



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

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Project ID# FC130

Overview Slide

➤ Timeline:

- Start date: 06/01/2015
- End date: 05/31/2017

➤ Budget Data:

- Total Project Value: \$ 760,000 (Federal), \$ 250,000 (cost share); Total \$ 1,010,000
- Cost Share Percentage: 20%
- Total Funds Spent*: 243,000
- * On 04/01/2016

➤ Barriers/Targets:

- Activity (catalyst, RDE, MEA)
- Integration in MEA (catalyst, ionomer)
- Manufacturability (catalyst, ionomer, MEA)

➤ Partners and PIs



Los Alamos National Laboratory,
Los Alamos: Dr. Yu Seung Kim



IRD Fuel Cells LLC, Albuquerque:
Ms. Madeleine Odgaard



Pajarito Powder LLC, Albuquerque,
Dr. Barr Halevi

- **Objectives**: Development of PGM-free 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 PGM-free catalyst with ionomer into the MEA will be performed.
- **Relevance to DOE Mission**: This will enable integration of the PGM-free anode materials into the optimized MEA structure. It can be expected that performance of PGM-free based AEMFC will be significantly improved ca. peak power density up to 250 mW cm⁻².
- **Targets**
 - RDE peak current density > 1 mA cm⁻²
 - RDE current density at 0.01V > 0.085 mA cm⁻²
 - MEA peak current density 250 mW cm⁻² (H₂/O₂ configuration)

Approach: Technical Details

- **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/cm².
 - (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

Date	Milestone	Status	Comments
Oct 2015	Synthesis and characterization Ni-based materials with: surface area $> 20 \text{ m}^2 \text{ g}^{-1}$, particle size $< 70\text{nm}$	100% completed	Materials were synthesized and characterized by SEM, TEM, XRD, BET and XPS
Jan 2016	Synthesis and characterization Ni-based materials with phase purity $> 95\%$	85% completed	Phase pure NiZn, Ni ₂ P/C and NiO were synthesized. Ternary systems (Ni-Mo-M, M=Cu, Co, Re etc) still have an oxides
Jan 2016	Scale-up down selected UNM catalyst and match $\pm 10\%$ of HOR current density by RDE tests	80% completed	Materials synthesized and electrochemically evaluated.
Feb 2016	Rank cationic functional groups in ionomers	90% completed	LANL ranked the cationic functional groups

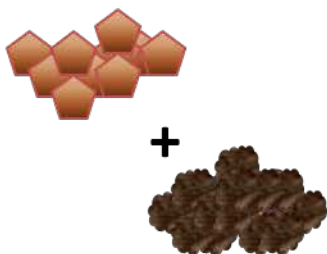


Accomplishments and Progress

Synthetic Approach

Thrust Area 1: Tasks 1-2 (UNM)

1. Combine solid nitrates and Mo-salt

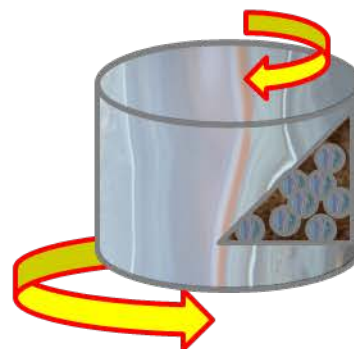


$\text{Ni}_2\text{P/C}$

2. Grind

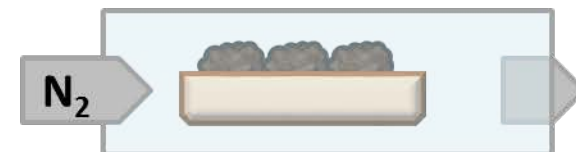


3. Ball mill

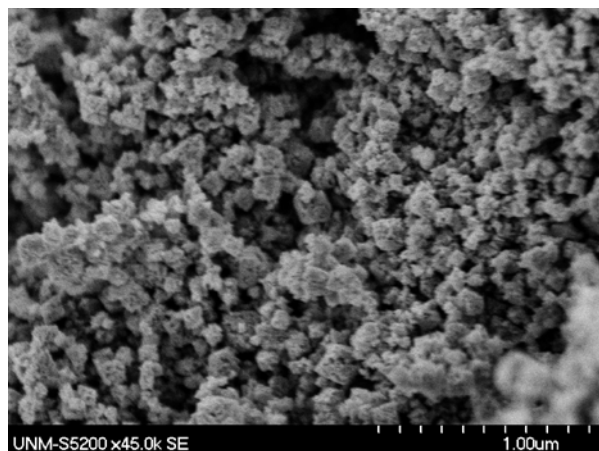
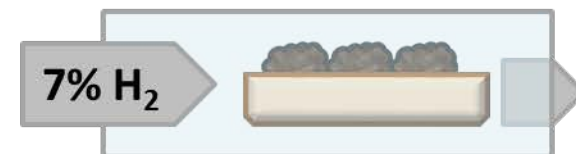


NiO

4. Dry at 250 °C for 1 h

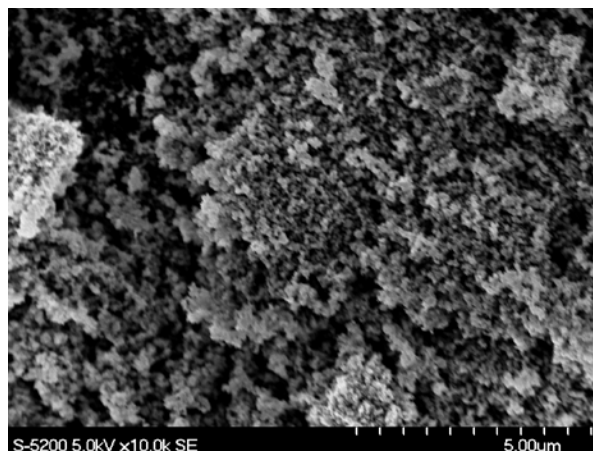


5. Reduction at 550 °C for 4 h



UNM-S6200 x45.0k SE

1.00um



S-5200 5.0kV x10.0k SE

5.00um

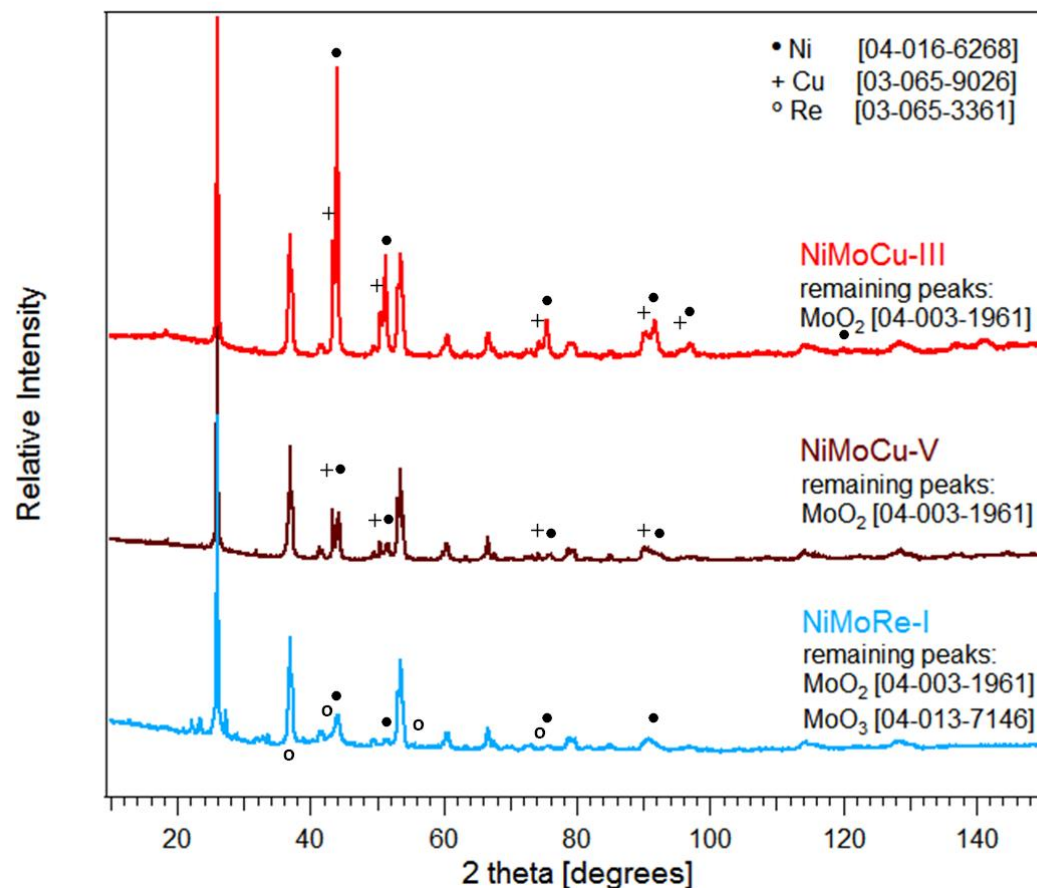
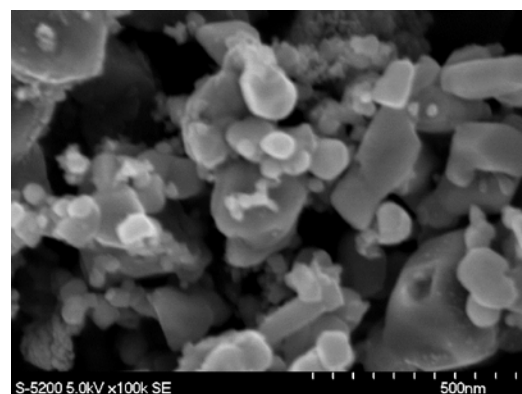
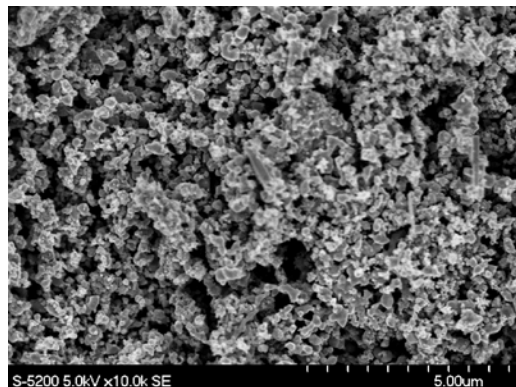
- Materials synthesized
- Characterization done
- Morphology control achieved

Accomplishments and Progress



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Binary and Ternary Catalysts

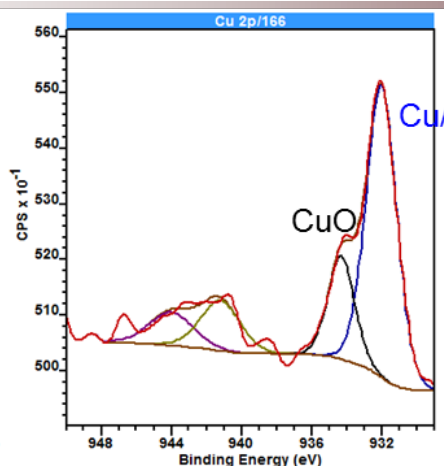
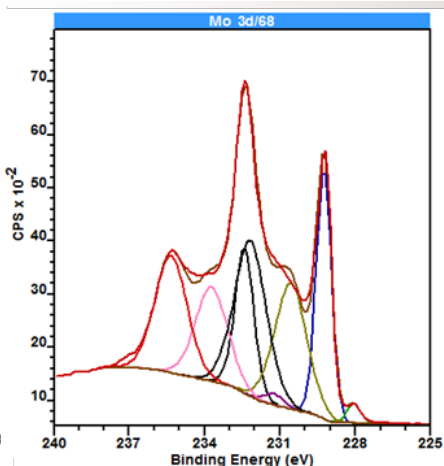
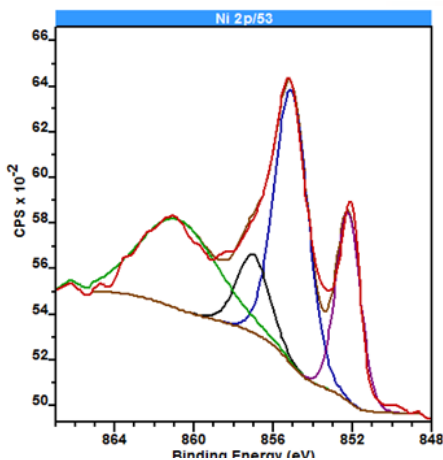


- Particle size <70nm, SA ~15-25 m² g⁻¹
- Binary materials phase pure, ternary have oxides

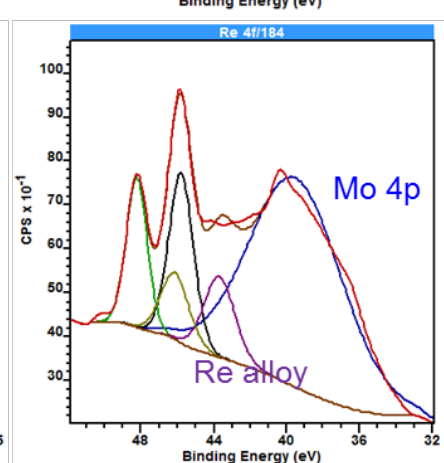
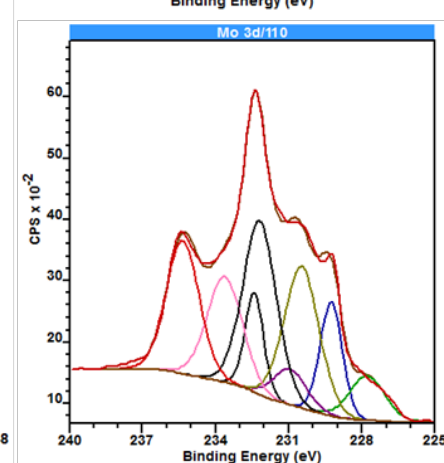
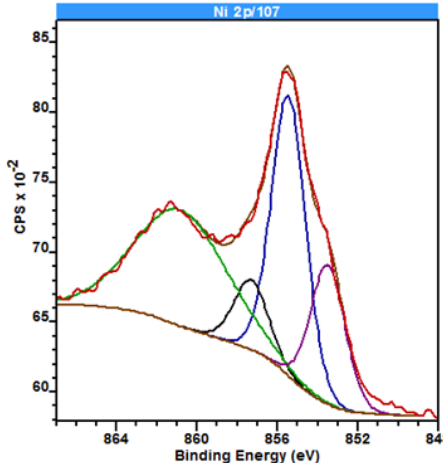


Accomplishments and Progress

Surface chemistry of ternary catalysts



NiMoCu



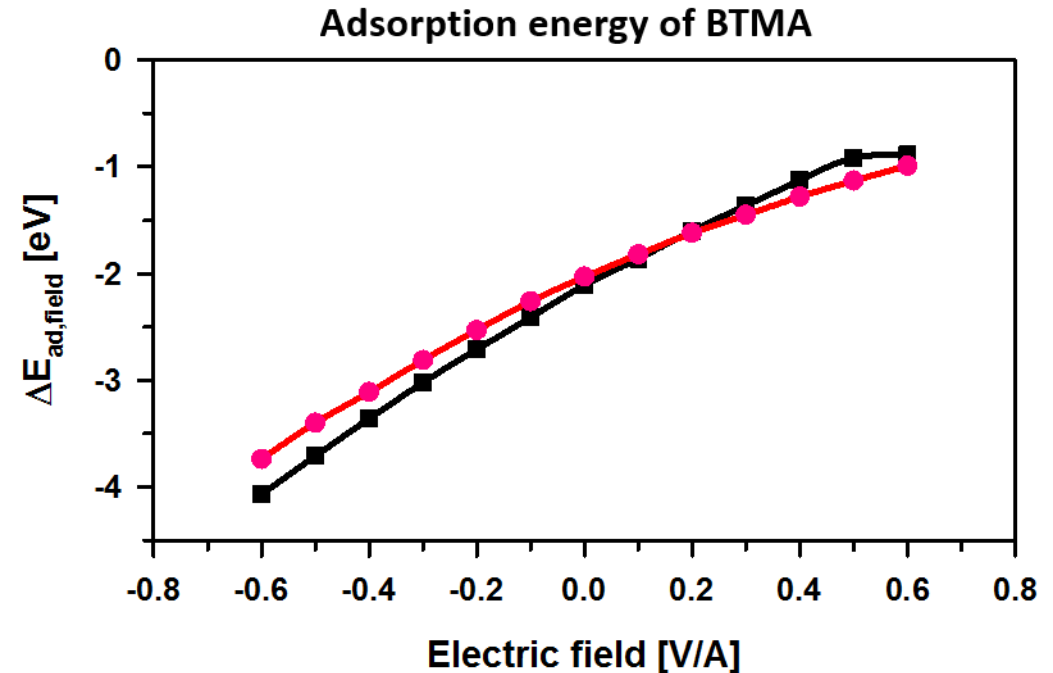
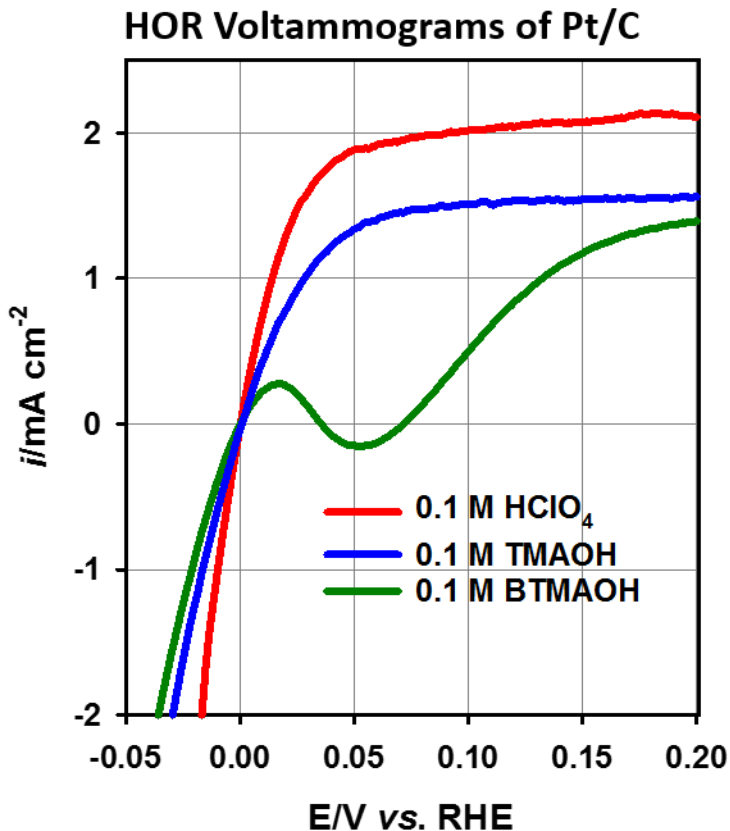
NiMoRe

- Surface of catalysts consists of metals and oxides
- Further optimization of synthesis is required

Accomplishments and Progress

Ionomer development

Thrust Area 2: Task 3 (LANL)



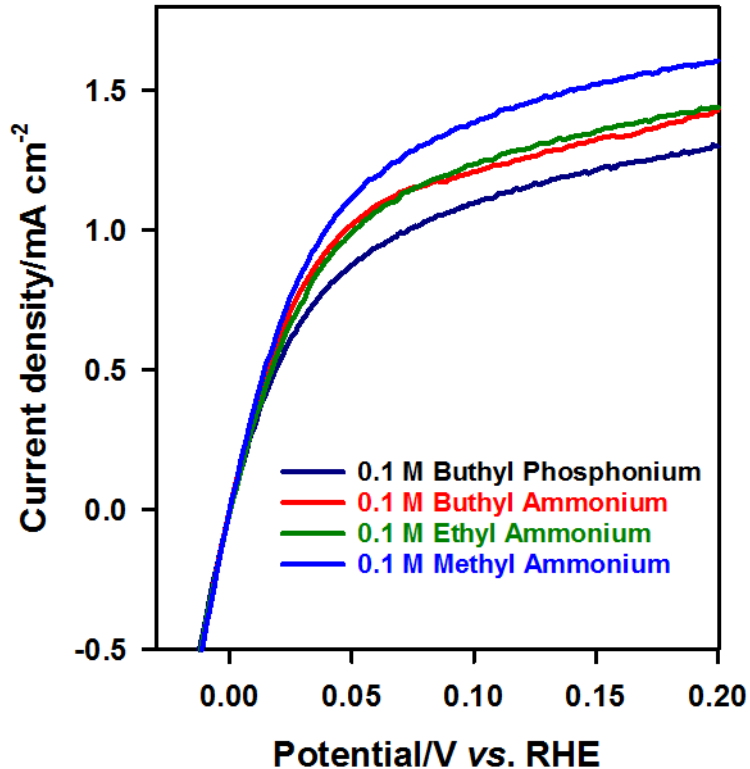
$U = 3\text{Å} \times E_{\text{field}}$; electrode potential assuming with the electric field over a Helmholtz layer with thickness of 3 Å.
(Karlberg et al., Phys. Chem. Chem. Phys., 9, 5158 (2007))

- HOR activity on Pt/C inferior in alkaline media
- Applied potential influence on interaction of Pt surface with ionomer

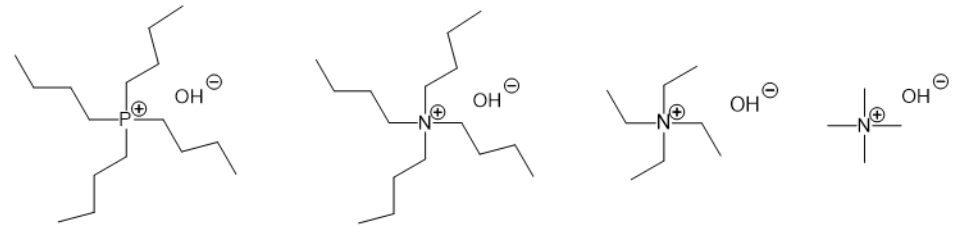
Accomplishments and Progress

Ionomer development

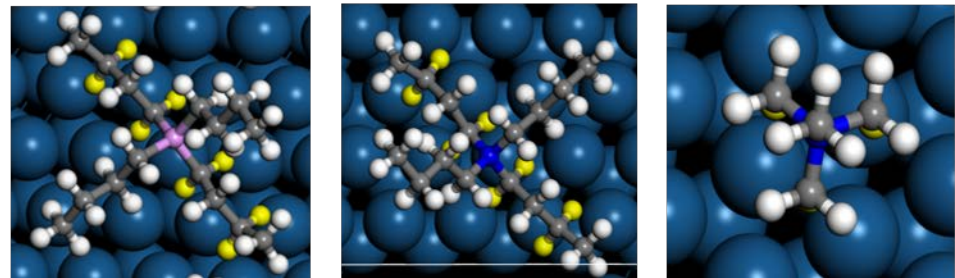
HOR Voltammograms of Pt/C



Adsorption energy from DFT modeling



TBP: -2.00 eV < TBA (\approx TEA): -2.33 eV < TMA: -2.79 eV



Geometrical and energetic features of each cation adsorption on Pt (111) surface at 0.0 V; yellow atom shown is interacted strongly with the Pt surface. *Courtesy, Dr. Choe at AIST*

- HOR depends on functional group in ionomer
- Experimental and DFT data are in good agreement
- Milestone on functional groups ranking met: TBP>TBA, TEA>TMA

Thrust Area 3: Task 4 (Pajarito Powder)

- **SSM process transferred (100% complete)**

- Several batches made to determine and optimize manufacturing conditions including: mixing method and drying; passivation after thermal treatment, etching and filtering
 - Sample delivered to UNM for testing
- Process yield low
- Costs determined to be high
- Filtration is bottleneck
 - Inline bagfilter and filterpress tested
 - Filterpress selected for implementation Q2/2016



- **Other manufacturing methods investigated**

- Dry/wet/and incipient impregnation of carbon supports is main thrust besides SSM

➤ Method scaled up to 10+ gram batches

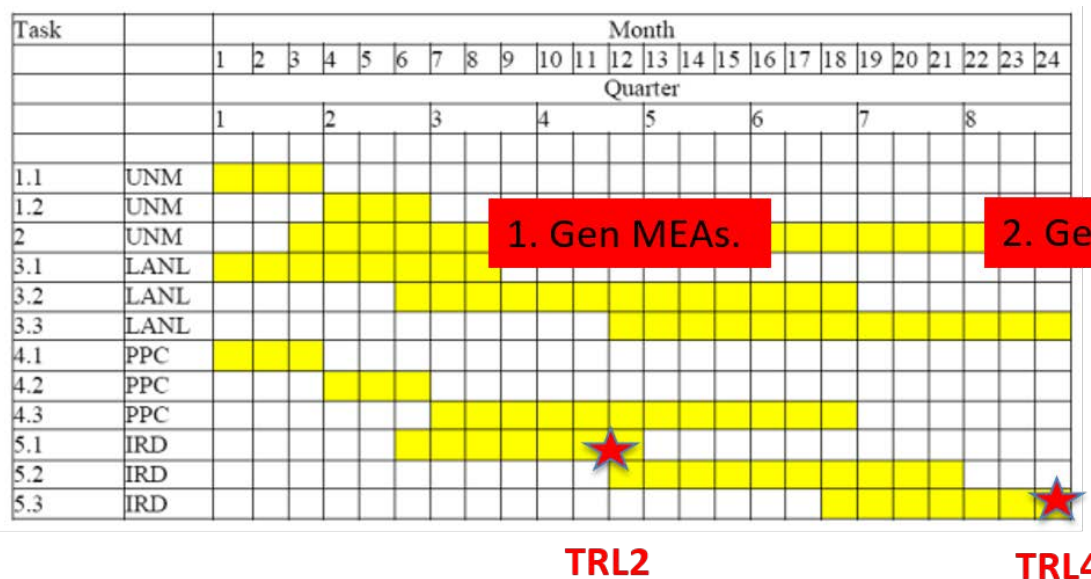
➤ Performance matches small size UNM batches in RDE tests

Accomplishments and Progress

MEA manufacturing

Thrust Area 4: Task 5 (IRD Fuel Cells)

- MEA Design and Testing (Initiated)
 - Work recently initiated. Design phase for modification of ink delivery system in order to reproducibly print difficult-to-disperse alkaline catalyst materials. Implementation planned to start at M12 according to the time plan.



➤ Work is performed according to the time schedule

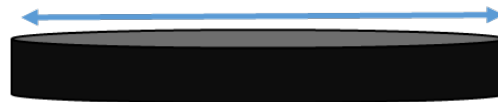
Accomplishments and Progress

Hydrogen Oxidation: RDE

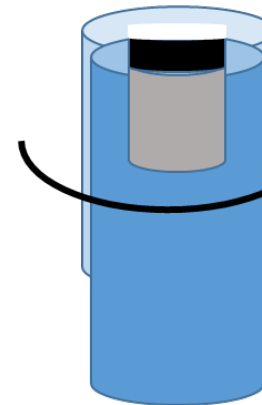
100 mg Activated Carbon + PTFE
100 mg NiCuMo

Mixed and pressed
(5000 pounds for 2 minutes)

1.8 cm



5 mm \rightarrow 7.72 mg of NiCuMo



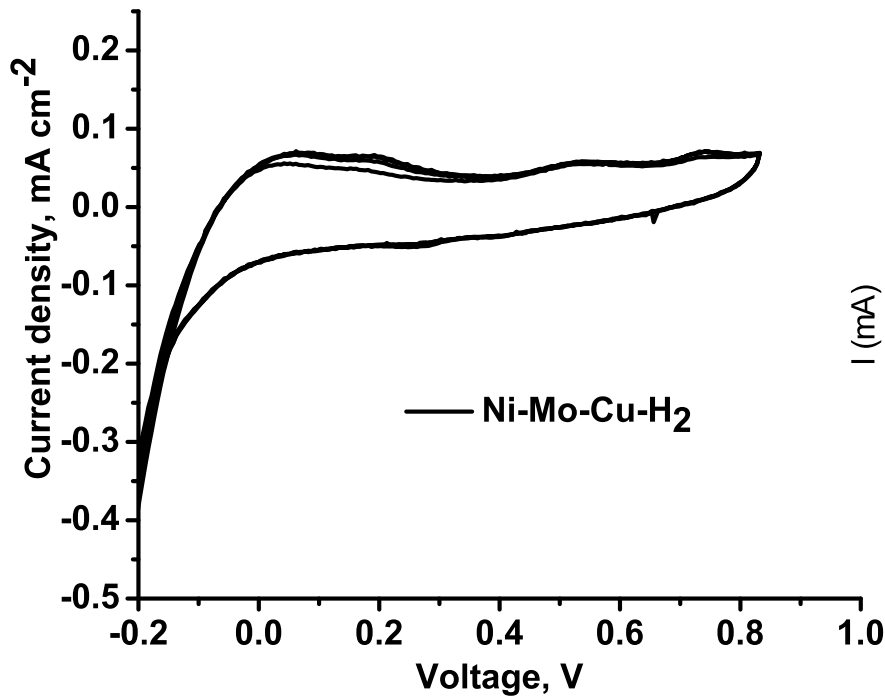
1600 rpm

- High loading of catalyst is needed
- Due to thick electrode layer, kinetic analysis is complicated

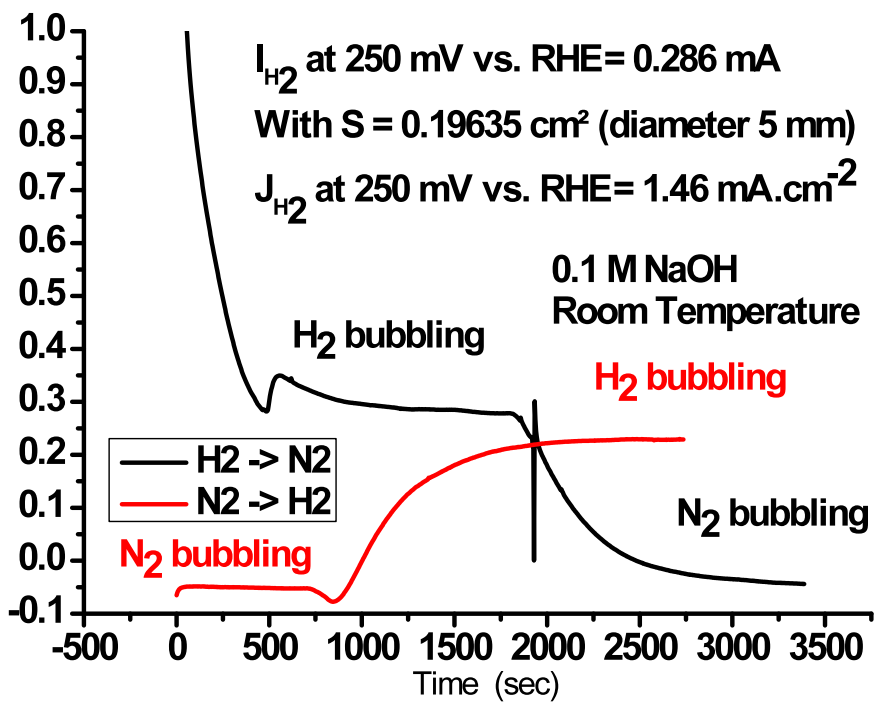


Accomplishments and Progress

Hydrogen Oxidation: RDE



Standard ink preparation. Loading of 0.2 mg cm⁻²



Pressed pellet

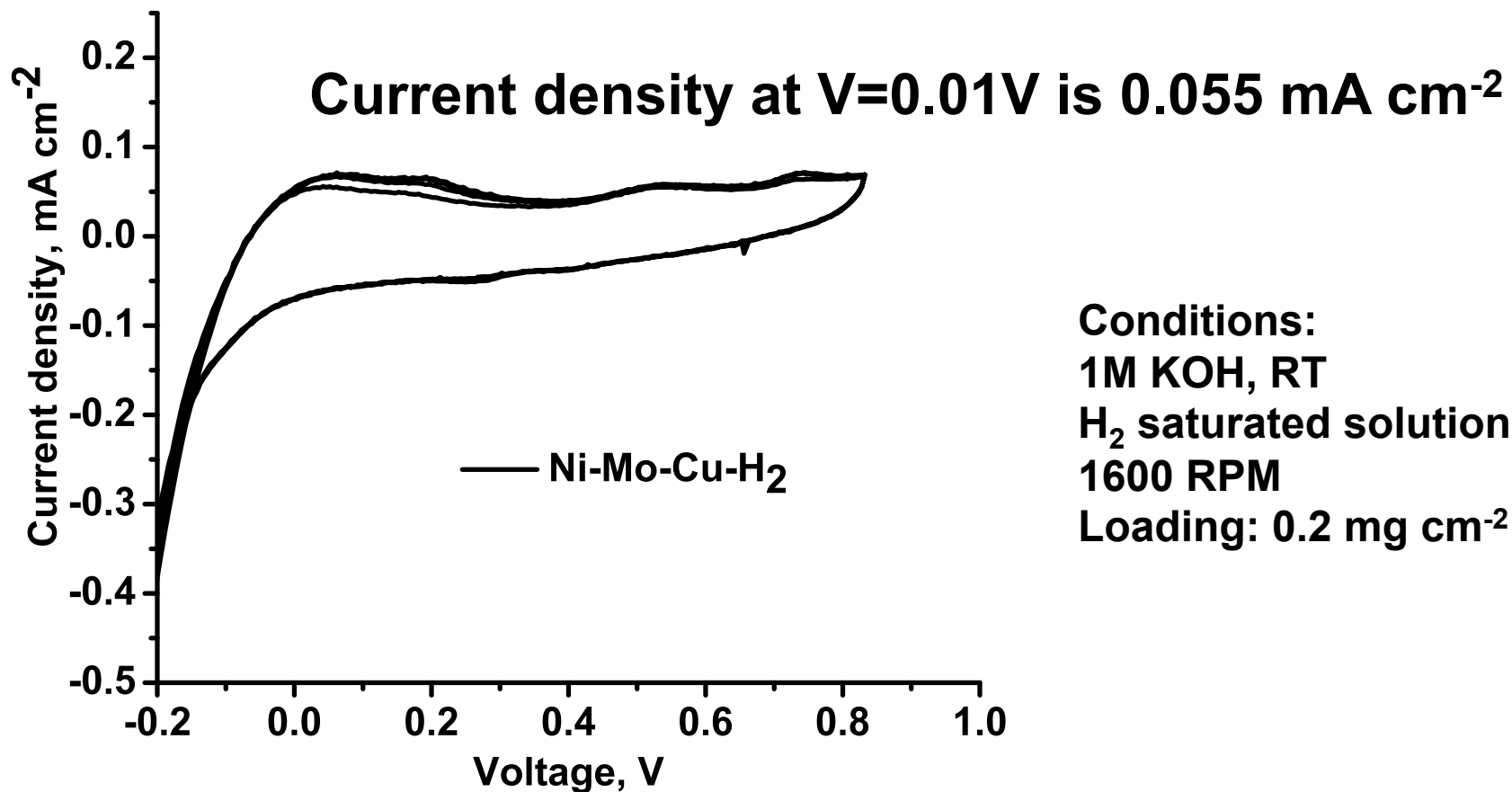
- Ternary catalysts active in HOR
- Current density > 1 mA cm⁻² was achieved (high loading)
- Milestone met

Accomplishments and Progress



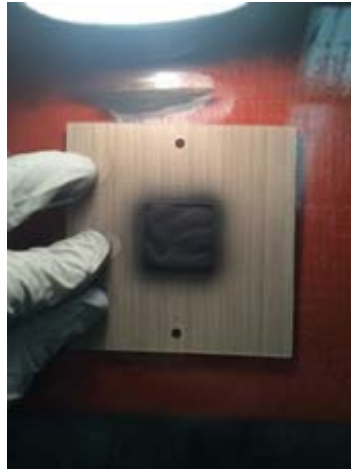
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Hydrogen Oxidation: RDE



- Ni-Mo-Cu sample approaching first Go/No-Go design point of:
 0.085 mA cm^{-2} at $V=0.01V$

MEA fabrication with Tokuyama ionomer



Mixture of catalysts, Tokuyama ionomer and alcohols were dispersed by ball-milling: 450RPM, $t=20$ min.

CCM sprayed. Converted to OH^- form by soaking in 1M KOH

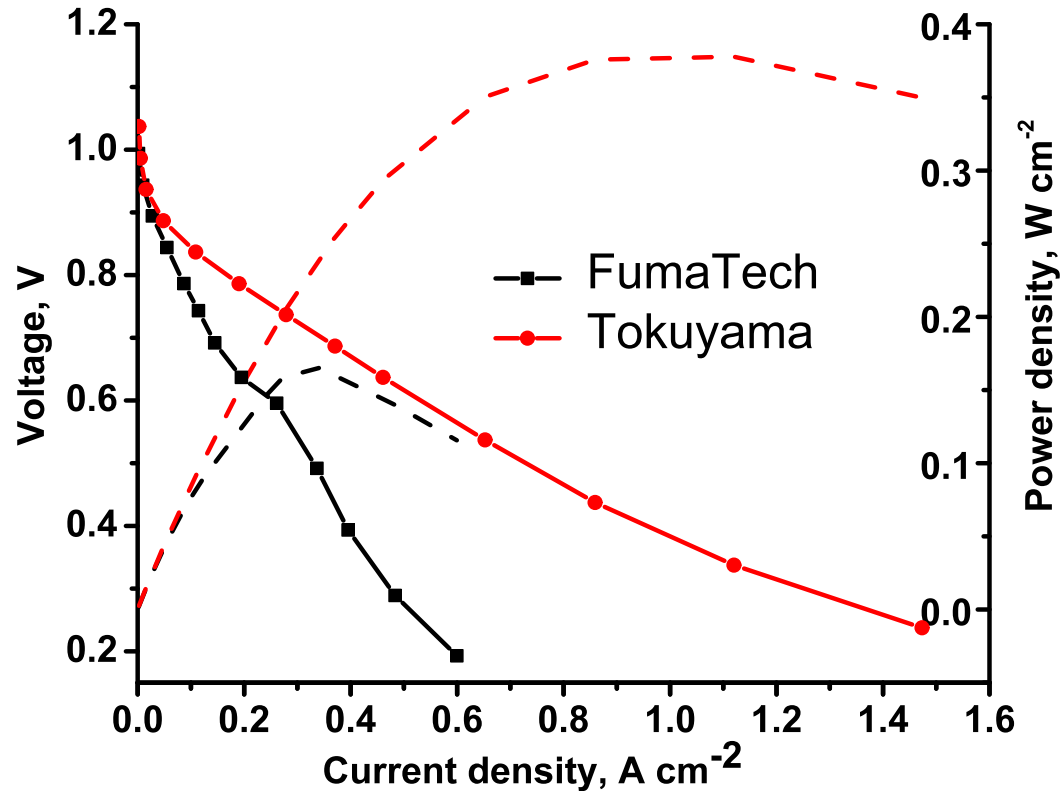
- Ink prepared by ball-milling was stable during the hand-spraying
- Membrane did not change the shape during the CCM fabrication
- No hot pressing required using CCM method

Accomplishments and Progress



Fuel Cell Tests: Model Experiments

Testing Pt/C catalysts with commercial ionomers



Anode/Cathode: Pt/C – 0.2 mg cm^{-2} , 100% RH, $T=60^{\circ}\text{C}$, $p=1.5b_g$, H_2/O_2 configuration

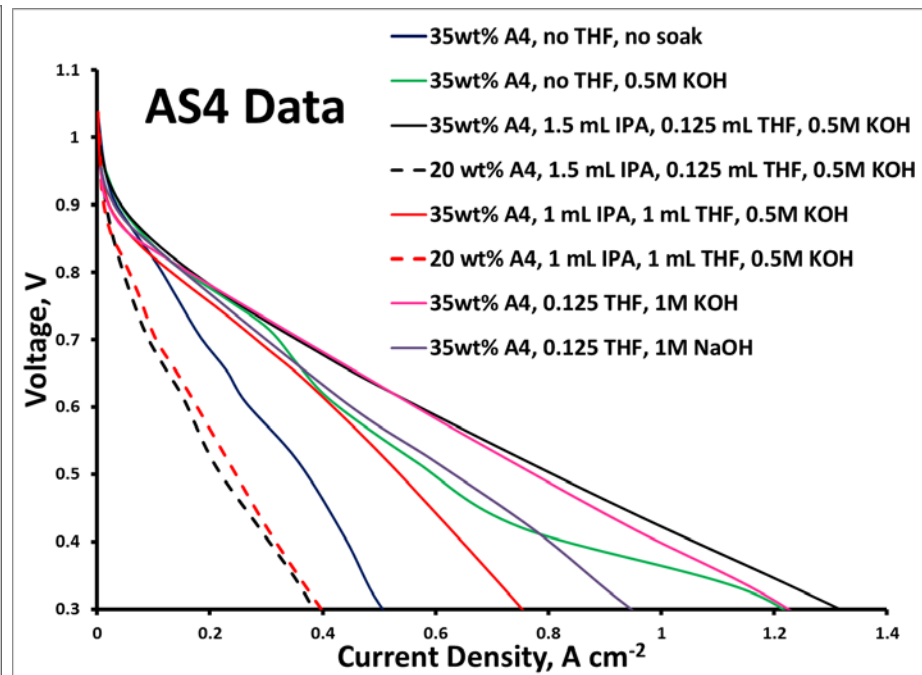
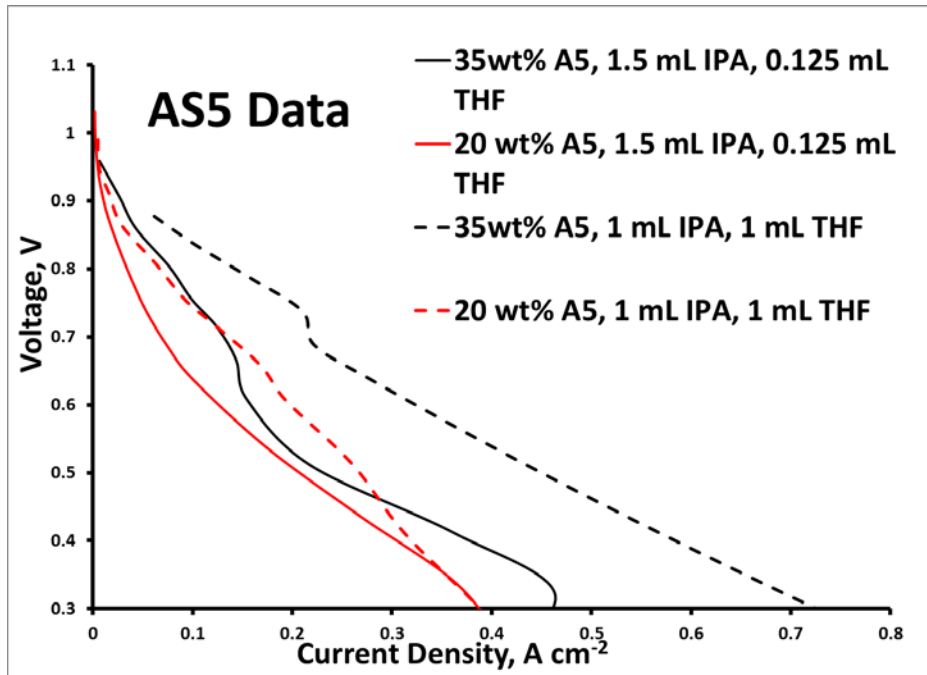
- Initial tests showed that MEA fabricated with Tokuyama ionomer has higher activity

Accomplishments and Progress



Fuel Cell Tests: Model Experiments

MEA tests with different Tokuyama ionomers



Anode/Cathode: Pt/C – 0.2 mg cm⁻², 100% RH, T=60°C, p=1.5b_g. H₂/O₂ configuration

- Further optimization on model Pt/C systems is ongoing
- MEA activation protocol should be established

Collaboration and Partners



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Catalyst design, characterization, project management:

Alexey Serov (Project Lead), Ashley Maes, Sarah Blair, Sarah Stariha, Sadia Kabir, Kateryna Artyushkova, Plamen Atanassov



Ionomer development and DFT calculations:

Yu Seung Kim (PI), Hoon Chung, Kwan-Soo Lee, Joseph Dumont, Ivana Matanovic



MEA Design:

Madeleine Odgaard (PI), James Brewster, Debbie Schlueter, S. Lucero

Scaling Up:

Barr Halevi (PI), Henry Romero, Samuel McKinney



Remained Challenges and Barriers

- Decrease particle size of Ni-Mo-M catalysts
- Optimize RDE working electrode preparation to establish kinetics parameters
- Integrate PGM-free anode into MEA structure
- Design MEA fabrication and testing protocol

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.

- **Results**

- Sacrificial Support Method was applied for preparation of unsupported Ni-based materials
 - Morphology of catalysts was controlled and maintained to meet milestone criteria (particle size <70 nm and surface area 20 m² g⁻¹)
 - LANL met milestone requirements by ranking functional groups in ionomers. DFT calculations were found to be in good agreement with experiment
 - Pajarito Powder scaled up the SSM up to 10 g level and met criteria on electrochemical performance of the samples
 - IRD fuel cell initiated optimization of ink spraying techniques based on unsupported Ni-Mo-M catalysts
 - The Team met milestone on peak current density >1 mA cm⁻²
 - Team is approaching first Go/No-Go decision with powder density at 0.01V

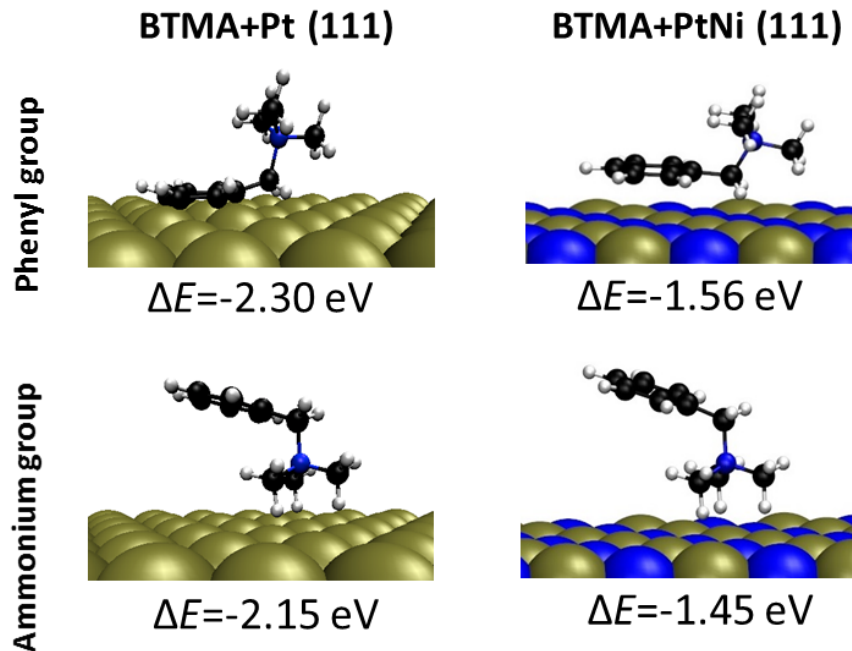
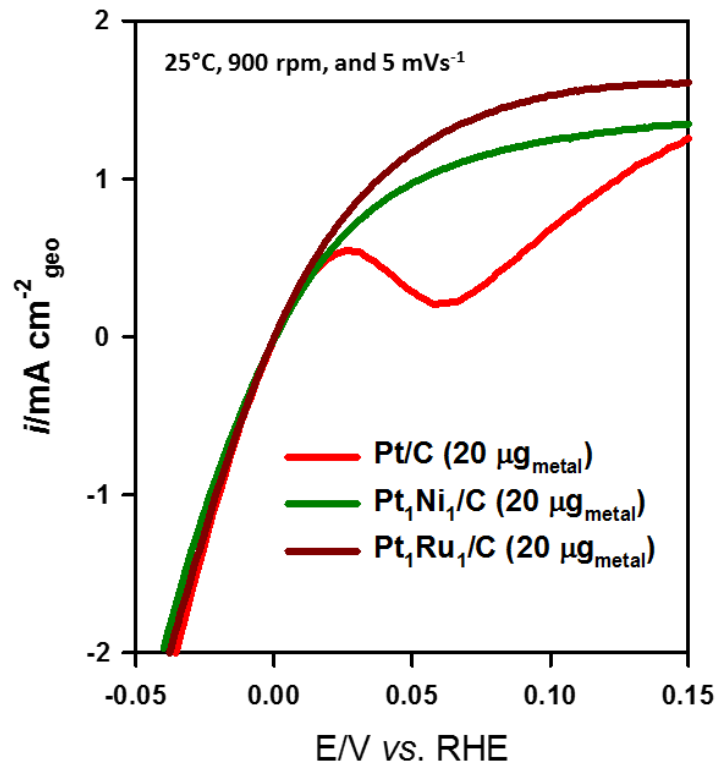
Future Activity

- Synthesis of phase pure Ni-Mo-M catalysts
- Establishing structure-to-properties relationships on multiple levels: catalysts, catalyst-to-ionomer, MEA etc.
- Synthesis of LANL ionomer with downselected functional groups
- Scaling up the catalyst production to 25g and 50g batched
- Integration of catalysts, ionomers and membranes into highly performed MEA
- IP protection, publishing obtained results, presenting on national and international conferences



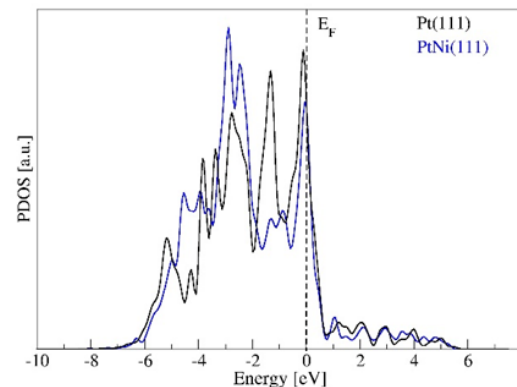
Technical Back-up Slides

HOR Voltammograms in 0.1 M BTMAOH



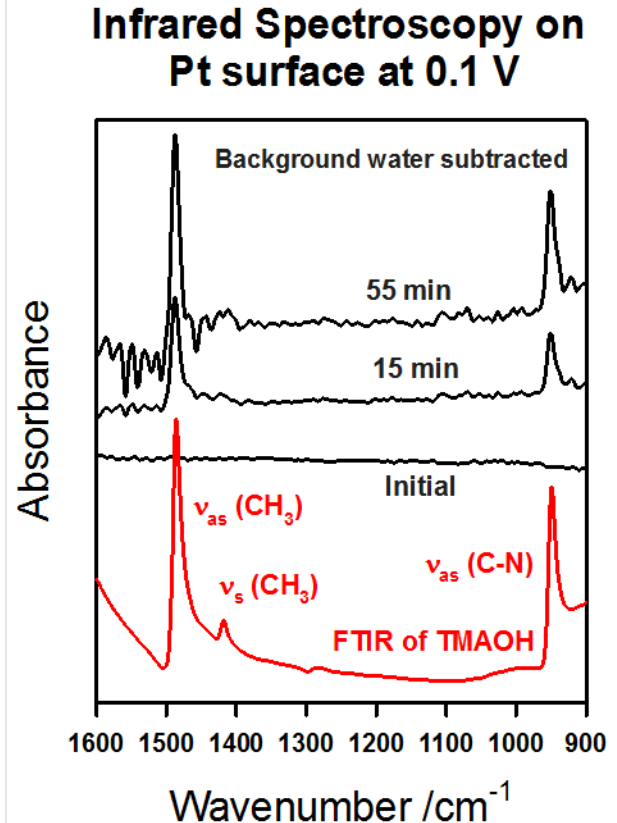
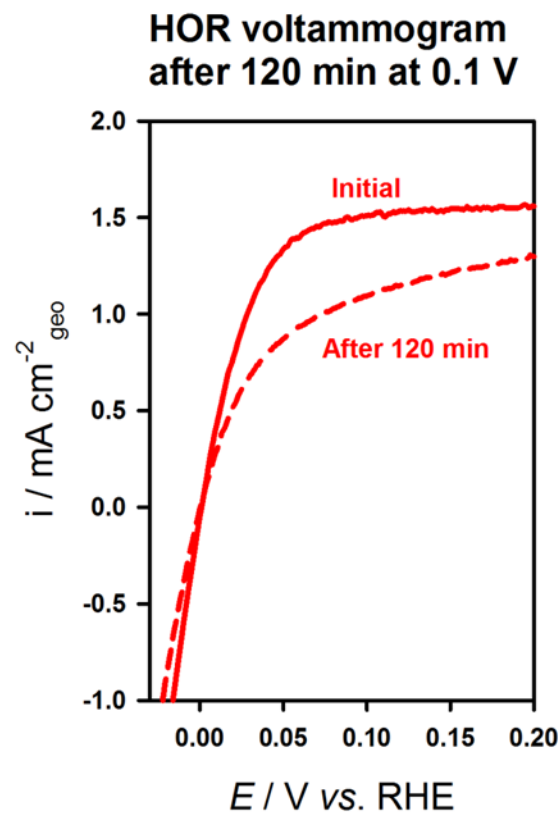
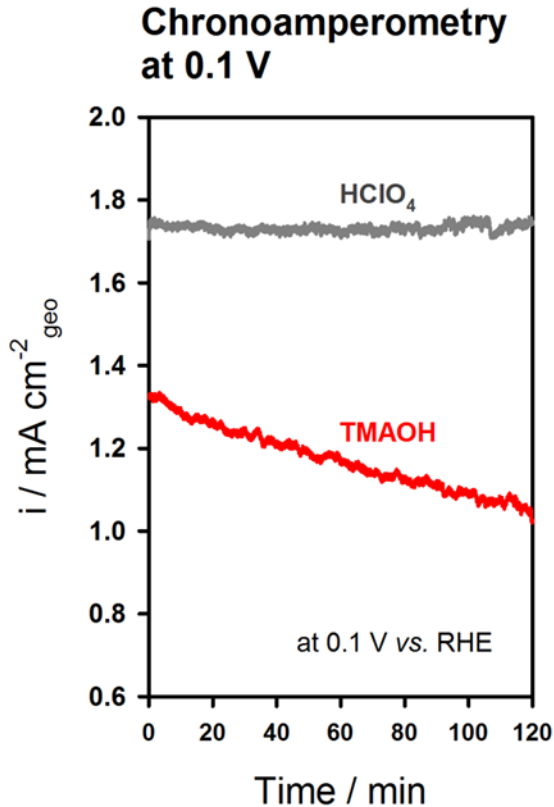
- Alloying with Ni decreases poisoning of the catalyst with both phenyl and ammonium group due to the change in the electronic structure with alloying –shift of d -states toward more negative values relative to Fermi level, which increases the filling of antibonding orbitals.

Highlight: Ni can change the electronic structure of catalyst, allowing less poisoned catalyst structure.



$$\epsilon_d - E_F = -1.90\ eV\ \text{for Pt(111)}$$

$$\epsilon_d - E_F = -2.13\ eV\ \text{for PtNi(111)}$$



- HOR activity of Pt/C electrode in tetramethyl ammonium (TMA) gradually decreased over time.
- Infrared spectroscopy indicates that the TMA group gradually chemisorbed and impacted the HOR current of Pt/C electrode.
- Cationic group adsorption is a complex chemisorption rather than a mere physisorption.

Highlight: Methyl ammonium group may not be a good choice for ionomer binder for AMFC anode.