Development of PGM-free Catalysts for Hydrogen Oxidation Reaction in Alkaline Media

Alexey Serov (PI June 1, 2015 – March 31, 2017) Email: serov@unm.edu
Plamen Atanassov (PI April 1, 2017 – March 31, 2018) Email: plamen@unm.edu

UNM Center for Micro-Engineered Materials and
Department of Chemical and Biological Engineering,
University of New Mexico
MSC01 1120 1 University of New Mexico
Albuquerque, NM 87131-0001

DOE Managers:

Nancy Garland

Gregory Kleen

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

Project Start Date: June 1st, 2015

Project End Date: March 31st, 2018

Overall Objectives

- Development and scale-up of a PGM-free electrocatalyst for hydrogen oxidation in alkaline media
- Develop a novel alkaline exchange ionomer
- Integrate PGM-free catalysts and novel ionomers into a high-performance Alkaline Exchange Membrane Fuel Cell
- Demonstrate a peak power density of 250 mW cm^{-2} in an MEA

Fiscal Year (FY) 2017 Objectives

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

Technical Barriers

(1.B)	Reduce/eliminate PGM-loading of catalysts
(1.B)	Design and demonstrate small-scale production of newly-developed and promising catalysts (minimum viable product)
(2.C)	Improve electrolyte conductivity, for both proton and alkaline systems, over the entire temperature and humidity operating range
(3.C)	Integrate catalysts with membranes and GDLs into MEAs

Technical Targets

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	≥1000	~10

The goal of this project is to integrate PGM-free anodic electrocatalysts with a novel anion exchange ionomer in a highly performing MEA. The project is in an earlier stage in comparison with well-established PEMFC technology; however, achieving the goals of this project will allow the following DOE fuel cell targets to be reached:

- Cost: $14/kWh net
- Start-up/shutdown durability: >5000 cycles
- Performance @ 0.8 V: 300 mA/cm^2

FY 2017 Accomplishments

- Two classes of electrocatalysts were found to be most active in HOR (alkaline): Ni-Mo/KB and NiCu/KB. These catalysts were synthesized at UNM by a thermal reduction method. The 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 the catalysts. These ionomers were supplied to UNM and EWII for integration with PGM-free catalysts in the amounts of 50 ml.
- EWII Fuel Cells optimized an automatic ink deposition system in order to manufacture MEAs by CCM and CCS methods. Several MEAs with areas of 5 cm^2 and 25 cm^2 were fabricated and tested.
- The overall goal of the project was achieved by successful accomplishment of all milestones and 2 Go-no-Go design points.

Introduction

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

Our proposed project has an enabling impact on the DOE alkaline membrane fuel cell portfolio for two major reasons: first, this is a novel project on PGM-free catalysts for the electro-oxidation of hydrogen in alkaline media; second, this is a project that catalyst and ionomer developers are teaming up on for industrial scale-up and MEA fabrication. Our project directly ties to the FCTO mission, goals and targets, both through addressing the capital cost targets for fuel cells, as well as advancing materials applicable for electro-oxidation of different liquid fuels.

Approach

In general, the approach towards successful achievement of the project goals can be described through the roles of the team members. UNM focuses on the development of several synthetic approaches for synthesis of Ni-based electrocatalysts for hydrogen oxidation in alkaline media that include: Sacrificial Support Method (SSM), thermal reduction, and chemical reduction. These methods will allow for the preparation of Ni-based materials with controlled properties. Pajarito Powder transfers the technology of SSM and other synthetic approaches for Ni-based materials from UNM and manufactures scaled-up batches of the best performing formulations using identical equipment as UNM and using down-selected formulations. Los Alamos National Lab focuses on preparation of perfluorinated anion exchange ionomers having selected cationic groups and electrochemical characterization at the catalyst-ionomer interface. EWII Fuel Cells focuses on the integration of the Hydrogen Oxidation Reaction (HOR) catalyst and Anion Exchange (AE) ionomers to a Membrane Electrode Assembly (MEA) with a peak power density > 250 mW cm^{-2} (2nd Gen.) as well as the development and manufacturing of alkaline exchange MEAs based on scalable processes with MEA areas of 5 cm^2 and 25 cm^2.

Results

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

From the perspective of materials synthesis, more than 15 different Ni-based catalysts were synthesized. The variable parameters were: co-catalytic elements to nickel and the ratio between these elements and synthetic parameters (temperature, duration, reducing atmosphere, etc). Among the studied systems, NiMo and NiCu supported on high surface area carbons (KetjenBlack [KB] and Denka) systems were selected as the most promising. Additional experiments were performed using nickel, molybdenum and copper as a main catalytic matrix. The synthesized materials were characterized by RDE methods. The performances (in alkaline HOR) for both NiMo/KB and NiCu/KB were higher than previously reported in literature. Materials were comprehensively characterized by: XRD, SEM, TEM, BET and XPS methods, which allowed further optimization of the synthesis methods and improvement of the electrocatalytic activity of Ni-based materials.

After full optimization of the synthetic parameters and choice of metal precursors, the UNM team decided to use NiMo/KB and NiCu/KB as main materials for the anode in a fuel cell. The optimization of synthesis allows to substantially suppress formation of the NiO phase. The RDE method was used for screening electrocatalytic activity of NiMo/KB and NiCu/KB electrocatalysts. Figure 1 demonstrates the electrochemical performance of the NiMo/KB material in the Hydrogen Oxidation Reaction. It can be seen that the material possesses high activity reaching 1 mA cm^{-2} with increased loading on the working electrode. Based on the results of these RDE HOR experiments, the preparation method of both unsupported and supported on carbon Ni-rich catalysts were transferred to the subcontractor Pajarito Powder for scale-up. The method was successfully adopted and scaled up to the level of 25 g of catalyst per single batch. The performance of the scaled material was ±10% by limiting current compared to the NiMo/KB and NiCu/KB synthesized at UNM.

LANL 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 show that platinum strongly interacts with AE ionomers, which leads to a decrease in activity. In contrast, NiMo/KB and NiCu/KB were substantially less prone to poisoning by alkaline exchange ionomers (Figure 2). The activity of the NiMo/KB electrocatalyst integrated with the ATMPP ionomer was similar to that of Pt/C (Figure 2). LANL optimized the synthesis of the ionomer on the level of 100 ml which allows integration of PGM-free electrocatalysts into MEAs by EWII Fuel Cells.

The highly performing NiMo/KB and NiCu/KB electrocatalysts were tested in fuel cell tests at UNM and EWII Fuel Cells. UNM prepared MEAs by hand spraying, while EWII used proprietary digital printing techniques to manufacture MEAs. Performance of the NiMo/KB in fuel cell tests are 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 the NiMo/KB catalyst was ~175 mW cm^{-2} (Figure 4). A similar trend was observed in the case of the NiCu/KB material, where the peak power density was demonstrated on the level of 350 mW cm^{-2}. Such results allow our team to successfully accomplish the final goal of the project: achieve a peak power density of 250 mW cm^{-2}.

Figure 1

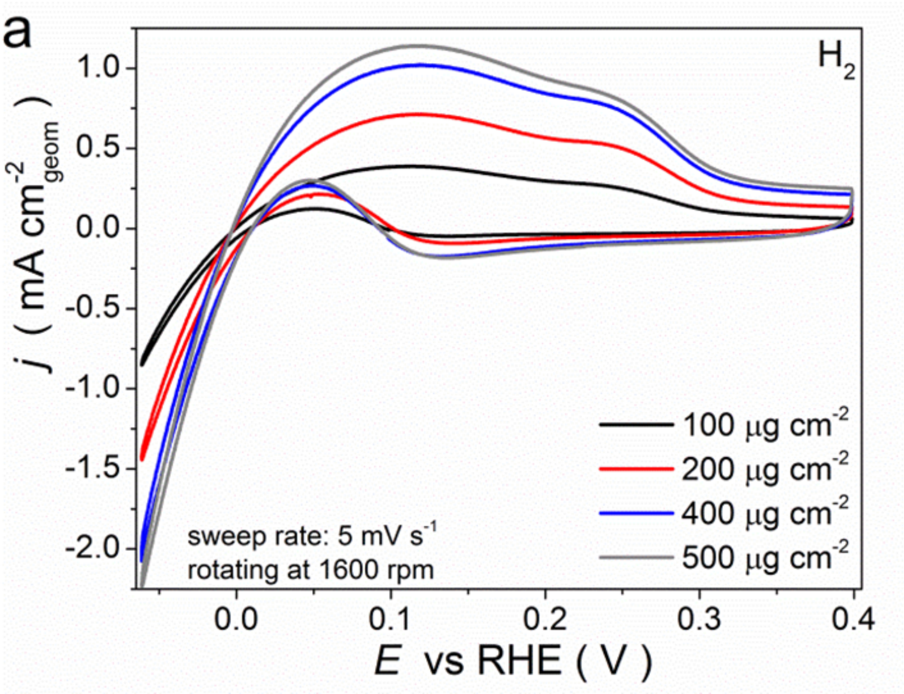


Figure 2

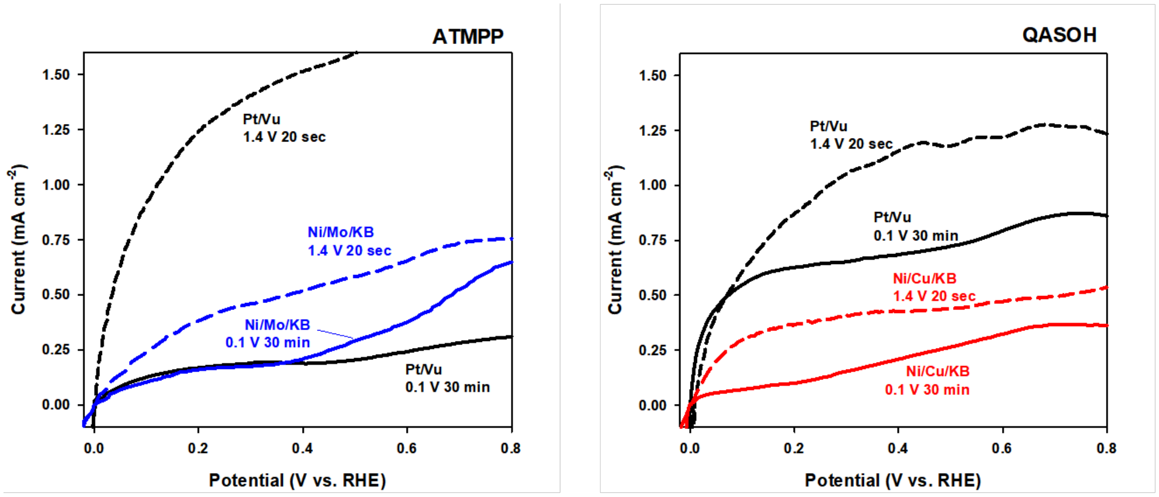


Figure 3

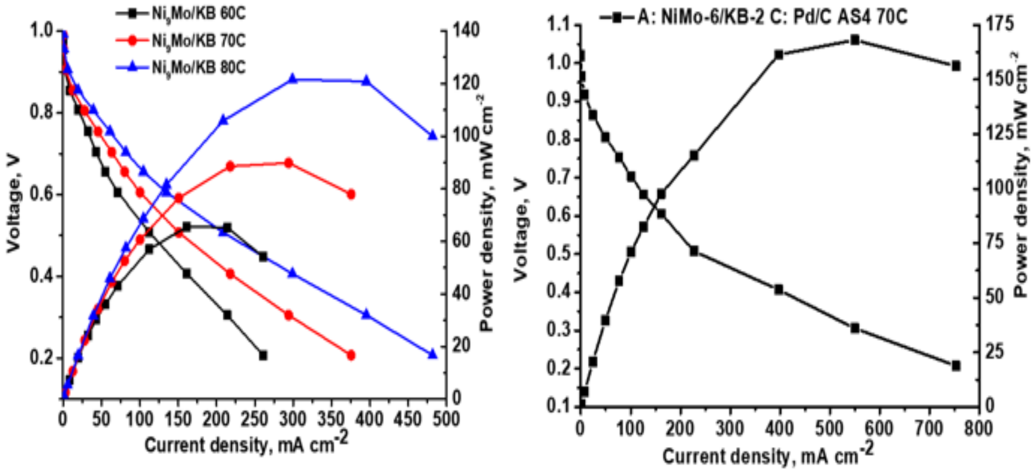
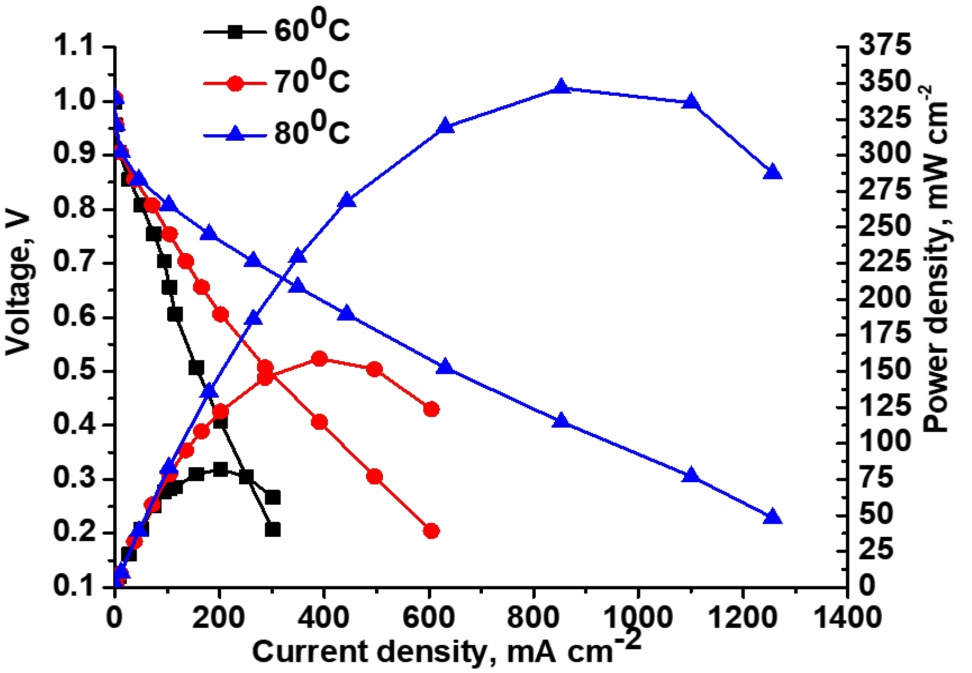


Figure 4



Conclusions and Future Directions

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

- Materials were synthesized and all milestones were met: particle size, phase purity, and surface area. Two RDE protocols were developed. Milestones on performance were met.
- LANL developed an ionomer that was supplied to UNM and EWII for integration of PGM-free catalysts into MEAs.
- EWII Fuel Cells optimized the automatic ink deposition system in order to manufacture MEAs by CCM and CCS methods. Several MEAs with an area of 5 cm^2 and 25 cm^2 were fabricated and tested.
- The final goal of project was achieved with an MEA performance of 350 mW cm^{-2}

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

- Integration of UNM NiMo/KB and NiCu/KB catalysts with a LANL ionomer.
- Manufacturing of state-of-the-art MEAs.
- Development of activation and testing protocols.

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.

Acronyms

AEMFC	Anion Exchange Membrane Fuel Cell
PEMFC	Proton Exchange Membrane Fuel Cell
PGM	Platinum Group Metal
MEA	Membrane Electrode Assembly
SSM	Sacrificial Support Method
ORR	Oxygen Reduction Reaction
HOR	Hydrogen Oxidation Reaction
CCM	Catalyst Coated Membrane
CCS	Catalyst Coated Substrate

RDE	Rotating Disk Electrode
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
BET	Brunauer–Emmett–Teller
TEM	Transmission Electron Microscopy
XPS	X-Ray Photoelectron Spectroscopy

Figure Captions

Figure 1. RDE data of the NiMo/KB material in HOR in dependence of catalyst loading on a working electrode. Conditions: 0.1M NaOH, 1600RPM

Figure 2. Interaction of AE 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% RH, at room temperature and ambient pressure, saturated with H_2. Catalyst Loading: 0.1 mg_{metal}/cm^2

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

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

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