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

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Subcontractors:
- Los Alamos National Laboratory (LANL) Los Alamos, NM
- IRD Fuel Cells LLC, Albuquerque, NM
- Pajarito Powder LLC, Albuquerque, NM

Project Start Date: June 1, 2015
Project End Date: May 31, 2017

Overall Objectives

- Develop and scale up a 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 performed alkaline exchange membrane fuel cell.

Fiscal Year (FY) 2016 Objectives

- Screen possible candidates for hydrogen electro-oxidation.
- Scale up best performing material.
- Down-select ionomers for integration of materials into a membrane electrode assembly (MEA).

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 highly perform MEA. The project is in earlier stage compared with well-established polymer electrolyte membrane fuel cell technology, however achieving the goals of project will allow to reach DOE fuel cell targets (Table 1).

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

FY 2016 Accomplishments

- Most active Ni-Mo-Cu catalysts were synthesized at UNM by sacrificial support method (SSM). Technology was transferred to Pajarito Powder and scaled up to 25 g per batch.

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	$mg\text{-}PGM/cm^2_{geo}$	≤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

- The LANL team screened several alkaline exchange ionomers with different cationic groups and studied their interaction with catalyst. Ionomer was supplied to UNM for integration of PGM-free catalysts.
- IRD Fuel Cells optimized the automatic ink deposition system in order to manufacture MEAs by catalyst coated membrane (CCM) and catalyst coated substrate (CCS) methods. Several MEAs with area of 5 cm^2 and 25 cm^2 were fabricated and tested.

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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. Contrary to proton exchange 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 (HOR) kinetics of electrocatalyst under high pH conditions. Gasteiger et al. reported that the HOR of platinum electrocatalysts is several orders of magnitude slower in alkaline electrolytes 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 the first project on PGM-free catalysts for electro-oxidation of hydrogen in alkaline media; second, this is a project that catalyst and ionomer developers are teamed up for industrial scale-up and MEA fabrications. Our project directly ties to the Fuel Cell Technologies Office 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 project goals can be described through the roles of team members. UNM focuses on the modification of SSM to create Ni-based materials with controlled properties as well as synthesis, characterization, and electrochemical performance of several Ni-based classes of materials. LANL prepares perfluorinated anion exchange ionomers having selected cationic groups and electrochemical characterization at the catalyst-ionomer interface. Pajarito Powder focuses on technology transfer of SSM approach for Ni-based materials and direct scale-up using identical equipment as UNM and using down-selected formulations, scale up of the SSM approach, and manufacture batches of best performing formulations developed by UNM. IRD Fuel Cells focuses on integration of the HOR catalyst and anion exchange ionomers to an MEA with a peak power density >50 mW cm^{-2} (first generation), development and manufacture of alkaline exchange MEAs based on scalable processes, and manufacture and proof of concept of MEAs based on the scaled up catalyst and ionomer (second generation).

RESULTS

The overall goals of first phase of the project were (1) down-selection of most active PGM-free electrocatalysts for HOR in alkaline media, (2) ranking and synthesis of novel anion exchange membrane ionomer, and (3) establishing of the MEA fabrication protocols.

From the point of materials synthesis more than 45 different Ni-based catalysts were synthesized, the variable parameters were co-catalytic elements to nickel, ratio between elements, and SSM parameters (temperature, duration, atmosphere, etc.). Among the studied systems, the Ni-Mo system was selected as most promising, and additional experiments were performed using nickel and molybdenum as a main catalytic matrix. An influence of the addition of a third element was studied by rotating disk electrode (RDE) method. It was shown that Ni-Mo-Re, Ni-Mo-Cu, and Ni-Mo-Co catalysts were most active. Taking into account that rhenium, even though not PGM, has a high price, the continuation of experiments was conducted with inexpensive Ni-Mo-Cu and Ni-Mo-Co systems.

After full optimization of SSM parameters and choice of metal precursors, the UNM team decided to use a Ni-Mo-Cu as the main material for the anode in the fuel cell. The main problem of ternary system was a phase separation of Ni and Mo as well as substantial formation of oxides. Oxides are not conductive and substantially decrease the overall performance. Further, this issue was solved via modification of SSM and addition of carbon support. As can be seen on Figure 1, phase pure $Ni_{87}Mo_{13}$/KB was prepared.

In order to obtain reliable and reproducible RDE data, the UNM team developed two methods: (a) based on ink drop-cast and (b) using a pressed gas diffusion electrode. Both methods allow the team to achieve performance milestones (Figure 2). Based on the results of RDE HOR experiments, the preparation method of Ni-rich unsupported and supported on carbon catalysts 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 Ni-Mo-Cu synthesis at UNM. Using most active materials, the UNM team could achieve the current density at low potential (0.01 V) with the value of 0.095 mA cm^{-2}, which is higher than the go/no-go design point of 0.085 mA cm^{-2} (Figure 3).

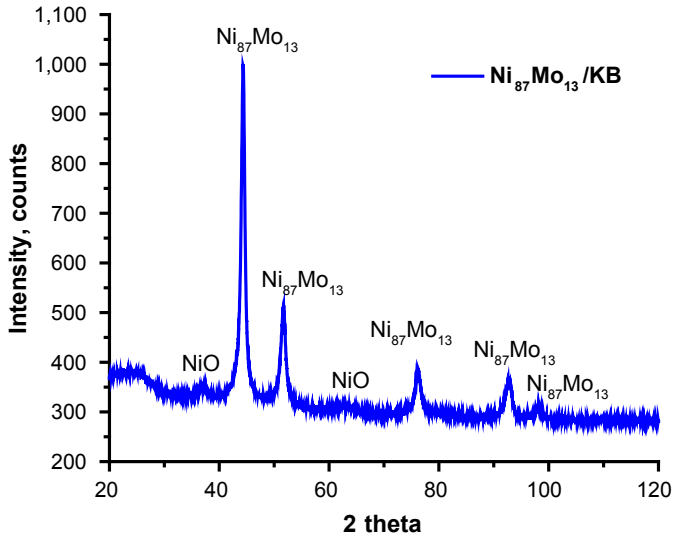
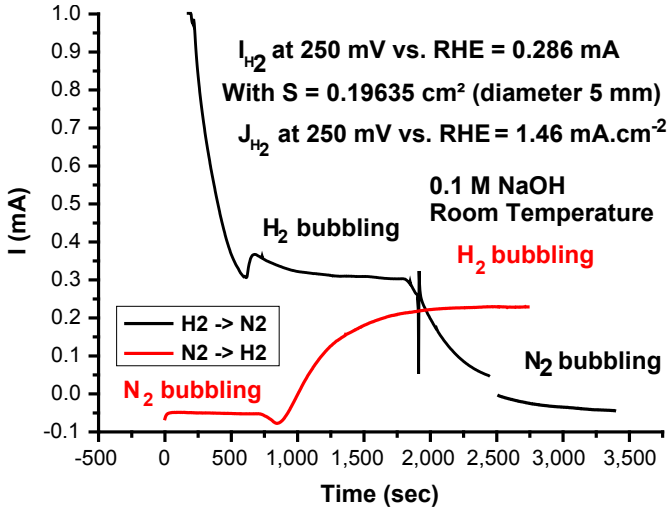


FIGURE 1. X-ray diffraction diffractogram of NiMo/KB electrocatalyst



RHE – Reference hydrogen electrode; RPM – revolutions per minute

FIGURE 2. RDE data in NiMoCu materials in HOR. Conditions: 0.1 M NaOH, 1,600 RPM.

In the preparation to Phase II and namely integration of Ni-Mo catalyst with LANL ionomer into MEA, IRD Fuel Cells performed optimization of automatic ink deposition. The initial experiments were started with commercial Pt/C and ionomers from Tokuyama and FumaTech. IRD Fuel Cell successfully deposited catalysts on carbon paper (CCS) and on membrane (CCM). The results of MEA tests using two different ionomers and platinum catalysts are shown on Figure 4.

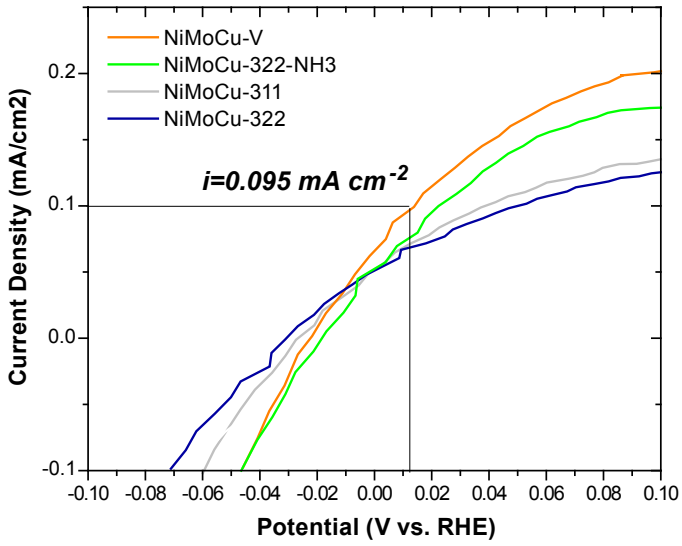


FIGURE 3. RDE data for best performing NiMoCu materials in HOR. Conditions: 0.1 M NaOH, 1,600 RPM.

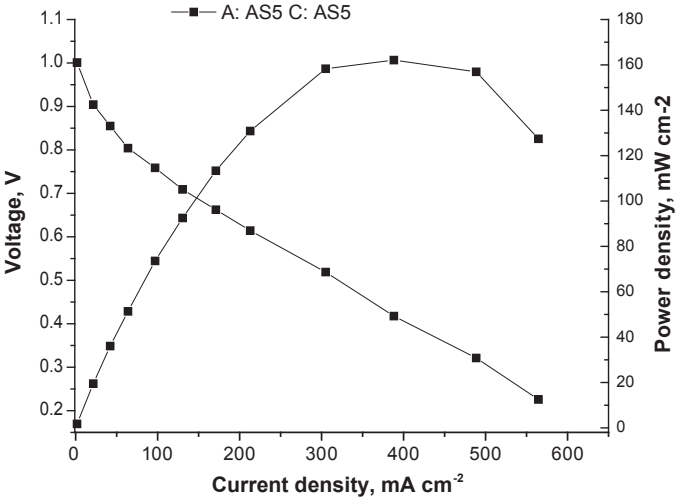


FIGURE 4. Fuel cell performance of MEA prepared by IRD Fuel Cells. Conditions: Pt/C (anode and cathode, 0.4 mg cm^{-2}), Tokuyama AS5 ionomer (anode and cathode), CCS, T_{cell} = 60°C, 100 relative humidity, 20 psi_g back pressure.

CONCLUSIONS AND FUTURE DIRECTIONS

The conclusions from the first year of the project can be summarized as:

- Materials were synthesized, and all milestones were met: particle size, phase purity, surface area. Two RDE protocols were developed. Milestones on performance were met.
- LANL developed ionomer was supplied to UNM for integration of PGM-free catalysts.

- IRD Fuel Cells optimized the automatic ink deposition system in order to manufacture MEAs by CCM and CCS methods. Several MEAs with area of 5 cm^2 and 25 cm^2 were fabricated and tested.
- First go/no-go design point was successfully passed.

The conclusions from the first year of the project can be summarized as:

- Integration of Ni-Mo catalysts with LANL ionomer.
- Manufacturing MEAs.
- Development of activation and testing protocols.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. A. Serov, Y. S. Kim, M. Odgaard, B. Halevi, P. Atanassov "Electrocatalysts for H_2/Air(O_2) Anion Exchange Membrane Fuel Cells: Building a New non-PGM Materials Set", PACIFICHEM (2015).

REFERENCES

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