V.A.2 Development of PGM-Free Catalysts for Hydrogen Oxidation Reaction in Alkaline Media

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Subcontractors:
- Los Alamos National Laboratory, Los Alamos, NM
- EWII Fuel Cells LLC, Albuquerque, NM
- Pajarito Powder LLC, Albuquerque, NM

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Project End Date: May 31, 2017

Overall Objectives

- Develop and scale up platinum group metal (PGM)-free electrocatalyst for hydrogen oxidation in alkaline media.
- Develop novel alkaline exchange ionomer.
- Integrate PGM-free catalysts and novel ionomers into high performance alkaline exchange membrane fuel cell.
- Demonstrate peak power density of the membrane electrode assembly (MEA) of 250 mW cm^{-2}.

Fiscal Year (FY) 2017 Objectives

- Screen possible candidates for hydrogen electro-oxidation.
- Scale up best performing material.
- Synthesize ionomers for integration of materials into MEA.
- Achieve performance in MEA of 250 mW cm^{-2} using completely PGM-free anode.

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.

(B) Cost
- (Task 1.B) Reduce/eliminate PGM loading of catalysts
- (Task 1.B) Design and demonstrate small-scale production of newly developed and promising catalysts (minimum viable product)

(C) Performance
- (Task 2.C) Improve electrolyte conductivity, for both proton and alkaline systems, over the entire temperature and humidity operating range
- (Task 3.C) Integrate catalysts with membranes and GDLs (gas diffusion layers) into MEAs

Technical Targets

The goal of this project is an integration of PGM-free anodic electrocatalysts with novel anion exchange ionomer in high performance MEAs. The project is in an early stage of development compared with well-established polymer electrolyte membrane fuel cell technology; however, achieving the goals of the project will allow us to reach DOE fuel cell targets (Table 1).

- Cost: $14/kW net
- Start-up/shutdown durability: >5,000 cycles
- Performance @ 0.8 V: 300 mA/cm^2

FY 2017 Accomplishments

- Two classes of electrocatalysts were found to be most active in hydrogen oxidation reaction (alkaline): NiMo/KetjenBlack and NiCu/KetjenBlack. These catalysts

TABLE 1. Progress towards Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

Characteristic	Units	DOE 2020 Electrocatalyst and MEA Targets	Project Status (5 cm^2 cell, H_2/O_2)
PGM total loading	mg-PGM/cm^2_{geo}	≤0.125	0.1, cathode
PGM-free catalyst activity	A/cm^2 @ 900 $mV_{IR\text{-}free}$	0.044	0.005
MEA performance	mW/cm^2_{geo} @ 675 mV	≥1,000	~10

were synthesized at UNM by a thermal reduction method. Technology was transferred to Pajarito Powder and scaled up to 25 g per batch.

- The Los Alamos team screened several alkaline exchange ionomers with different cationic groups and studied their interaction with catalyst. Ionomer was supplied to UNM and EWII for integration of PGM-free catalysts in the amount of 50 mL.
- EWII Fuel Cells optimized the automatic ink deposition system to manufacture MEAs by catalyst-coated membrane and catalyst-coated substrate methods. Several MEAs with areas of 5 and 25 cm^2 were fabricated and tested.
- The overall goal of the project was achieved by successful accomplishment of all milestones and two go/no-go design points.

INTRODUCTION

Alkaline membrane fuel cells have been drawing attention because they have the potential to convert hydrogen fuel to electricity without using precious metal catalysts in the electrodes. Unlike polymer electrolyte membrane fuel cells that require substantial amounts of expensive Pt catalyst to catalyze the inherently sluggish oxygen reduction reaction, alkaline membrane fuel cells are able to operate using inexpensive and earth-abundant PGM-free oxygen reduction reaction catalysts. One of the most significant reasons for the substitution of anode materials from Pt to other catalysts is much slower hydrogen oxygen reduction kinetics of electrocatalyst under high pH conditions. Gasteiger et al. reported that the hydrogen oxidation reaction (HOR) of platinum electrocatalysts is several orders of magnitude slower in alkaline electrolytes compared to acidic electrolytes [1].

This project has an enabling impact on the DOE alkaline membrane fuel cell portfolio for two major reasons: first, this is the first project on PGM-free catalysts for electro-oxidation of hydrogen in alkaline media; second, catalyst and ionomer developers have teamed up in this project for industrial scale-up and MEA fabrication. This project directly ties to the mission, goals, and targets of DOE's Fuel Cell Technologies Office, both by addressing the capital cost targets for fuel cells and by advancing materials applicable for electro-oxidation of different liquid fuels.

APPROACH

In general, the approach towards successful achievement of project goals can be described through the roles of team members. UNM focuses on the development of several synthetic approaches for synthesis of Ni-based electrocatalysts for hydrogen oxidation in alkaline media: sacrificial support method, thermal reduction, and chemical reduction. These methods will allow preparation of Ni-based materials with controlled properties. Los Alamos National Laboratory's role is the preparation of perfluorinated anion exchange ionomers having selected cationic groups and electrochemical characterization at the catalyst-ionomer interface. The sacrificial support method and other synthetic approaches for Ni-based materials developed at UNM will be transferred to Pajarito Powder, where direct scale-up using identical equipment as UNM and using down-selected formulations will be conducted. Pajarito Powder will scale up the sacrificial support method/thermal reduction approaches and manufacture batches of the best performing formulations developed by UNM. EWII Fuel Cells will integrate the HOR catalyst and anion exchange ionomers to an MEA with a peak power density >250 mW cm^{-2} (2nd Generation) and will develop and manufacture alkaline exchange MEAs based on scalable processes with MEA areas of 5 and 25 cm^2.

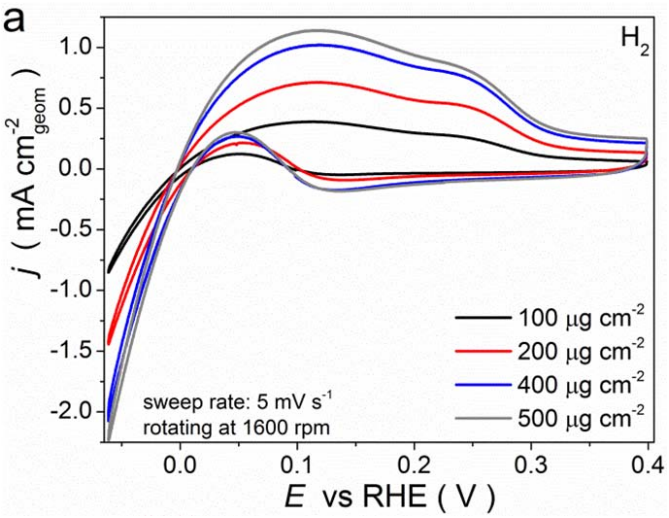
RESULTS

The overall goals of the second phase as well as of the whole project were: (1) down-selection of the most active PGM-free electrocatalysts for HOR in alkaline media, (2) ranking and synthesis of novel anion exchange membrane ionomer, (3) establishment of MEA fabrication protocols using completely PGM-free electrocatalyst, and (4) demonstration of peak power density in MEA of 250 mW cm^{-2}.

More than 15 different Ni-based catalysts were synthesized. The variable parameters were co-catalytic elements to nickel, the ratio between elements, and synthetic parameters (temperature, duration, reducing atmosphere, etc.). Among studied systems, NiMo and NiCu supported on high-surface-area carbons (KetjenBlack [KB] and Denka) were selected as the most promising, and additional experiments were performed using nickel, molybdenum, and copper as a main catalytic matrix. The synthesized materials were characterized by rotating disk electrode, and performance (in alkaline HOR) of both NiMo/KB and NiCu/KB was higher than previously reported in literature. Materials were comprehensively characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Brunauer–Emmett–Teller, and X-ray photoelectron spectroscopy, which allow the further optimization of synthesis and improvement of electrocatalytic activity of Ni-based materials.

After full optimization of synthetic parameters and choice of metal precursors, the UNM team decided to use NiMo/KB and NiCu/KB as the main materials for the anode in a fuel cell. The optimization of synthesis allows us to substantially suppress formation of the NiO phase.

Rotating disk electrode method was used for screening electrocatalytic activity of NiMo/KB and NiCu/KB electrocatalyst. Figure 1 demonstrates electrochemical performance of NiMo/KB material in HOR. It can be clearly seen that the material possesses high activity, reaching 1 mA cm^{-2} with increased loading on the working electrode. Based on the results of the rotating disk electrode HOR experiments, the preparation method of Ni-rich unsupported and supported on carbon catalyst was transferred to scale-up subcontractor Pajarito Powder. The method was successfully adopted and scaled up to the level of 25 g of catalyst per single batch. The performance of scaled material was ±10% by limiting current compared to NiMo/KB and NiCu/KB synthesis at UNM.



RHE – reference hydrogen electrode

FIGURE 1. Rotating disk electrode data of NiMo/KB material in HOR in dependence of catalyst loading on working electrode. Conditions: 0.1 M NaOH, 1,600 revolutions per minute.

Los Alamos National Laboratory synthesized two ionomers: methyl ammonium poly(phenylene) (ATMPP) and ethyl ammonium poly(styrene) (QASOH). Comparison of the HOR activity of PGM-free anodes with Pt/C shows that platinum strongly interacts with anion exchange ionomers, which leads to decrease in activity. NiMo/KB and NiCu/KB are substantially less prone to poisoning by alkaline exchange ionomers (Figure 2). The activity of NiMo/KB electrocatalyst integrated with ATMPP ionomer was similar to that of Pt/C (Figure 2a). Los Alamos National Laboratory optimized synthesis of ionomer on the level of 100 ml, which allows integration of PGM-free electrocatalysts into MEAs by EWII Fuel Cells.

The high performance NiMo/KB and NiCu/KB electrocatalysts were tested in fuel cell tests performed at UNM and EWII Fuel Cells. UNM prepared MEAs by hand spraying, while EWII used proprietary digital printing techniques to manufacture MEAs. The performance of NiMo/KB in the fuel cell test is illustrated in Figure 3. It was found that an increase in temperature from 60°C to 80°C resulted in a substantial increase in peak power density up to 120 mW cm^{-2}. The highest performance in MEA tests with NiMo/KB catalyst was ~175 mW cm^{-2} (Figure 4). A similar trend was observed in the case of NiCu/KB material, where peak power density was demonstrated on the level of 350 mW cm^{-2}. Such results allow our team to successfully

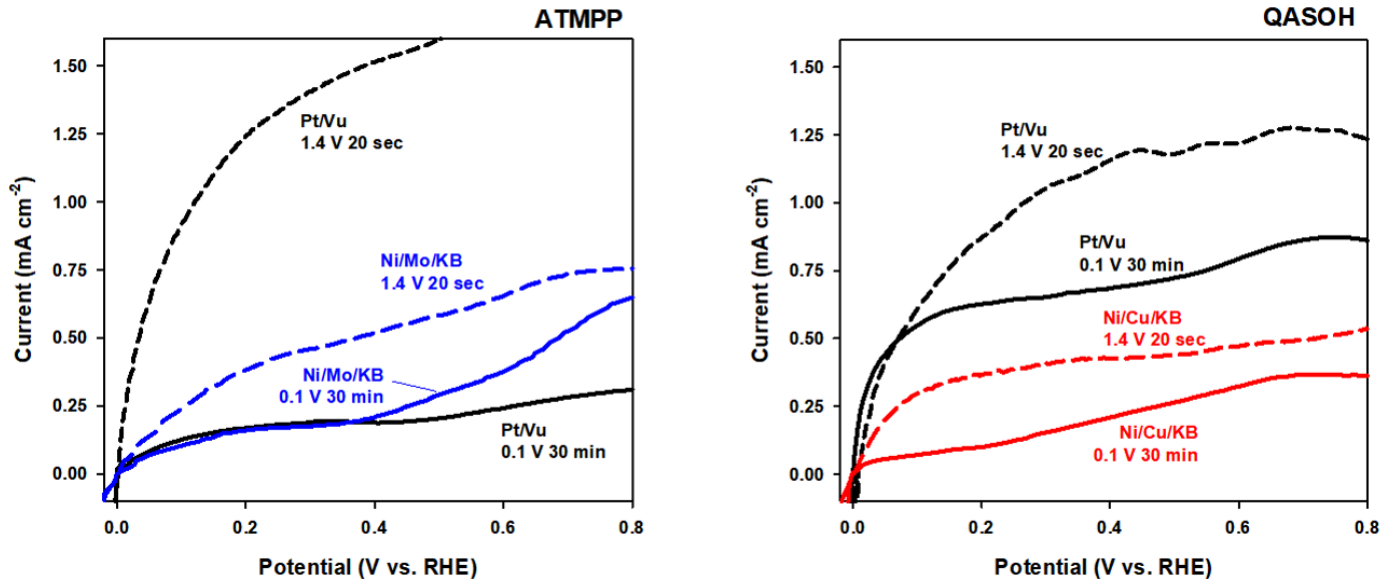


FIGURE 2. Interaction of anion exchange ionomers with Pt/C and PGM-free HOR catalysts (NiMo/KB and NiCu/KB) studied in micro electrode studies. Conditions: electrode with 100 μm diameter at 100% relative humidity, at room temperature and ambient pressure, saturated with H_2. Catalyst loading: 0.1 mg_{metal}/cm^2.

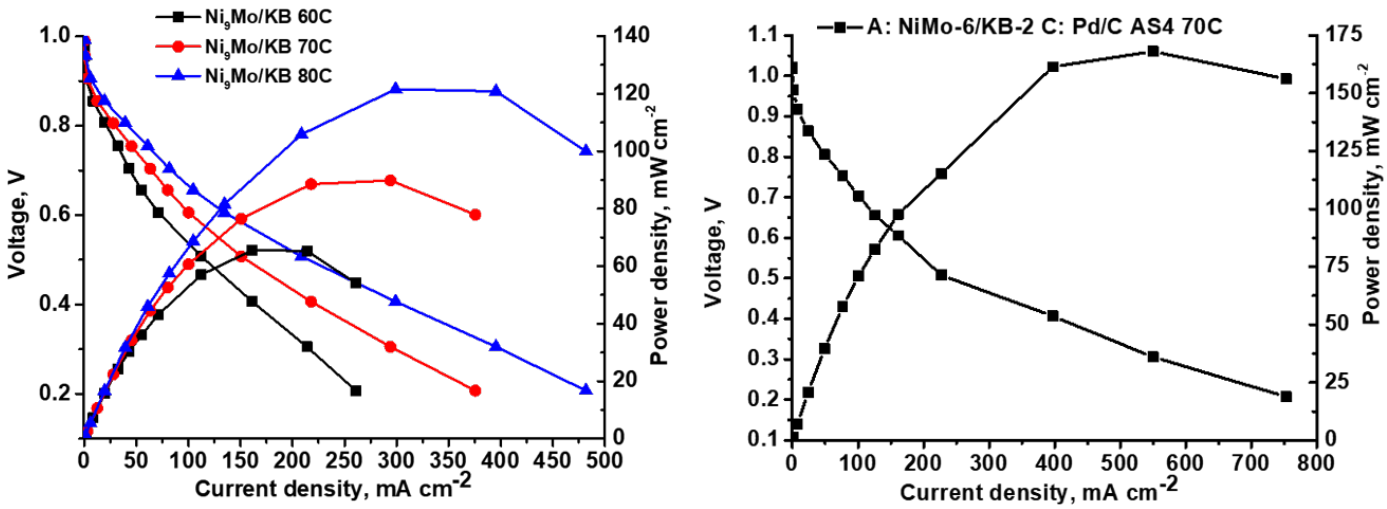


FIGURE 3. Fuel cell performance of MEA prepared with NiMo/KB electrocatalyst. Conditions: NiMo/KB (anode, 4 mg cm^{-2}); Pt/C (cathode, 0.4 mg cm^{-2}); Tokuyama AS4 ionomer (anode and cathode); catalyst coated membrane; T_{cell} = 60, 70, and 80°C; 100% relative humidity; 20 psi_g backpressure.

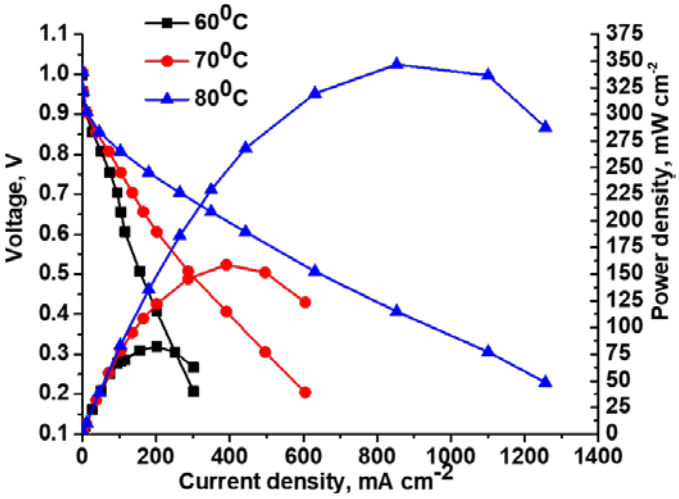


FIGURE 4. Fuel cell performance of MEA prepared with NiCu/KB electrocatalyst. Conditions: NiCu/KB (anode, 4 mg cm^{-2}); Pt/C (cathode, 0.4 mg cm^{-2}); Tokuyama AS4 ionomer (anode and cathode); catalyst coated membrane; T_{cell} = 60, 70, and 80°C; 100% relative humidity; 20 psi_g backpressure.

accomplish the final goal of the project: peak power density of 250 mW cm^{-2}.

CONCLUSIONS AND UPCOMING ACTIVITIES

The conclusions from the second and final year of the project can be summarized as follows:

- Materials were synthesized and all milestones were met: particle size, phase purity, surface area. Two rotating disk electrode protocols were developed. Milestones on performance were met.
- Ionomer developed by Los Alamos National Laboratory was supplied to UNM and EWII for integration of PGM-free catalysts into MEAs.
- EWII Fuel Cells optimized the automatic ink deposition system to manufacture MEAs by catalyst coated membrane and catalyst coated substrate methods. Several MEAs with areas of 5 and 25 cm^2 were fabricated and tested.
- The final goal of project was achieved with MEA performance of 350 mW cm^{-2}.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. A. Serov, Y.S. Kim, M. Odgaard, B. Halevi, P. Atanassov, "Novel Electrocatalyst for Hydrogen Oxidation in Alkaline Media," ECS PRiME (2016).

2. A. Serov, S. Kabir, K. Lemire, K. Artyushkova, A. Roy, M. Odgaard, D. Schlueter, A. Oshchepkov, A. Bonnefont, E. Savinova, D.C. Sabarirajan, P. Mandal, I.V. Zenyuk, P. Atanassov, "NiMo Electrocatalysts for Hydrogen Oxidation Reaction for Alkaline Exchange Membrane Fuel Cells," to be submitted (2017).

3. T. Reshetenko, M. Odgaard, D. Schlueter, A. Serov, "Analysis of alkaline membrane fuel cells performance at different operating conditions using steady-state DC and AC methods," under review (2017).

4. H.T. Chung, U. Martinez, I. Matanovic, Y.S. Kim, "Cation-Hydroxide-Water Coadsorption Inhibits the Alkaline Hydrogen Oxidation Reaction," J. Phys. Chem. 7, 22, 4464–4469 (2016).

5. H.T. Chung, Y.-K. Choe, U. Martinez, J.H. Dumont, A. Mohanty, C. Bae, I. Matanovic, Y.S. Kim, "Effect of Organic Cations on Hydrogen Oxidation Reaction of Carbon Supported Platinum," J. Electrochem. Soc. 163, 14, F1503–F1509 (2016).

REFERENCES

1. W. Sheng, H.A. Gasteiger, Y. Shao-Horn, J. Electrochem. Soc. 157, (2010), B1529–B1536.