.72 V at 1 A/cm^2, which meets the Fuel Call Technology Office (FCTO) efficiency target of ≤$2/kg at an efficiency of 43 kWh/kg. Component performance targets have been established using a porous electrode model to support the overall cell performance target. At the modeled scale of 50,000 kg/day and operating at 1 A/cm^2, the hydrogen cost is $2.15'kg, $1.82/kg, or $1.76/kg, respectively, for 2, 20, or 200 plants. In the low-volume

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

manufacturing case, it is still possible to meet the cost target by operating near 1 A/cm^2, sacrificing some efficiency. The overall project goals described above will be achieved by meeting the component targets outlined in Table 1.

FY 2019 Accomplishments

- NiFeCo/Raney Ni catalyst was demonstrated to lower the OER overpotential by 30 mV at 500 mA/cm^2.
- Achieved an AEM MEA performance of 1.80 V at 1 A/cm^2.
- Crosslinked the multi-cation anion exchange polymer developed in the previous year to enhance the mechanical properties of the membrane.
- Identified novel electrode architecture to enhance the clearing of produced gases to minimize interfacial resistance.
- Leveraged the expertise in molecular dynamics and density functional theory of our EMN collaborators to gain key insights into chemical processes at the electrode surface. The main findings from this collaboration are:
    - Assessed the importance of catalyst layer thickness when operating an AEMEl that uses K_2CO_3 as an electrolyte
    - Established that the presence of carbonate ions has no effect on membrane conductivity
    - Correlated Nernstian voltage loss observed in carbonate fed systems to experimentally obtained data.

Table 1. Technical Targets

Target	Units	End of Project	Budget Period 2
Cell voltage	V	1.72	1.82
Current density	A/cm^2	1	1
Operating temperature	°C	90	90
Membrane ASR	Ω·cm^2	0.08	.12
Membrane OH^- conductivity	S/cm	0.1	.076
Cathode overpotential at design point	mV	150 mV @ 0.5 A/cm^2	200 @ 0.5 A/cm^2
Anode overpotential at design point	mV	100 mV @ 0.5 A/cm^2	125 @ 0.5 A/cm^2

INTRODUCTION

Reducing the materials cost of water electrolyzers, in particular, the platinum metal group (PGM) OER and HER catalysts, is a key component for meeting the DOE's goal of a $2.00/kg levelized cost of hydrogen by 2020. The relatively recent development of AEMs allows for the use of low-cost non-PGM catalysts. In terms of OER, many studies indicate that Ni-Fe mixed oxides provide a greatly increased OER activity in comparison to pure Ni electrodes or other binary mixed oxides [1]. On the HER side, enhanced HER has been reported on Ni/MO_x by Markovic et al. [2] and Gong et al. [3] – both of whom suggested that at adjacent metal/metal-oxide sites, the metal-oxide facilitates the formation of OH_{ads}, thus weakening the H-OH bond in "activated water" and reducing activation energy for the Volmer reaction.

Operating AEMEls at elevated temperatures will increase the reaction kinetics and improve performance. However, the most technologically mature anion exchange polymers cannot be used at operating temperatures >60°C for extended periods of time. Novel AEMs will also be developed in the course of this project that will be thermally stable and incorporate multiple ion-exchange sites.

APPROACH

This project will improve the existing NiFe OER catalyst reported in the previous budget period via the incorporation of cobalt into the alloy. The synthetic route involved a modified impregnation method using aniline to form a mixed-metal oxide as a 2D film on Raney-Ni support. Previous data reported by our research group shows that the presence of cobalt in the catalyst results in the activation of the catalyst at lower potentials relative to NiFe increases its performance [4]. Building off the efficacy of Ni alloys from the previous year, NiMo and NiCu-cup (cupferron (cup)) were selected as candidates for HER catalysts. NiCu-cup is a progression of the HER catalyst used previously by our group, where metal ions are chelated by cupferron

and subsequently reduced via heat treatment. During the heat treatment, the cupferron degrades and forms several layers of graphene around the metal. The theory is that the graphene protects the metal from oxidation at anodic potentials and limits the formation of poisoning hydride species at cathodic potentials.

Effective removal of gases produced during catalysis is an important consideration for water electrolysis systems. Therefore, an electrode structure must have enough porosity yet provide a flat surface for catalyst deposition. Two novel HER electrode architectures were considered: a non-woven carbon veil and a carbon cloth with a microporous layer (MPL) deposited as a thick ink. The former is an incredibly porous material, and the latter preserves the porosity of the carbon cloth as the thick MPL ink does not penetrate the bulk relative to the standard ink.

The multi-cation poly(aryl piperidinium) (PAP) AEM developed during the first budget period allowed for AEMEls capable of relatively high-temperature operation (>60°C) and low operating potentials. However, the addition of a second cation group resulted in increased swelling from water and lower tensile strength, making the material difficult to use. This year, two approaches were considered to address these issues: introduction of a reinforcement matrix, and crosslinking of polymer molecules. A small amount of expanded polytetrafluoroethylene (ePTFE) introduced before membrane casting was used as the reinforcement material. The ionomer was crosslinked by reducing the amount of multi-cation repeat units by 10%, and 1,6-dibromohexane was used to alkylate the piperidinyl nitrogen of two repeat units

RESULTS

Figure 1 shows the polarization curves of three AEMEl electrolysis cells, each with a Pt/C HER electrode and PAP-TP-Me membrane. The OER catalysts are the NiFe/Raney catalyst used to achieve last year's performance goal of an overpotential 150 mV at 500 mA/cm^2, this year's NiFeCo/Raney catalyst, and iridium oxide to serve as a basis for comparison.

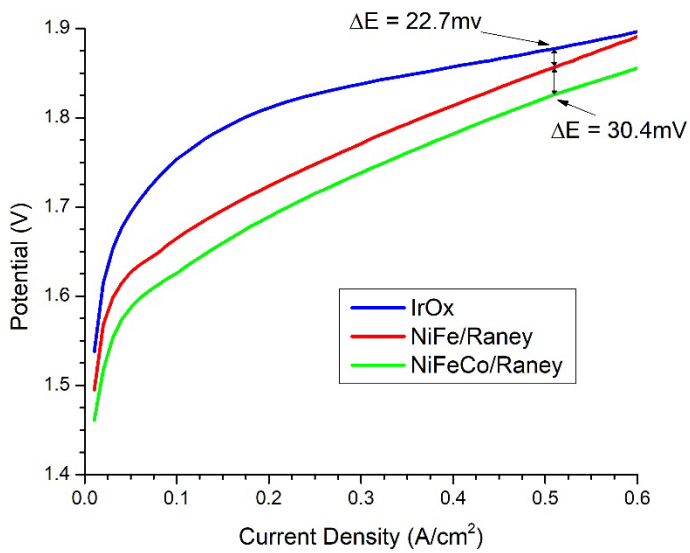

Figure 1: A comparison of the polarization curves of three AEMEls with a Pt/C HER catalyst and three different OER catalysts. A PAP-TP-Me membrane was used, and the cell was operated at 50°C. 1% K_2CO_3 solution was fed to the OER electrode while no electrolyte solution was fed to the HER electrode.

At 500 mA/cm^2, the cell using the NiFeCo catalyst achieved a 30.4 mV lower operating potential than last year's NiFe catalyst. Figure 1 shows that the Go/No-Go OER catalyst performance metric of a 25 mV reduction of overpotential has been exceeded. The HER Go/No-Go performance metric of 200 mV or less overvoltage at 500mA/cm^2 in hydrogen has not yet been achieved. However, preliminary hydrogen pump data shows NiMo/C and NiCu-cup/C operating at a lower overpotential at 500 mA/cm^2 than the catalysts used to

meet last year's HER performance metric. In addition, NiMo/C was used to meet this year's overall AEM MEA Go/No-Go performance metric.

The efficacy of the two electrode architectures was evaluated by measuring the interfacial resistance of the AEMEl cell at increasing current densities using impedance spectroscopy. As the current density increases and more hydrogen is produced, the interfacial resistance will increase as well. Therefore, an improved electrode architecture would display the least increase in interfacial resistance. Figure 2 compares the interfacial resistance as a function of the current density of AEMEls using HER electrodes made using Toray 90 carbon paper, carbon mat, carbon cloth with a standard MPL, a carbon cloth with a "flocked" MPL (i.e., an MPL applied via a thick ink). Flocked carbon cloth showed the least interfacial resistance followed by the carbon cloth with the standard MPL, the Toray 90 carbon paper, and the carbon veil. The flocked carbon cloth showed minimal penetration of the MPL ink by providing a flat surface for catalyst deposition on one side and a porous moiety to release produced gas on the other. Surprisingly, the carbon veil showed the highest interfacial resistance despite being a material that is the thinnest and most porous.

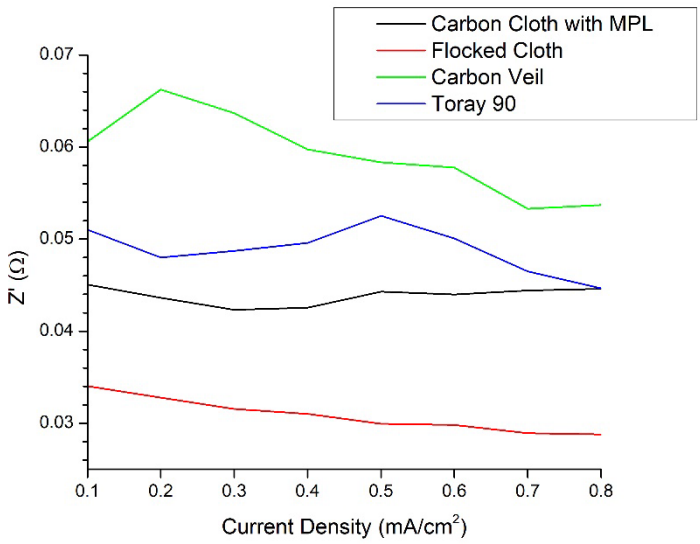

Figure 2: The interfacial resistance of AEMEls using different HER electrode materials as a function of current density. Each cell used a PAP-TP-Me membrane and a NiFe and Pt/C OER and HER electrode, respectively.

In addition to the MQN membrane reinforced with ePTFE (MQN-ePTFE), MQN membranes were prepared with 5% and 10% (referred to as MQN-5C and MQN-10, respectively) of the neutral piperidinyl nitrogens crosslinked. All of the membranes derived from MQN showed a dramatic increase in tensile strength and an equally dramatic decrease in swelling from water (Figure 3, left). Despite favorable mechanical properties, MQN-ePTFE was downselected for further analysis due to poor performance in an AEMEl relative to MQN-5C and MQN-10C. The remaining MQN derivatives were subjected to conductivity and degradation studies. Figure 3 (right) shows the ASR of MQN-5C and MQN-10C at 95% relative humidity as a function of temperature. Both membranes have an ASR of <0.12 Ωcm^2 at all temperatures relevant to normal AEMEl operation. The Go/No-Go performance milestone for the membranes this year is an ASR of <0.12 Ωcm^2 as well as a less than 15% loss of ion-exchange capacity (IEC) after a 1000-hour treatment of the membrane in 90°C 1M KOH. At this time, the 1000-hour treatment is ongoing; however, after a 500-hour treatment at 90°C 1M KOH, MQN-5C and MQN-10C show a 2.45% and 4.57% loss of IEC, respectively.

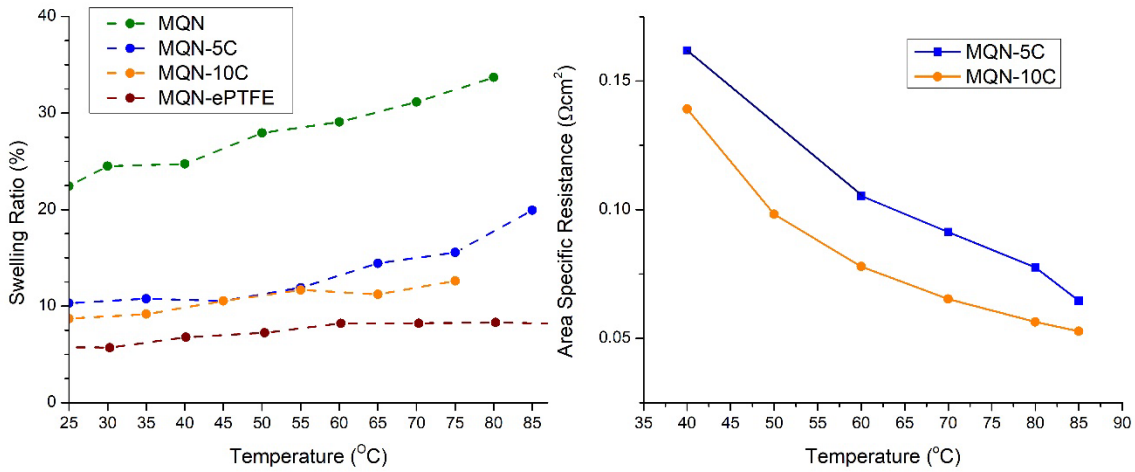

Figure 3: (left) The swelling ratios of MQN membrane derivatives as a function of temperature. (right) The ASRs of MQN-5C and MQN-10C as a function of temperature.

An AEMEl was assembled using NiFeCo/Raney and NiMo/C OER and HER catalysts, respectively. NiMo/C was selected as the HER catalyst because it has been investigated more thoroughly than NiCu-cup/C. MQN-10C was chosen as the membrane because of its superior mechanical properties and its higher IEC. The cell was operated at 90°C, and 3% K_2CO_3 solution was fed to the anode. No electrolyte was fed to the cathode. Figure 4 compares the polarization curves of AEMEls cells obtained last year to those this year. The NiFeCo/NiMo cell achieved a potential of 1.80 V at 1 A/cm^2, 20 mV lower than the Go/No-Go milestone of 1.82 V at the same current density.

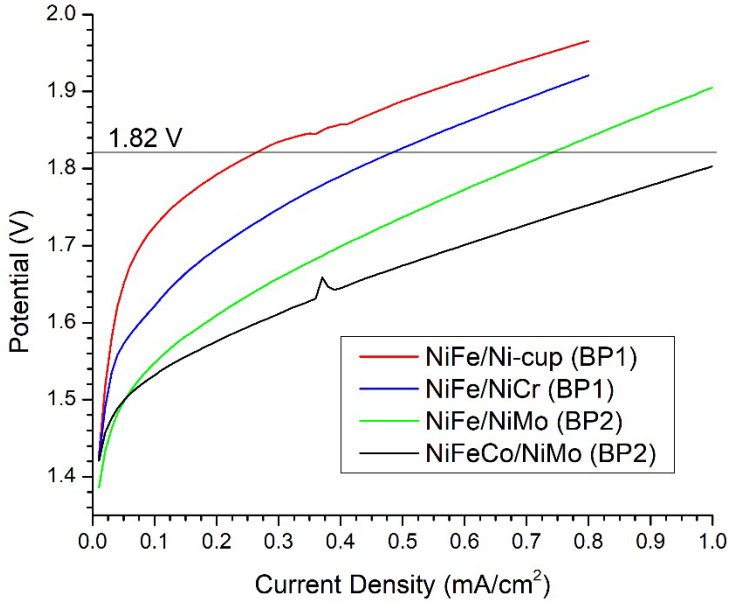

Figure 4: A comparison of the polarization curves from AEMEl cells equipped with different combinations of non-PGM OER and HER catalysts.

The NiFeCo/NiMo cell was held at 90°C and 1 A/cm^2 for 47 hours to demonstrate the stability of the catalyst and membrane. Interestingly, the potential dropped dramatically when the carbonate solution was replaced periodically. Figure 5 shows the potential of the NiFeCo/NiMo cell over a period of 47 hours. Last year, the

best stability test results showed a potential increase of 10 mV/hr. Here, we demonstrate that a net increase in the potential of 1.25 mV/hr can be achieved over intermediate lengths of time when the carbonate solution is periodically replaced. The Go/No-Go performance metric for potential stability is 5 mV/hr or less after 48 hours at 1 A/cm^2. Due to a software error, our test ran for only 47 hours although it is unlikely that a dramatic increase in potential will be observed in the remaining hour, we will attempt to complete the 48-hour test within this budget period.

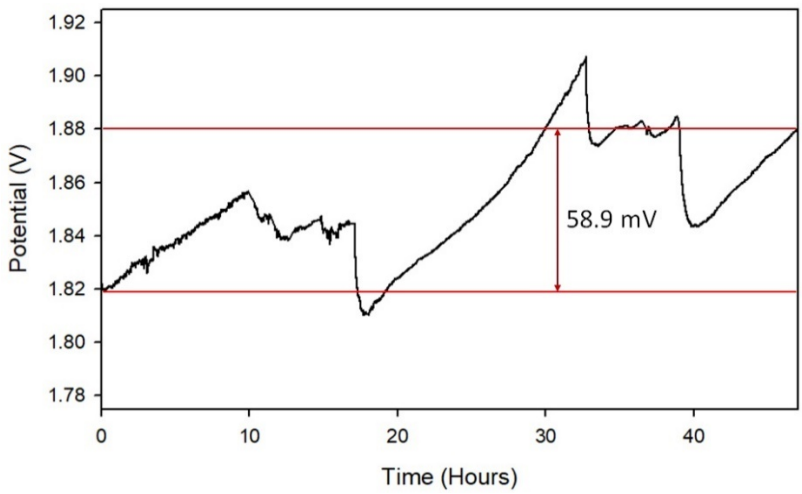

Figure 5: The stability of an AEMEl cell using a NiFeCo OER catalyst, NiMo HER catalyst, and an MQN-10C membrane. The stability test was performed at 90°C by holding the current density at 1 A/cm^2 for 47 hours.

CONCLUSIONS AND UPCOMING ACTIVITIES

This year we have made dramatic improvements the materials developed for anionic electrolysis. Crosslinking the PAP-TP-MQN membrane resulted in a 3x reduction in water swelling and a 3x improvement in tensile strength with a minimal sacrifice to IEC. The catalysts developed this year exceeded the performance of last year's catalysts by 170 mV at 800 mA/cm^2 and exceeded the Go/No-Go performance metric by 20 mV. We also demonstrated a 10x improvement to AEMEl performance stability at intermediate temperatures and high current density. Next year we plan to continue to identify, characterize, and implement high performance catalyst materials while at the same time increasing the IEC of AEMs without sacrificing mechanicals stability. We also intend to investigate the possibility of carbonate consumption at high current densities to understand how to increase potential stability.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. I. Gunasekara, I. Kendrick, S. Mukerjee. "Interfacial Kinetics of HOR/MOR at the AEM/Pt Microelectrode Interface: Investigation of the Influence of CO_3^{2-} on the Reaction Kinetics and the Mass Transport through Membrane." *Journal of The Electrochemical Society.* 166 (2019): F889-F896.
2. E. Liu, J. Li, L. Jiao, H.T.T. Doan, Z. Liu, Z. Zhao, Y. Huang, K.M. Abraham, S. Mukerjee, Q. Jia, "Unifying the Hydrogen Evolution and Oxidation Reactions Kinetics in Base by Identifying the Catalytic Roles of Hydroxyl-Water-Cation Adducts." *Journal of the American Chemical Society*, 141 (2019): 3232-3239.
3. N. Ramaswamy, S. Mukerjee, "Alkaline Anion-Exchange Membrane Fuel Cells: Challenges in Electrocatalysis and Interfacial Charge Transfer." *Chemical Reviews,* (2019) article in press.
4. I. Kendrick, S. Mukerjee, A.Z. Weber, M.R. Gerhardt. "Elucidating the Electrode/Electrolyte Interface of Anionic Exchange Membrane Electrolyzers." In *Meeting Abstracts*, no. 30, pp. 1502-1502. The Electrochemical Society, 2019.

5. S. Mukerjee, P. Kolla, Q. Jia, I. Kendrick, Y. Yan. "Enabling Cost Effective Hydrogen at Low Temperatures." In *Meeting Abstracts*, no. 38, pp. 1766-1766. The Electrochemical Society, 2019.
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