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

2015 DOE Hydrogen and Fuel Cell Program Review

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Project ID# FC130

Overview Slide

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- **Timeline**:
  - Start date: 4/15/2015
  - End date: 4/31/2017
- **Budget Data**:
- Total Project Value: $ 1,000,000 (Federal), $ 250,000 (cost share); Total $ 1,250,000
- Cost Share Percentage: 20%
- Total DOE Funds Spent*: $

*Negotiation period

- **Barriers/Targets (DOE Technical Plan 2020):**
  - Electrical and overall CHP efficiency: >45% and 90%, respectively
  - Equipment cost (5kW system): $\$1,500/kW_{avg}$
  - Degradation with cycling: 0.3% per 1000h
  - Operating lifetime: 60,000h
  - System availability: 99%
- **Partners**
  - *Univ. of New Mexico*, Albuquerque: Dr. Alexey Serov - PI
  - *Los Alamos National Laboratory, Los Alamos*: Dr. Yu Seung Kim
  - *IRD Fuel Cells LLC, Albuquerque*: Ms. Madeleine Odgaard
  - *Pajarito Powders*, Albuquerque, Dr. B. Halevi

Relevance

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- **Objectives:** This project will develop new classes of non-PGM electrocatalysts for HOR in alkaline media; the catalysts will be scaled up to 50 g batches; a new type of ionomer for AEMFC will be synthesized and full integration of non-PGM catalyst with ionomer into the MEA will be performed.

- **Relevance to DOE Mission:** This will enable integration of the non-PGM anode materials into the optimized MEA structure. It can be expected that performance of non-PGM based AEMFC will be significantly improved ca. peak power density up to 550 mW/cm^2.

- **Impact**
  - Lower MEA cost to less than or equal to $ 3/KW
  - Independence from Pt and other PGMs - global availability
  - Higher kinetics of HOR in alkaline media

Approach

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- **Overall technical approach:**
  - **Comprehensive materials development strategy encompassing:**
    - Novel new catalysts for Hydrogen Oxidation Reaction in alkaline media
      - High Performance Catalysts
      - Tailored Catalysts for Understanding Structure Property Relationships
    - Controlling Metal/Alloys support interactions
      - Efficient mass transport of charged and solute species
    - Ensuring Stability via careful control of reaction center's electronic structure
  - **Synthesis of novel alkaline exchange ionomers**
    - Development of several synthetic approaches (copolymerization, chloromethylation, etc.)
  - **Scaling Up the catalyst synthesis**
    - Technology transfer from small lab-scale batches to 50 g batch level
    - Inter-batch reproducibility on the level of 10% by activity
  - **Integration of scaled-up catalysts and ionomers into AEMFC MEA**
    - Influence of additives onto MEA performance
    - Design of catalyst layers by deposition method
- **Program Technical Barriers and Approach to Overcome them:**
  - Meeting and Exceeding Program Activity Target of HOR current density at 0.01 V: > 0.085 mA/cm^2.
    - (a) Development of new classes of materials
    - (b) Scaling-up the technology
    - (c) Understanding mechanism of HOR electrocatalysis
    - (d) Integration of electrode materials into high-performance MEAs

Approach: Milestones and Go/No-Go

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- **Milestones (2015)**
  - Catalysts Development by Sacrificial Support Method (SSM):
    - Surface area of catalysts >20 $m^2\ g^{-1}$, particle size <70 nm (characterization by: XRD, SEM, BET, TEM and XPS) **FY15M1-3**
    - Phase pure Ni and Ni_3Mo alloy with no significant (<5wt%) oxides formation **FY15M4-6**
    - Phase pure alloys, oxides, carbides and phosphides. Observing electrochemical response of catalytic system to the introduction of hydrogen into the cell **FY15M3-24**
  - Ionomer Development:
    - Rank cationic functional groups in terms of HOR activities and locate cationic adsorption site **FY15M1-8**
    - Preparation of perfluorinated ionomer dispersions **FY15M6-18**
  - Tech Transfer and Scale-up
    - Match base catalyst to within 10% of UNM catalyst **FY15M1-12**
  - MEA Design
    - Manufacturing concepts defined and verified for the 1. Generation MEAs **FY15M6-12**
- **Go/No Go Decisions (2016)**
  - HOR current density at 0.01 V: > 0.085 mA/cm^2 (RDE Data)

Accomplishments and Progress

Program Management and Implementation

Non-PGM HOR Catalysts Design
Thrust Area 1: Tasks 1 - 2

Optimization of SSM (Task 1)
UNM

Synthesis of different types of Ni-base materials (Task 2)
UNM

Ionomer development for Ni-M Catalysts
Thrust Area 3
LANL

Technology Transfer of SSM for Nickel-Based Materials
Thrust Area 4
PPC

MEA Design
Thrust Area 5
IRD Fuel Cells

Accomplishments and Progress

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Thrust Area 1: Tasks 1-2 (UNM)

- **Task 1: SSM Adoption for Synthesis of Nickel-Based Materials (M1-M6)**
  - **Subtask 1.1** Optimization of Sacrificial Support Type (M1-M3)
    - Commercial silica vs UNM made
    - Ratio between silica and precursors
  - **Subtask 1.2** Optimization of Heat Treatment parameters (M4-M6)
    - Effect of H_2 atmosphere on Ni materials will be evaluated
  - **Milestone 1**
    - Catalyst material with surface area >20 m^2 g^{-1}, particle size <70 nm

- **Task 2: Synthesis and Characterization of Different Classes of Ni-based Catalysts (M3-M24)**
    - Ni-M alloys (where M=Zn, Co, Fe, Pb, Cu, etc.)
    - Ratio of Ni:M 50:50 and 75:25at% according to corresponding phase diagram
    - The mixed oxides will be prepared by SSM with variation of ratio of NiO to second oxide as 50:50 and 75:25at%.
    - Carbides will be prepared by carburization of Ni-precursors with mild sources of carbon such as melamine and urea.
    - The phosphides will be made by SSM with phosphates as a source of phosphorus.
    - All materials will be characterized by XRD, SEM, TEM, XPS and electrochemical activity in H_2 oxidation will be studied by RDE.
  - **Milestone 2**
    - Phase pure alloys, oxides, carbides and phosphides. Clear electrochemical response to introduction of hydrogen into the cell.

Accomplishments and Progress

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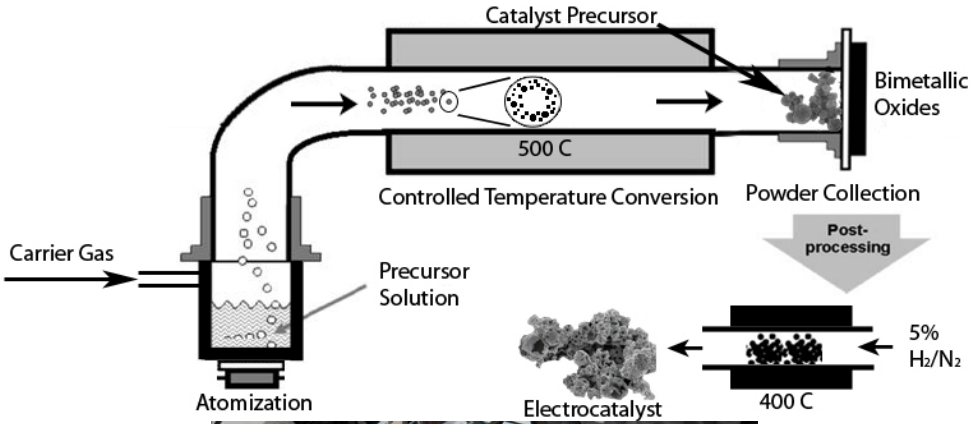
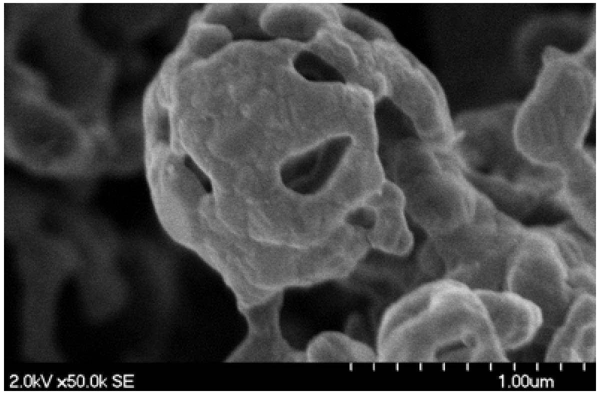
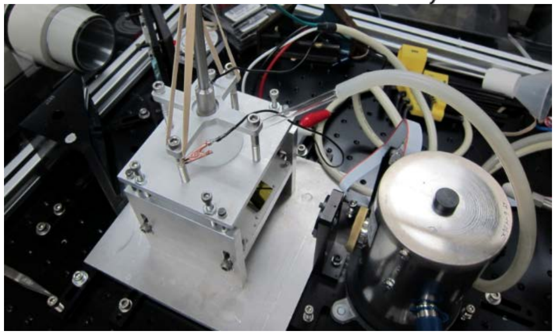
Thrust Area 1: Task 1 Preliminary Data







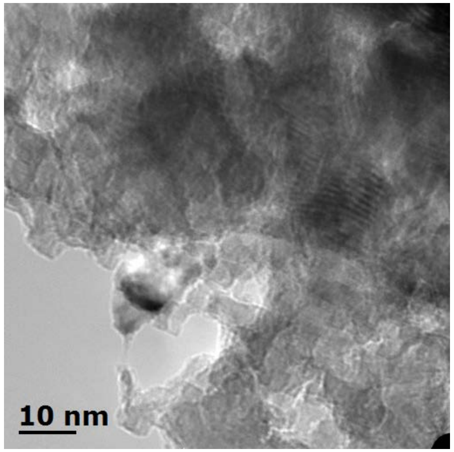
	60wt% $Ni_{87}Zn_{13}$, BM	$Ni_{87}Zn_{13}$,SP
OCV	0.832	0.826
mW cm^{-2}	354	258
NH_3 (ppm)	15	25

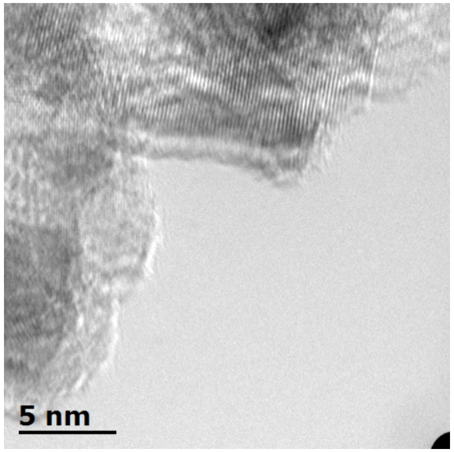
A. Serov, M. Padilla, A. J. Roy, P. Atanassov, T. Sakamoto, K. Asazawa, H. Tanaka "Anode Catalysts for Direct Hydrazine Fuel Cells: From Laboratory Test to an Electric Vehicle", Angewandte Chemie Int. Ed. 126 (39) (2014), 10419–10715.

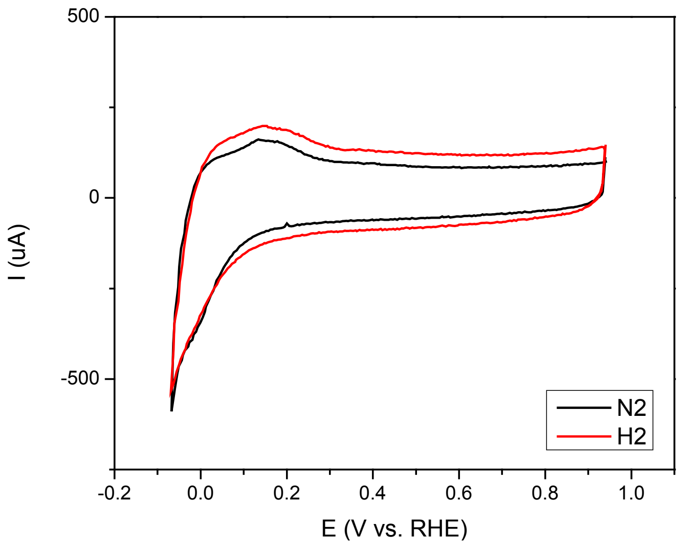
NiZn and NiZn/KB were synthesized for electrooxidation of hydrazine hydrate

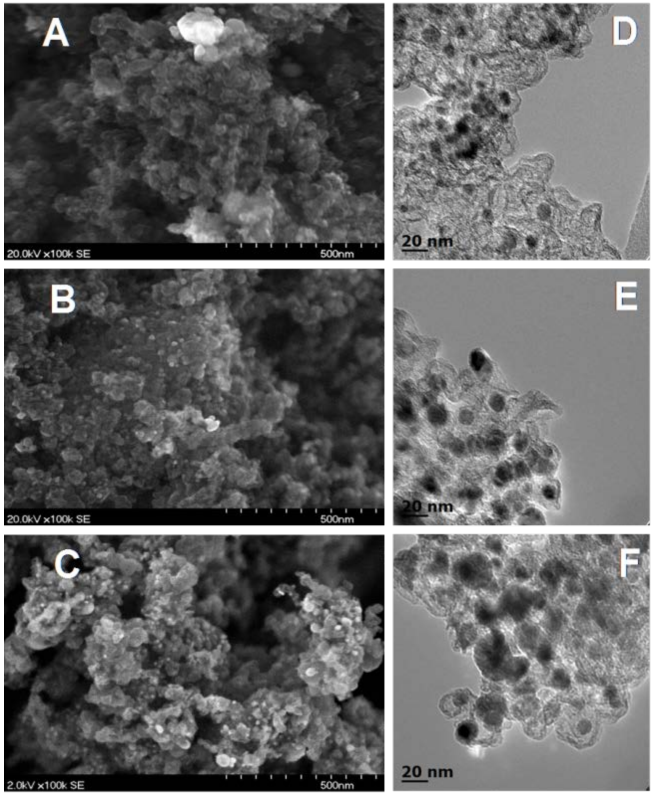
Accomplishments and Progress

Thrust Area 1: Task 1 Preliminary Data









Preliminary Ni-Pb system can be promising candidate.

Accomplishments and Progress

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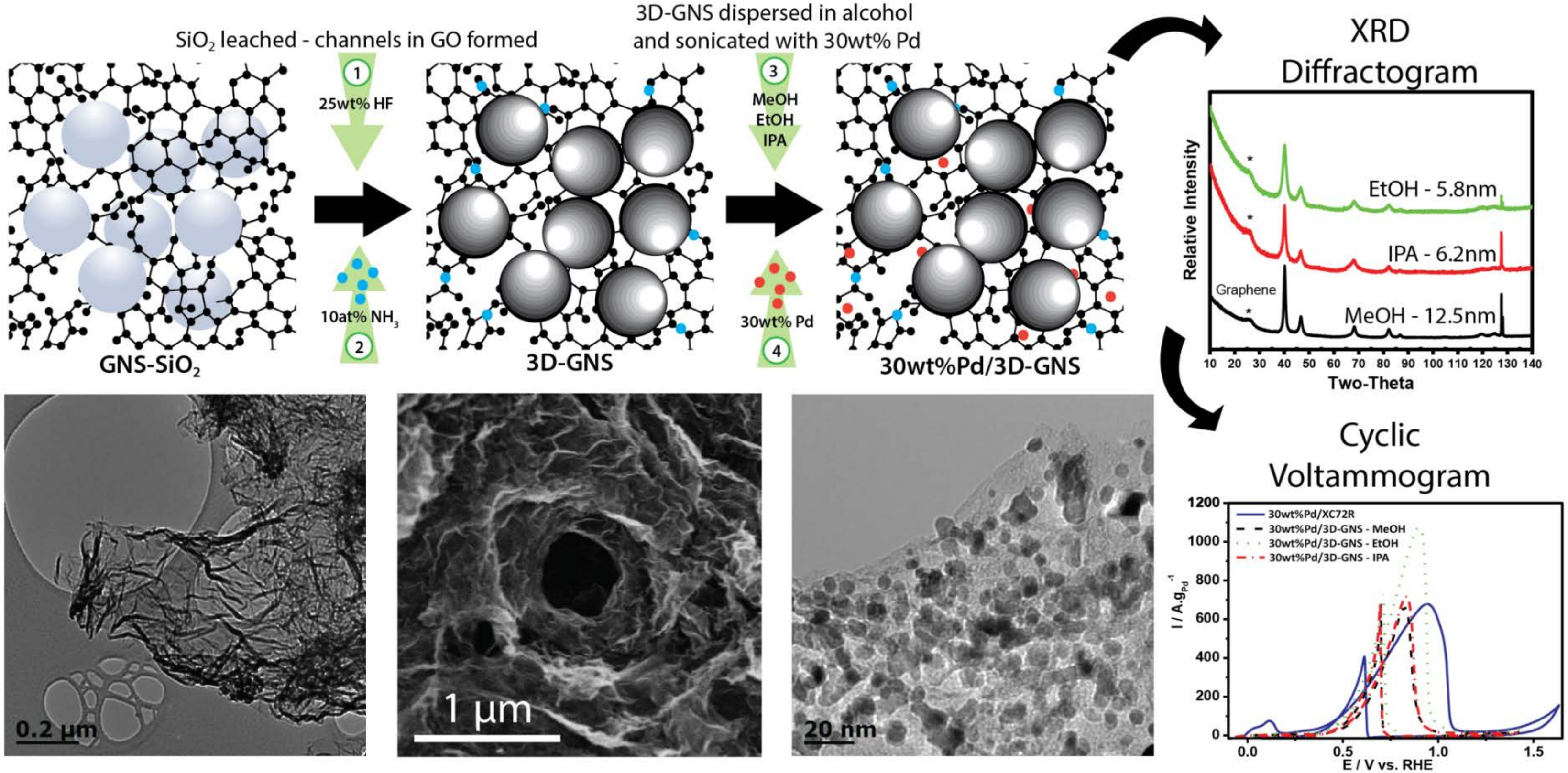
Thrust Area 1: Task 1 Preliminary Data



Novel types of conductive carbon additives were developed.

Accomplishments and Progress

Thrust Area 2: Task 3 (LANL)

- **Task 3: Ionomer Development for Ni-M Catalysts (M1-M24)**
  - **Subtask 3.1** Screening cationic functional groups using RDE experiments and DFT modeling study (M1-M8)
    - Best cationic functional groups for Ni-M catalysts will be selected by RDE experiment
    - Periodic DFT calculations will provide the adsorption of hydrogen and different organic cations
  - **Milestone 3.1.1.**
    - <u>Rank cationic functional groups in terms of HOR activities for Ni-based catalysts and suggest three best cationic functional group for ionomer synthesis.</u>
  - **Subtask 3.2** Synthesis and characterization of perfluorinated ionomer having selected cationic functional groups (M6-M18)
    - Perfluorinated ionomers will be prepared by functionalization of carboxylic Nafion® precursor and subsequent polycondensation reactions.
    - Microwave synthesis will be used
  - **Milestone 3.2.1.**
    - <u>Preparation of perfluorinated ionomer dispersion</u>
    - <u>Amount: 20 ml (solid content: 2.5 wt.%) solutions of three different ionomers</u>
    - <u>Conductivity: > 20 mS/cm at 80ºC</u>
    - <u>Water uptake: < 30 %</u>

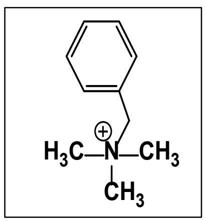
Accomplishments and Progress

Thrust Area 2: Task 3 Preliminary Data

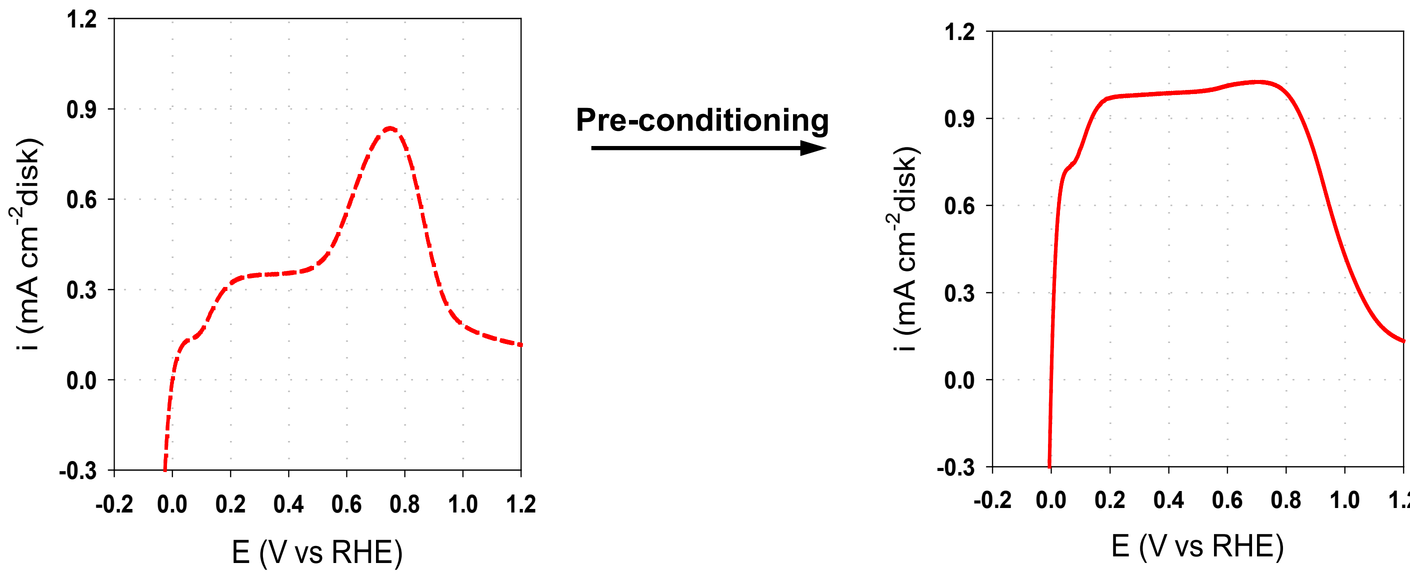
HOR of Pt in 0.1 M BTMAOH

HOR voltammograms were obtained:

1. 30 min after immersion of the microelectrode
2. After pre-conditioning: at 1.4 V for 10 sec



0.1 M BTMAOH
(pH 12.6)



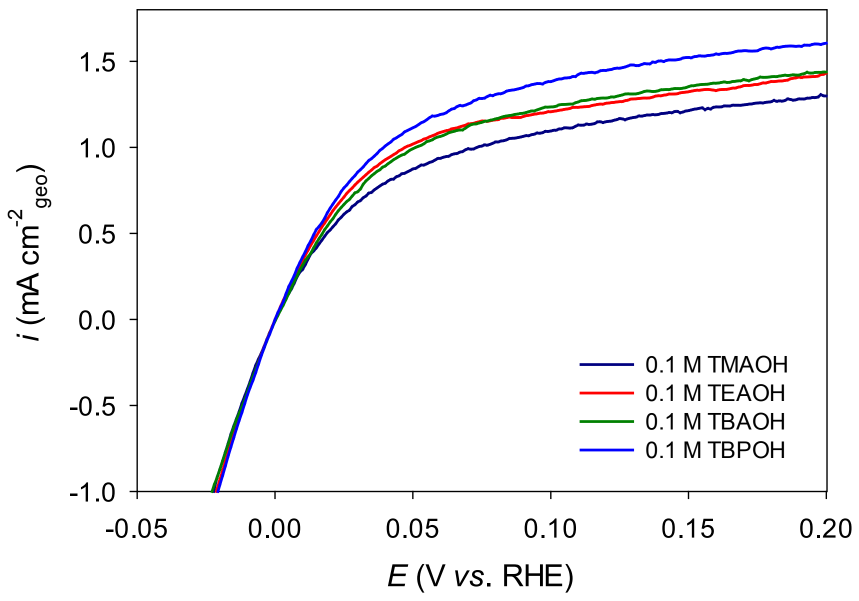
Measured HOR Activities of Pt in 0.1 M BTMAOH Solution.

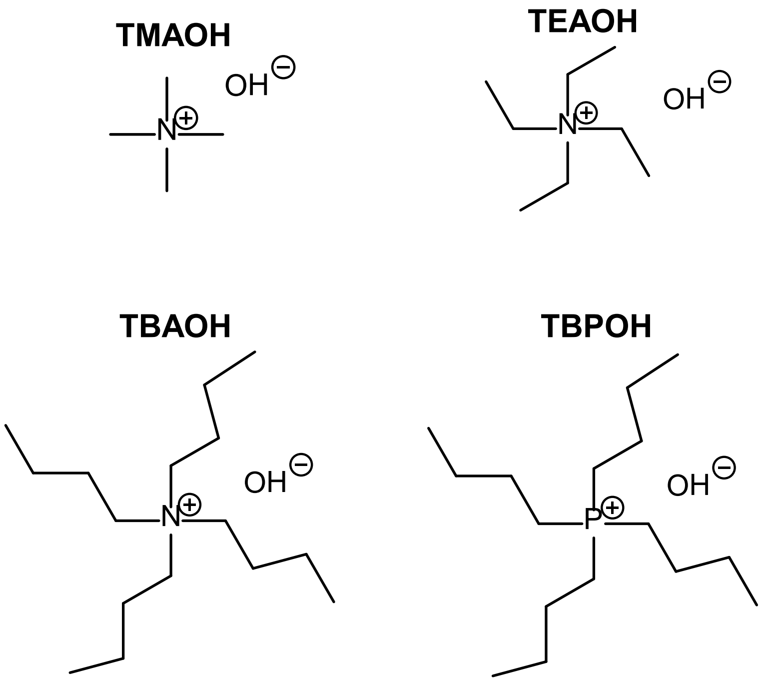
Accomplishments and Progress

Los Alamos NATIONAL LABORATORY

Thrust Area 2: Task 3 Preliminary Data

Effect of Organic Cation on HOR





Ranked the HOR Activities of Pt in Four Organic Cation Solutions

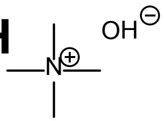
Accomplishments and Progress

Los Alamos NATIONAL LABORATORY

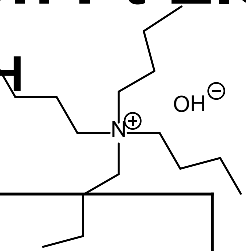
Thrust Area 2: Task 3 Preliminary Data

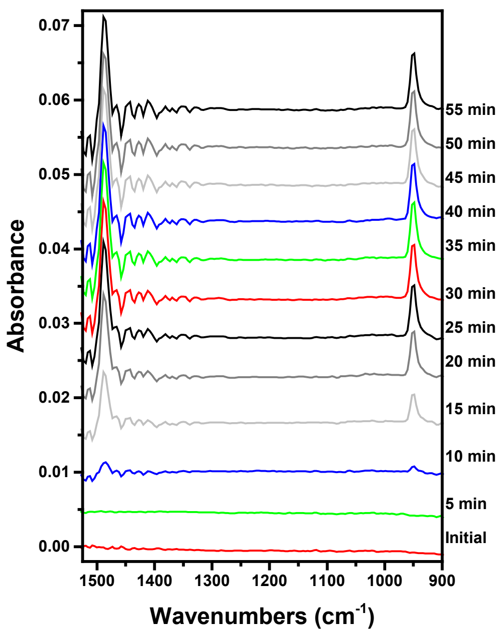
Cation Adsorption on Pt Electrode –FTIR Study

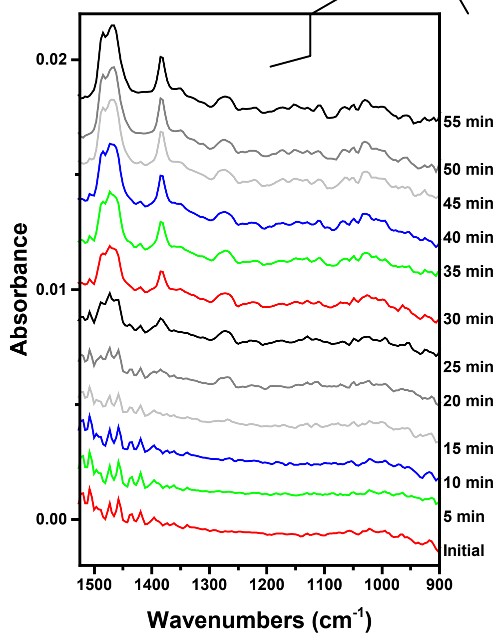
TMAOH



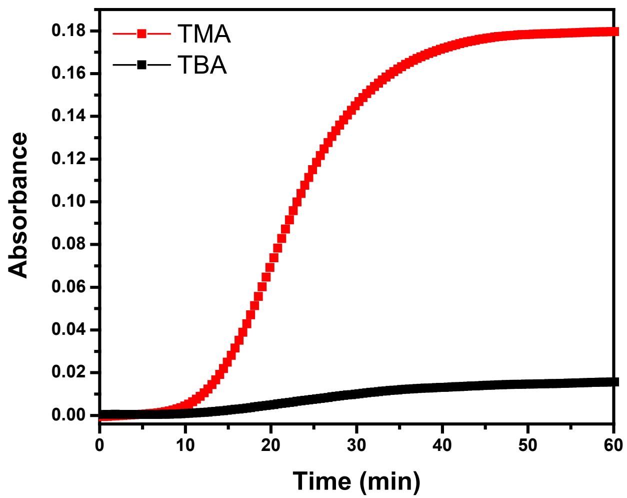
TBAOH







Total absorbance of C-H bend (~1485 cm^{-1})



Direct Observation of Organic Cation Adsorption at HOR Potential (0.1 V) using Surface FT-IR

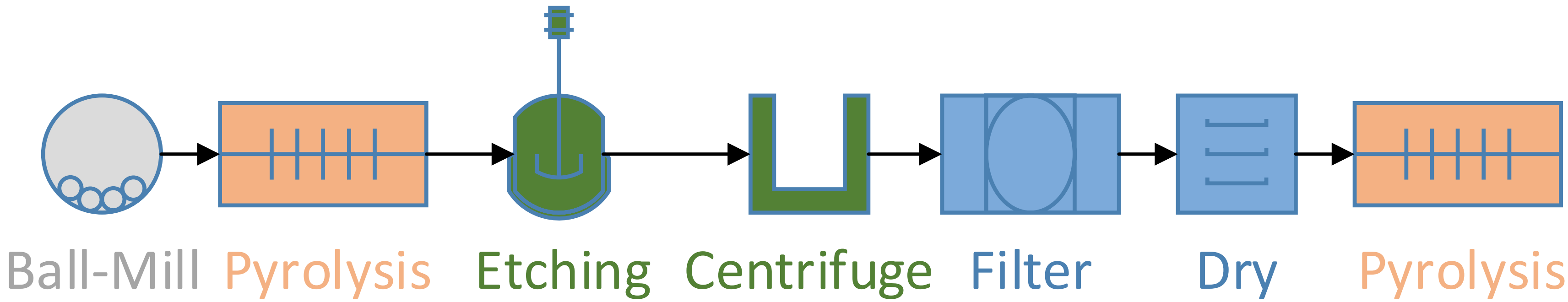
Accomplishments and Progress

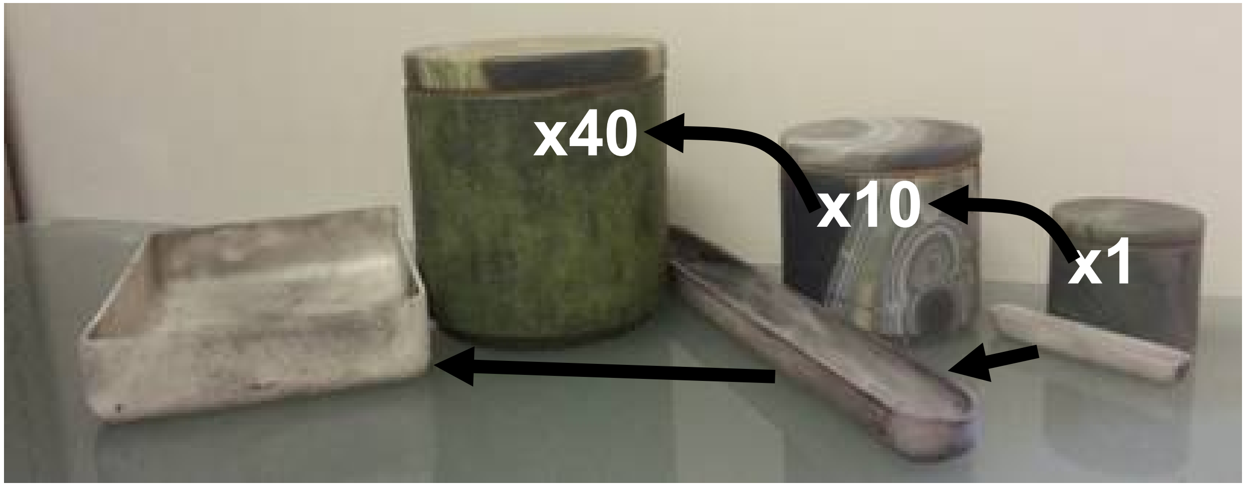
Thrust Area 3: Task 4 (Pajarito Powder LLC)

- **Task 4: Technology Transfer of SSM for Nickel-Based Materials (M1-M24)**
  - **Subtask 4.1** Technology Transfer of SSM for Nickel-Based Materials. (M1-M3)
    - Technology transfer using designated catalyst composition.
  - **Subtask 4.2** Scale-up of process to 50+gr batch size (M3-M6)
    - Scale up of representative catalyst 10, 25, and 50gr per batch levels.
  - **Subtask 4.3** Scaled-up manufacturing of leading formulation on 50gr scale (M6-M12)
    - Manufacture best UNM developed catalysts on 50gr per batch levels.
  - **Milestones 4.1-4.3**
    - <u>Technology Transfer of designated catalyst, measured by matching UNM catalyst to be within 10% by electrochemical performance and physical characterization on the batch level 10, 25 AND 50 g, respectively.</u>

Accomplishments and Progress

Thrust Area 3: Task 4 Preliminary Data





<u>Synthesis process transferring and processing conditions for scale-up being established</u>

Accomplishments and Progress

Thrust Area 3: Task 4 Preliminary Data

MEA materials on order and testing using reference catalysts (Pd/Pt) begun

Accomplishments and Progress

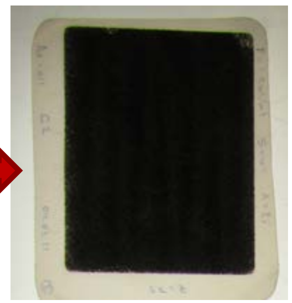
POWERING PEOPLE ANYWHERE

Thrust Area 4: Task 5 (IRD Fuel Cells LLC)

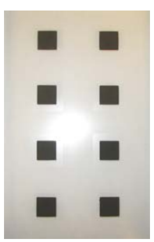
- **Task 5: MEA Design (M1-M24)**
  - **Subtask 5.1** MEA Design concepts with new materials (M6-M12)
    - Integration of the novel Ni-M catalyst alloys and anion exchange ionomers into fabrication of 1. Generation MEAs.
  - **Milestones 5.1**
    - MEA manufacturing concept (M12). Manufacturing concepts defined and verified for the 1st Generation of MEA (TRL2)
  - **Subtask 5.2**
    - Develop scalable manufacturing processes of alkaline exchange MEAs based on the Ni-M catalyst scaled in subtask 4.3
    - Develop scalable manufacturing processes of alkaline exchange MEAs based on the perfluorinated ionomer dispersions synthesized in subtask 3.3.
  - **Milestones 5.2**
    - Development of fabrication routes for alkaline exchange MEAs based on scalable processes (M20)

Accomplishments and Progress

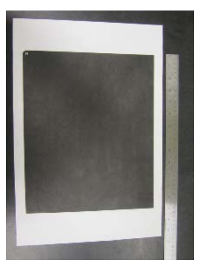
Thrust Area 4: Task 4 Preliminary Data



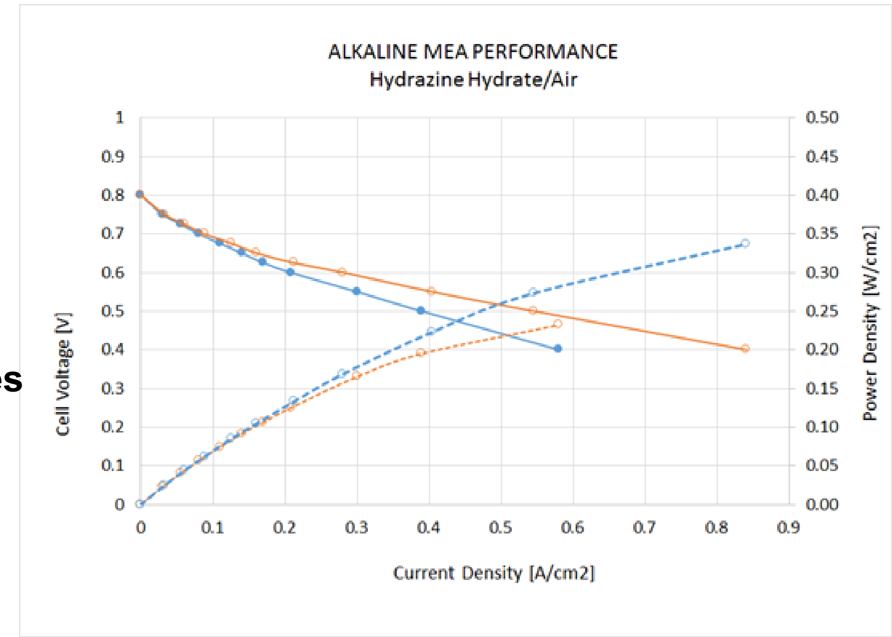
Coating optimization of Ni-based electrodes
Scalable process



25 cm^2 CCM



400 cm^2 CCM



Preliminary Ni-based catalyst: optimization of electrode and process manufacture development

Summary Slide

- Kick off meeting was held at UNM on April 16th with participation of all subcontractors. The presenters discussed the project scope, goals and the way to achieve the milestones as well as go/no-go design point.

Preliminary results and ongoing activity.

- Task 1.1 Optimization of Sacrificial Support Type (UNM): Initial experiments with nickel materials were started at UNM. Several commercially available Ni-alloys were obtained and MEA fabrication is started.
- Task 1.2 Optimization of Heat Treatment parameters (UNM): Based on previous UNM results with NiZn materials: Ni-Mo and Ni-W catalysts are in the preparation stage with temperature down-selected to 450 ° C.
- Task 3 Ionomer Development for Ni-M Catalysts (LANL): Los Alamos National lab team started the optimization of ionomer dispersion in different solvents.
- Task 4 Technology Transfer of SSM for Nickel-Based Materials (Pajarito Powder LLC): The experimental set-ups were re-designed in order to synthesize nickel-based materials on the level of 5-10 g.
- Task 5 MEA Design (IRD Fuel Cells LLC): IRD Fuel Cells started preparation of CCM-made anode with Tokuyama membrane in order to supply them to UNM team.

Future Activity

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- Optimization of Sacrificial Support Method in order to synthesize nickel-based Hydrogen Oxidation Reaction electrocatalysts.
- Establishing structure-to-properties relationships on multiple levels: catalysts, catalyst-to-ionomer, MEA etc.
- Technology transfer to Pajarito Powders LLC of most advanced electrocatalysts
- Integration of catalysts, ionomers and membranes into highly performed MEA.
- IP protection, publishing obtained results, presenting on national and international conferences.

Technology Transfer Activities

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1. Publications, Patents and Provisional Patents Filed:

Publications:

1 A. Serov, M. Padilla, A. J. Roy, P. Atanassov, T. Sakamoto, K. Asazawa, H. Tanaka "Anode Catalysts for Direct Hydrazine Fuel Cells: From Laboratory Test to an Electric Vehicle", Angewandte Chemie Int. Ed. 126 (39) (2014), 10419–10715.

2 T. Asset, A. Roy, T. Sakamoto, M. Padilla, I. Matanovic, K. Artyushkova, A. Serov, F. Maillard, M. Chatenet, K. Asazawa, H. Tanaka, P. Atanassov, "Highly active and selective nickel molybdenum catalysts for direct hydrazine fuel cell", Submitted, (2015)

Patents:

1. A. Serov, P. Atanassov, Method of Preparation of Nano-Sized Materials Provisional Application 61/992,732 filed on May 12, 2014, (UNM 2014-109)
2. A. Serov, N. Andersen, P. Atanassov, Facile Method for Making of Monodispersed Particles Provisional Application 61/996,799 filed on May 12, 2014, (UNM 2014-108)
3. A. Serov, H. Tanaka, P. Atanassov, K. Asazawa, T. Sakamoto Supported Ni-M Materials for Electrooxidation of Hydrazine Provisional Application 61/896,471 filed on October 28, 2013, (UNM 2014-047)
4. A. Serov, P. Atanassov, Design of Smart-MEAs for High Power Fuel Cells Provisional Application 61/952,067 filed on February 22, 2013, (UNM 2013-073)
5. U. Martinez, A. Serov, P. Atanassov Bimetallic Non-PGM Alloys for the Electrooxidation of Gas Fuels in Alkaline Media Provisional Application 14/149,905 filed on December 20, 2012 (UNM 2013-055)
6. A. Serov, Kateryna D. Artyushkova, Barr Halevi and Plamen B. Atanassov "Silver Based Catalyst for Effective Oxidation of Organic and Inorganic Fuels", Appl. Number: 2012-021 Appl. Date: Aug 29, 2011

Technology Transfer Agreements in negotiated between PPC and UNM groups for scale up procedure.

Collaborations

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Partners (this project)

- University of New Mexico, (Prime) Albuquerque, NM: Dr. A. Serov (P.I)
- Los Alamos National Laboratory, Los Alamos, NM: Dr. Y. S. Kim (National Lab., subcontractor)
- Pajarito Powder, Albuquerque, NM: Dr. B. Halevi (Industry subcontractor)
- IRD Fuel Cells, Albuquerque, NM: Ms. M. Odgaard (Industry subcontractor)