Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Developing Novel Platinum Group Metal-Free Catalysts for Alkaline Hydrogen and Oxygen Evolution Reactions
(DE-EE0008082)

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360 Huntington Ave, Boston, MA 02115

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Project ID: P156

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Northeastern University
Center for Renewable Energy Technology

Project Overview

Project Partners

PI: Sanjeev Mukerjee - Northeastern University

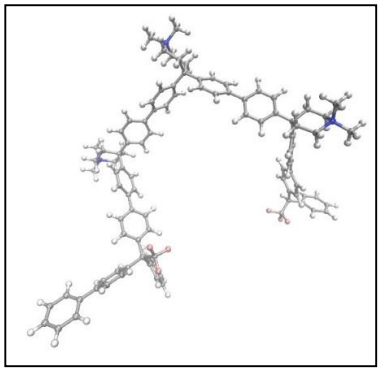
Partner organizations:

- **University of Delaware – Prof. Yushan Yan**
- **Advent North America – Dr. Emory De Castro**

Award #	EE0008082
Start Date Year 1 End Date Project End Date	10/1/2017 12/31/2018 12/31/2020
Year 1 Funding* Year 2 Funding*	$277,777 $422,222

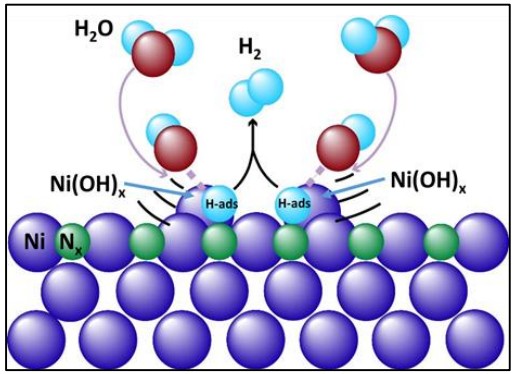
Project Vision

This project will develop stable, high-conductivity, and high-strength AEMs, stable and active PGM-free catalysts for hydrogen and oxygen evolution reaction (HER/OER), and high-performance electrode architectures.



Project Impact

The materials being developed under this project have the potential to unlock the cost advantages of AEM electrolyzers, enabling a clear pathway for achieving <$2/KgH2 (on scale) with efficiency of 43 kWh/kg H2 via anion exchange membrane (AEM)-based electrolysis.



**this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Approach - Summary

Project Motivation

The focus of this project is on durable, high-performance materials advanced water splitting, enabling a pathway for achieving <$2/Kg$_{H2}$ with efficiency of 43 kWh/kg H_2 via anion exchange membrane (AEM)-based electrolysis. We aim to advance these goals via an understanding of both hydrogen and oxygen evolution reactions leading to novel platinum group metal (PGM)-free catalyst materials in conjunction with improvements in membrane and ionomers and gas evolution electrodes with corresponding characterization and testing.

Barriers

Current state-of-the-industry anionic exchange membranes are subject to degradation above 60 ^{O}C. This project aims to develop a new anionic exchange membrane capable of operating at elevated to temperatures, thereby increasing the kinetics of electrolysis.

Key Metrics

	Units	Year 1	Year 2
Cell voltage	V	1.92	1.82
Current density	A/cm^2	0.8	1
Operating temp	^{O}C	80	90
Membrane ASR	Ω cm^2	0.15	0.12
HER overvoltage @500 mA/cm^2, 25 ^{O}C	mV	300	200
OER overvoltage @500 mA/cm^2, 25 ^{O}C	mV	150	125
Model voltage	V	1.74	1.69
Unexplained voltage loss	V	0.18	0.13

Approach - Summary

Partnerships and Roles

- *Northeastern Univ.*, (Prime) Boston, MA: S. Mukerjee (P.I):
  - **Novel HER catalysts:**
    - Metal-Metal Oxides
    - Functionalized mono-metallic
    - Embedded Metal-N-C Systems
  - **Novel OER Catalysts:**
    - Double layer metal oxides on Raney Ni (strategies for increasing active site density)
  - **Half and Single Cell Tests** (NEU)
  - **In situ Raman and Synchrotron X-ray Spectroscopy**
- *University of Delaware (Sub-awardee)*, Newark, DE: Prof. Y. Yan
  - **Novel Membranes and Ionomers**
    - Design of multi-cation Poly(aryl-piperidinium) Tri-quaternary-ammonium (PAP-TQN) membranes and ionomers for high temperature operation (90°C).
- *Advent North America (Sub-awardee),* Cambridge, MA: Dr. Emory De Castro
  - **Novel Electrodes** designed for gas evolution with and without liquid flow
- *National Lab Partners*:
  - NREL – MEA Prep and testing
  - LBNL – Small Angle Scattering and Transport Modeling
  - Sandia National Labs – Interfacial modeling

Approach - Innovation

NUCRET will leverage its expertise in catalyst development to synthesize and characterize catalysts for both OER and HER.

- HER catalysts
  - Metal/metal oxide – NiCr/C synthesized through borohydride reduction
  - Metal nitride – Ni^{2+} was chelated using cupferron, a nitrogenous compound. The complex was reduced via heat treatment in argon.
  - Metal organic framework – Ni and N precursors were incorporated into the ZIF-8 template.
- OER catalyst – Metal/metal oxide
  - NiFe/Raney Ni has been shown to be an effective non-PGM catalyst for OER

BP1 activities focused on identifying the most promising HER catalysts, validating the OER catalyst, and establishing baseline performance of an electrolysis equipped with these materials.

The University of Delaware has developed a polyaryl piperidine-based AEM with robust physical properties capable of operating at elevated temperatures (60 ^{O}C <). BP1 activities related to AEM development included:

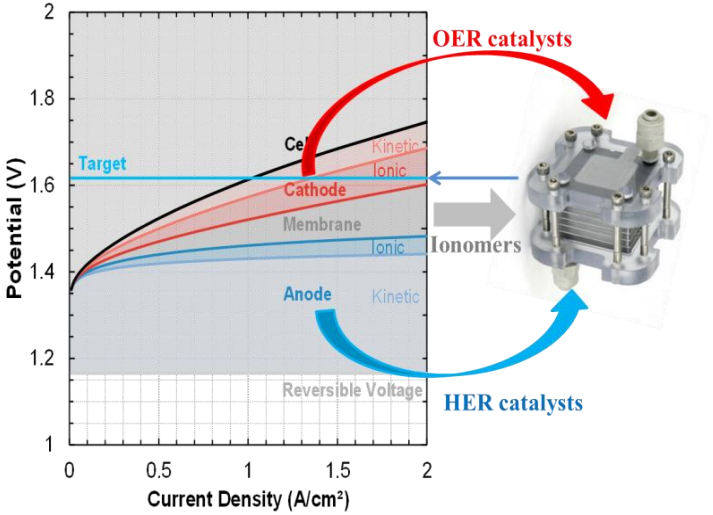
- Thorough characterization of physical properties
- Quantifying thermal stability
- Increasing the ion-exchange capacity (IEC) through the introduction of an additional active site

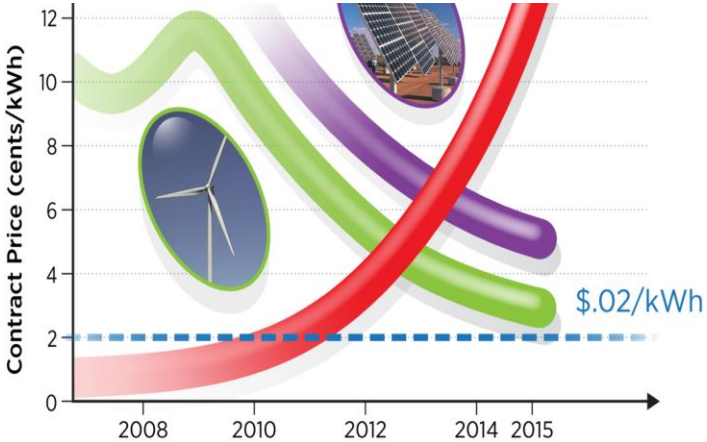
Relevance and Impact

- This program aims to develop thermally sustainable anionic membranes that will enable the use of cost-efficient transition metal catalysts.

- Our group will be able to leverage the capabilities of the ENM to generate multiscale modeling and molecular dynamics generated simulations of the membrane catalyst interface. In addition, its expertise with advanced ionomer materials, the EMN will provide durability and validation protocols of electrolyzer materials

- These activities can be applied to other areas of electrolysis research to characterize ionomer stability and electrolyte ion flux.





Approach – HER in Alkaline

Volmer:

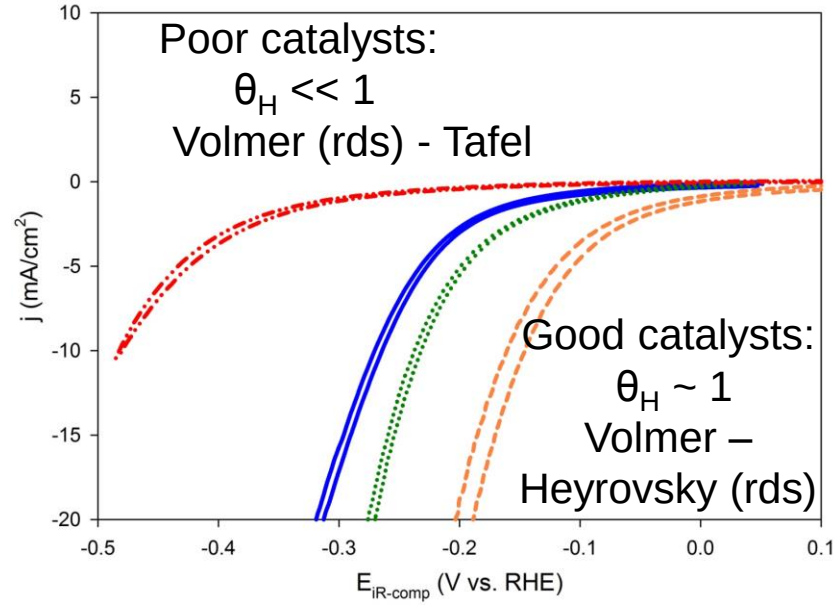
$M + H_2O + e^- \rightarrow M\text{-}H_{ads} + OH^-$

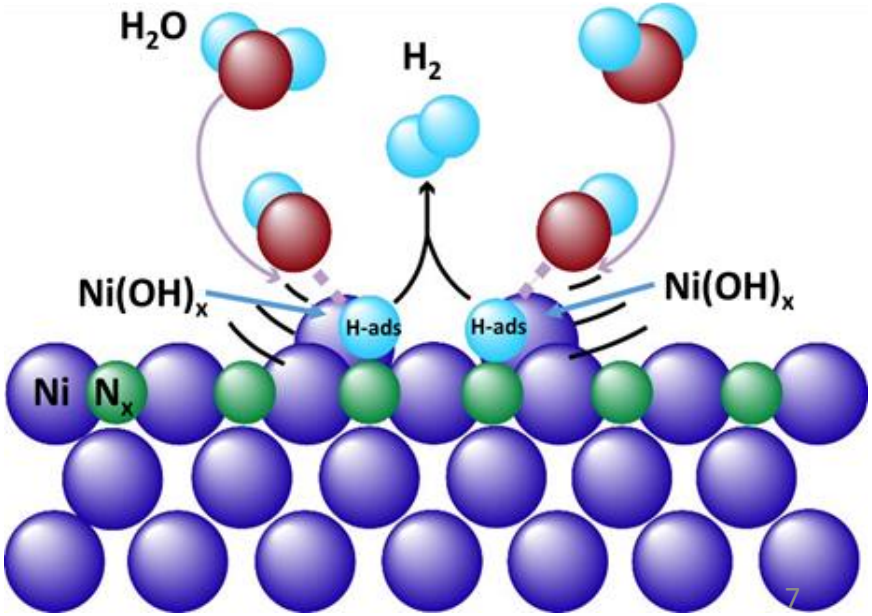
Heyrovsky:

$M\text{-}H_{ads} + H_2O + e^- \rightarrow \quad H_2 + OH^-$

Tafel:

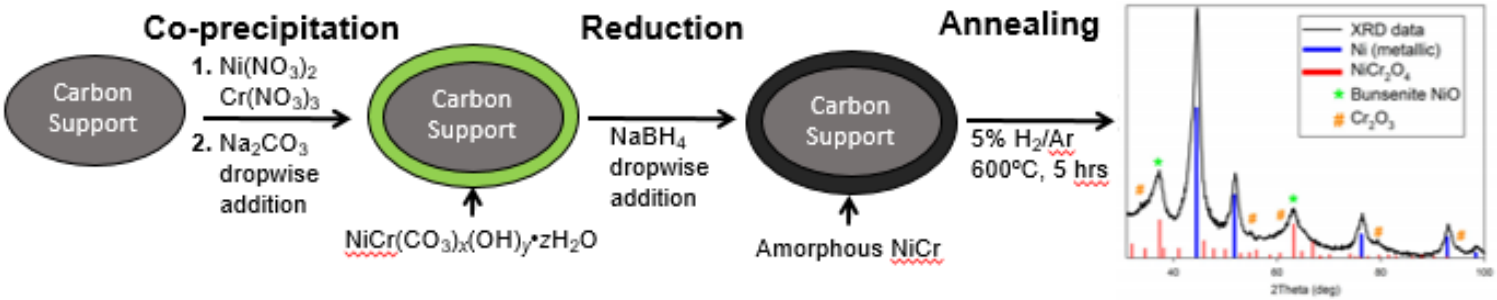
$2\ M\text{-}H_{ads} \rightarrow H_2$



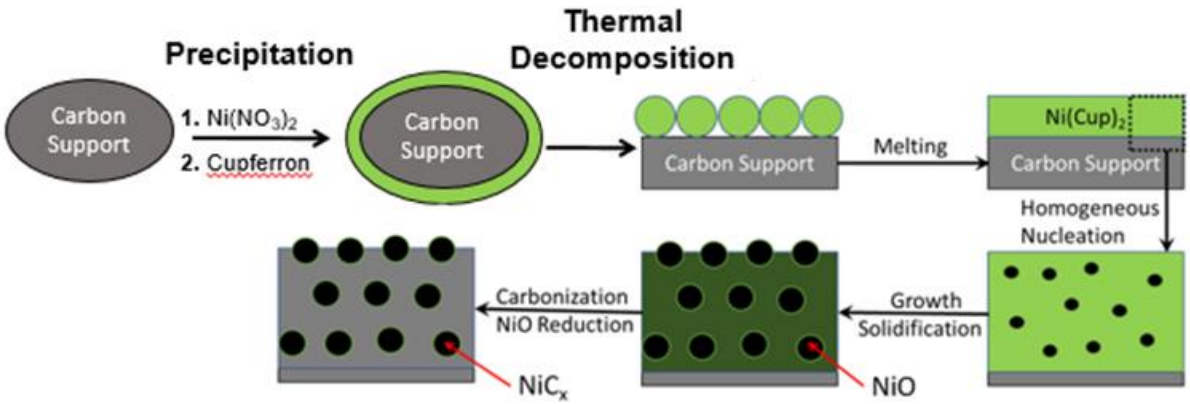


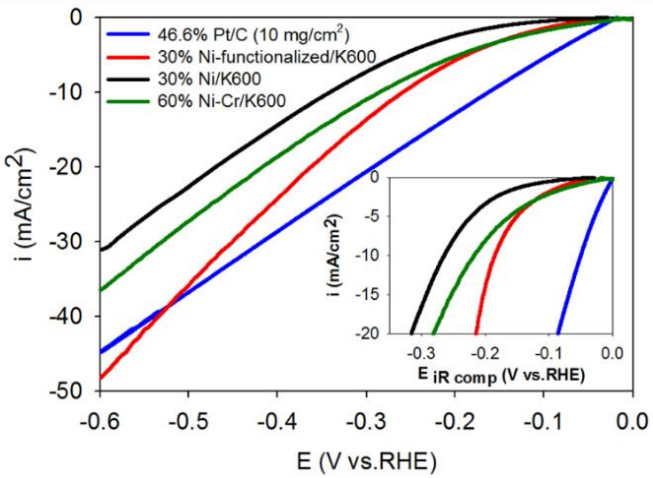
Approach - Materials Design Strategy: Non-PGM HER Electrocatalysts

❖ Strategy 1: State of the art Metal-Metal Oxide electrocatalysts

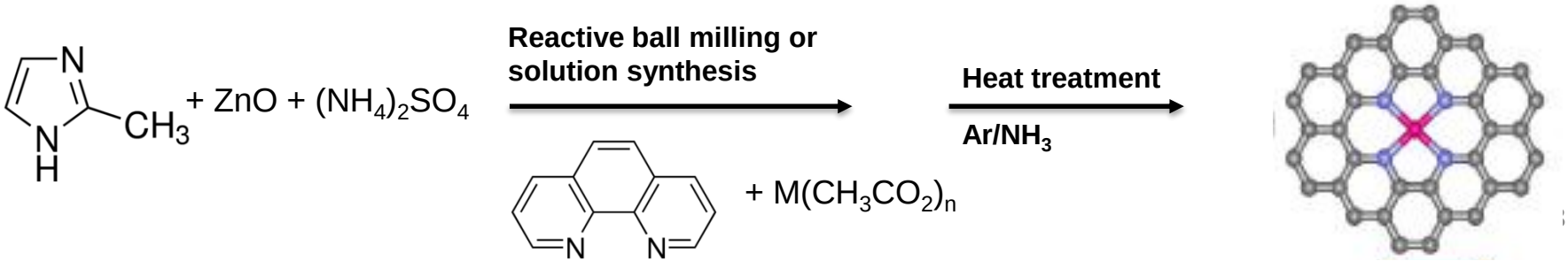


❖ Strategy 2: Functionalized mono-metallic electrocatalysts





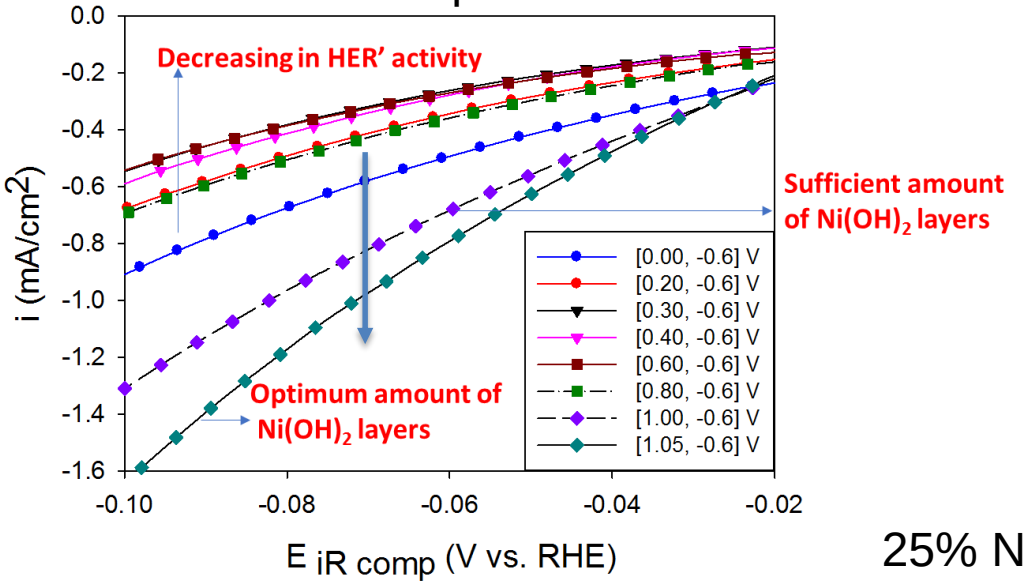
❖ Strategy 3: Embedded metal nanoparticle electrocatalysts



Approach - High Voltage Stability

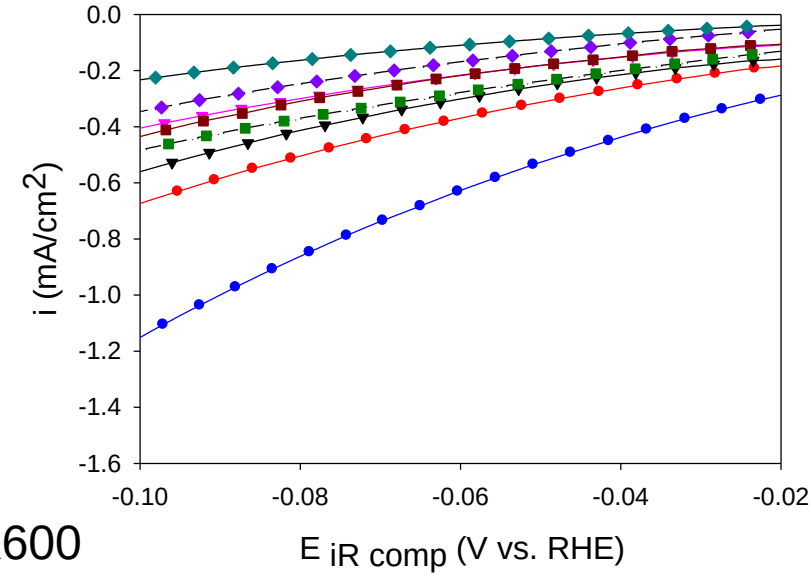
Improved HER function

30% Ni-cup/K600

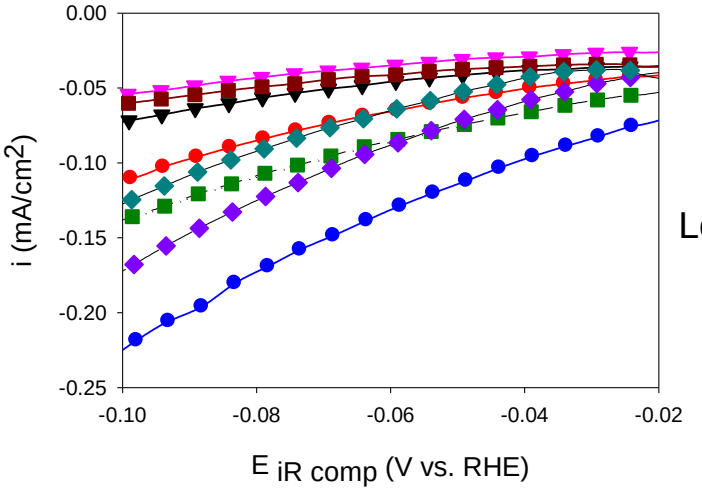


Lowered HER function

60% Ni-Cr/K600



25% Ni/K600

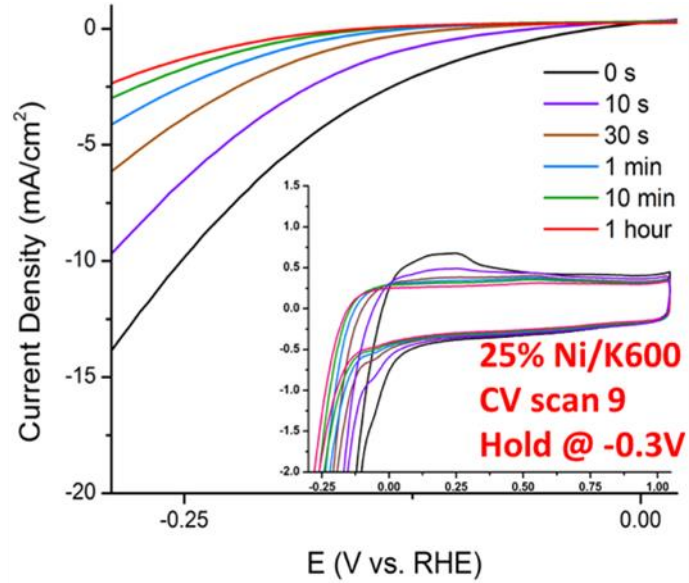


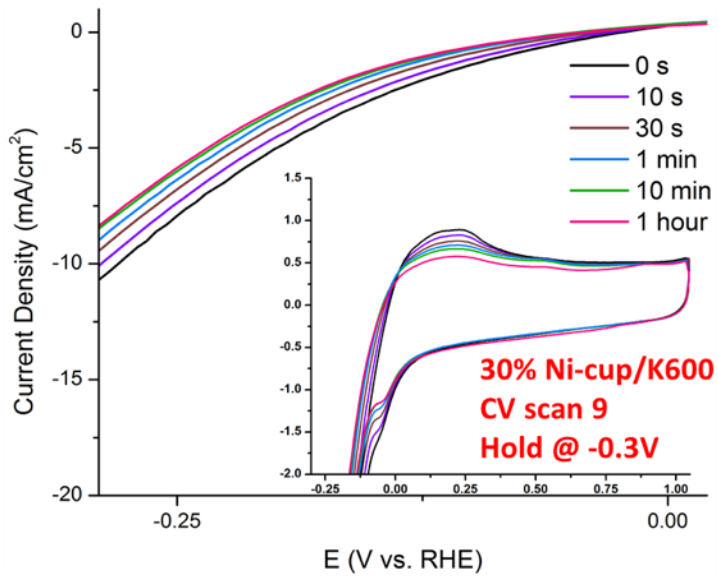
Lowered HER function

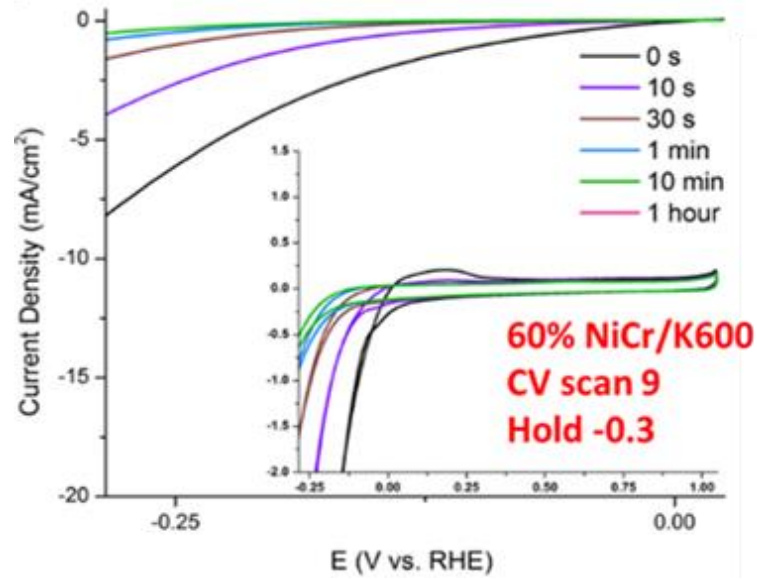
Approach - Cathodic Stability

- Hydride formation did not go past sub-surface in the case of Ni-cup/C, evidenced by stable HER's performance of initial and post 1h hold @ -0.3 V.
- In the case of both Ni/C and NiCr/C, hydride formation to go beyond surface and change the Ni lattice structure, resulting in lower HER performance
- Cycling the Ni-cup/C at high oxidation voltage did not oxidize the catalyst
- Opposite trend observed in the case of Ni/C and NiCr/C

Irreversible process for Ni metal.



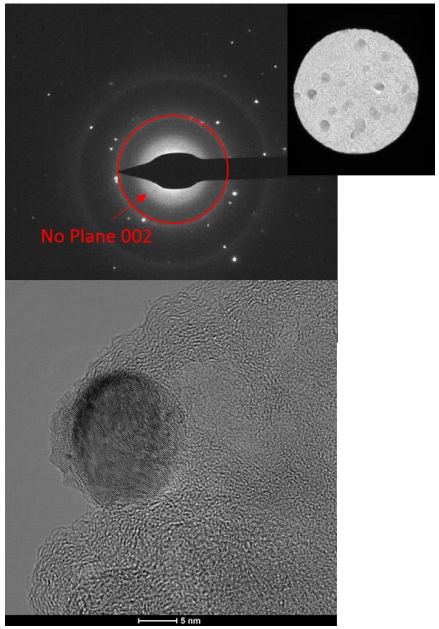




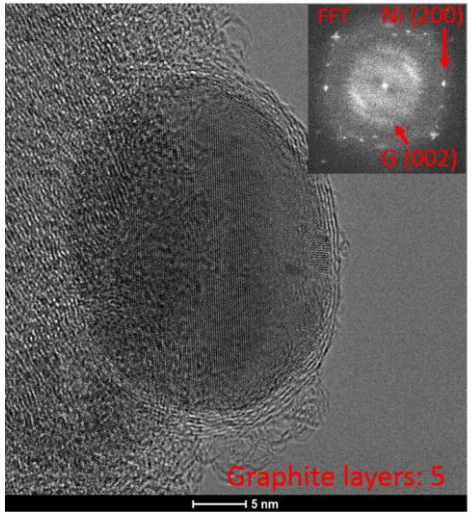
Approach – Surface Protection

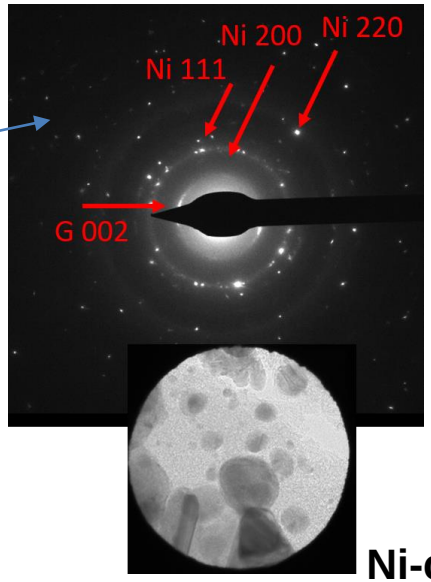
Ni reduced /K600 has no graphite.

Ni/K600



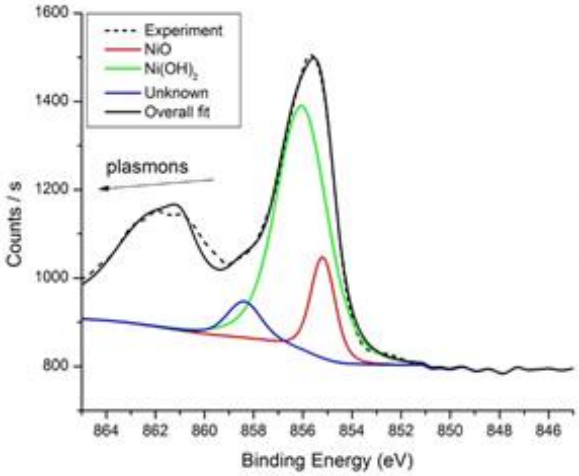
Ni-Cup

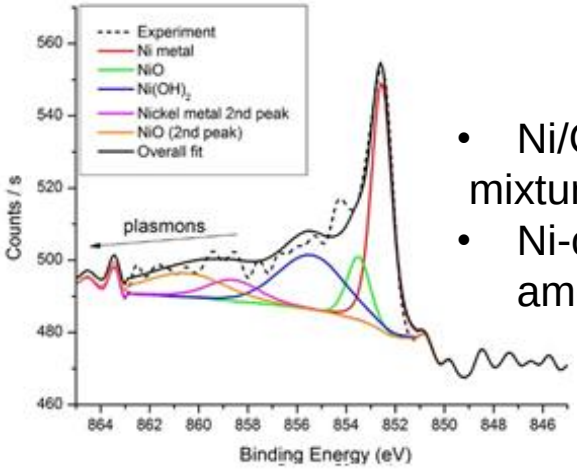




Ni-cup/ K600

- Multi SAD patterns show graphene plane (002)
- **Each Ni particle has about 5 graphite layers or more (some have 10 layers)**

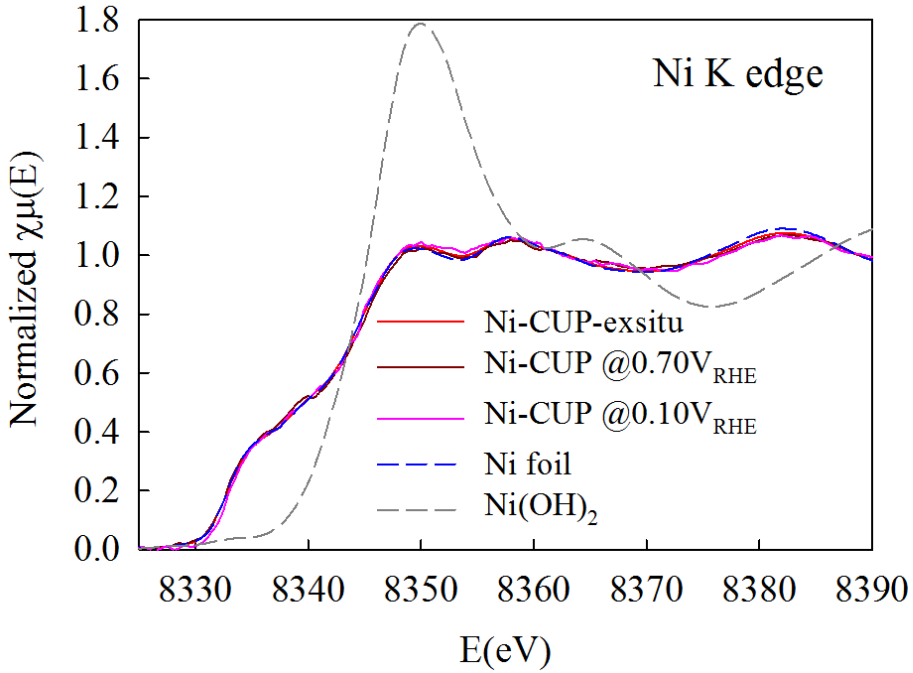


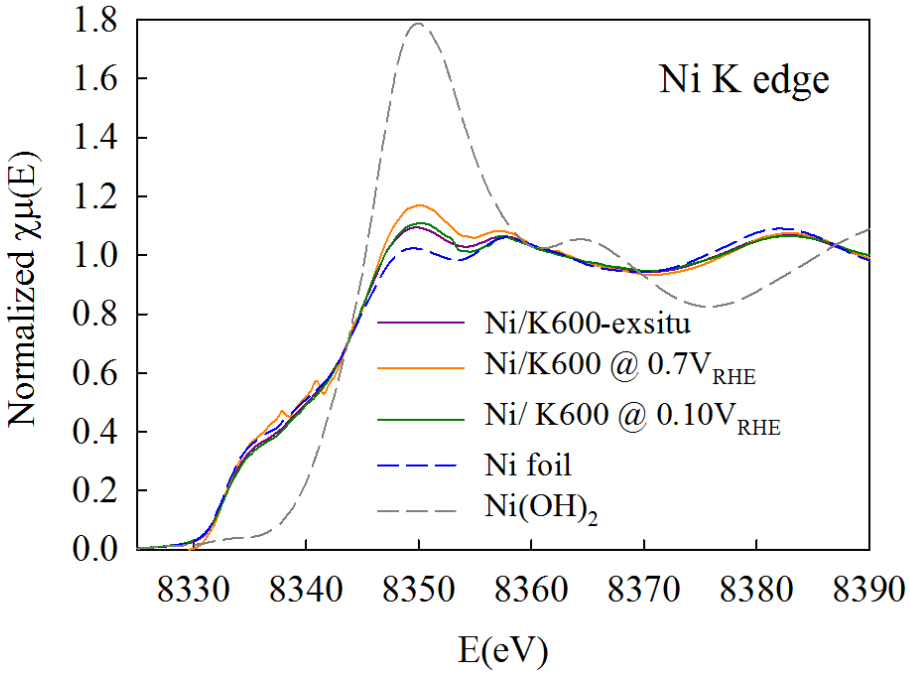


XPS

- Ni/C-No Metal-Surface comprised of a mixture of oxides
- Ni-cup/C-Surface Ni metal-Reduced amounts of surface oxides

Approach – Surface Protection



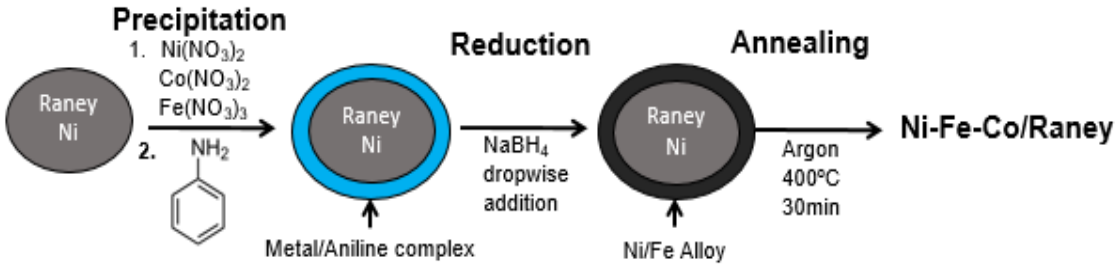


- At anodic potentials (0.1V and 0.7V vs. RHE), the Ni-cup/K600 remains at Ni(0) state, where the Ni/ K600 is oxidized even at 0.1 V vs. RHE.
- Hydrogen gas bubbles formed at cathodic potentials and interfered with the XAS acquisition.

Ni-Cup/C remains metallic (more noble) while Ni/C is oxidized

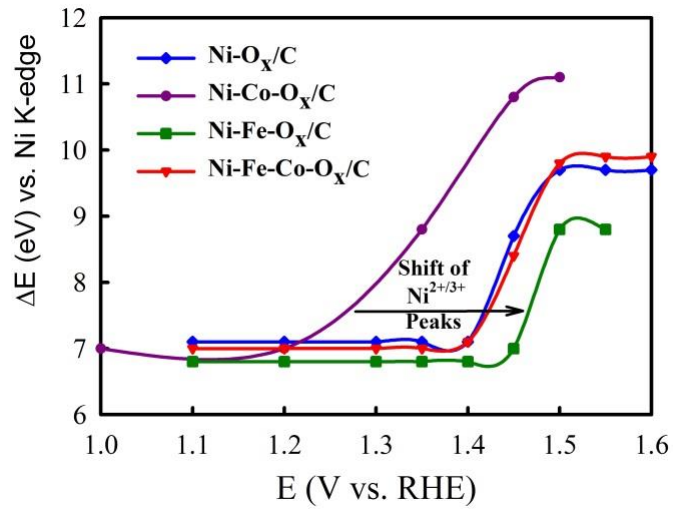
Approach - Mechanistic Aspects

Materials Strategy



- **Strategy 1: Improve surface area of Ni support**
- **Strategy 2: Improve active site density**
- **Strategy 3: Optimize Fe/Ni Ratio**

$\Delta\mu$ shift $\propto E$ in situ XAS



- ΔE (eV, XAS) vs
  - Fe stabilizes Ni in lower oxidation state
  - Co facilitates Ni oxidation

Yeager Mechanism (validated for base-metal oxides)

$2S^z + 2OH^-$ → $2S^z\text{-}OH + 2e^-$ (Fast adsorption of OH^-)

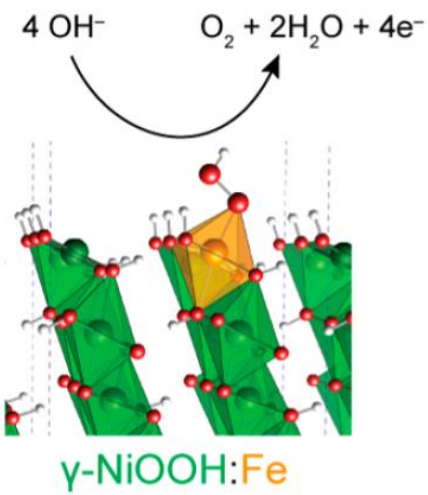
$2S^z\text{-}OH$ → $2S^{z+1}\text{-}OH + 2e^-$ (Oxidation of metal - rds)

$2\,S^{z+1}\text{-}OH + 2\,OH^-$ → $2S^z + O_2 + H_2O$ (Fast Acid-Base reaction)

- DFT results:

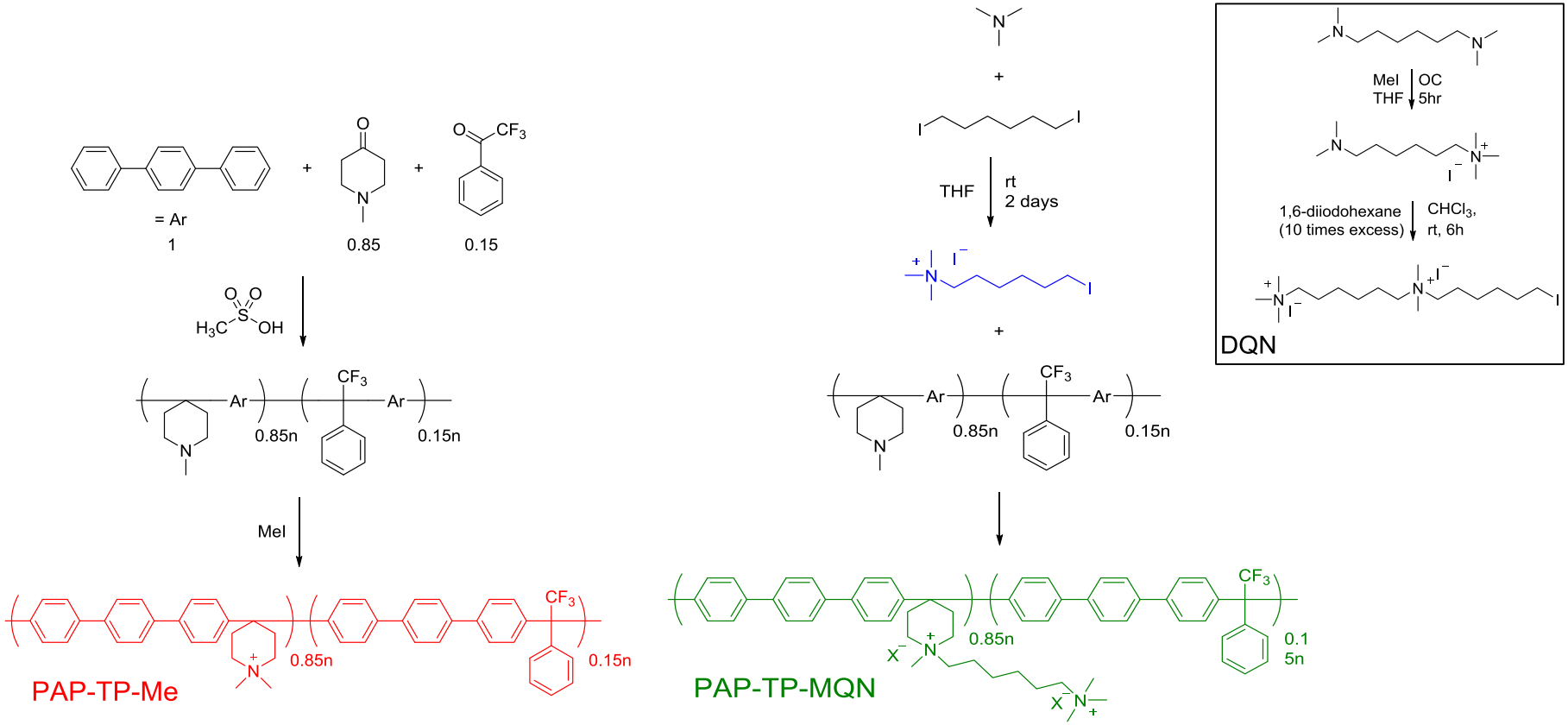
  Fe^{3+} sites exhibit optimized binding of -OH & -OOH intermediates

  Proton-transfer from Ni^{3+} redox shuttles



Bell et al. *JACS* **2015**

Approach – Ionomer Synthesis

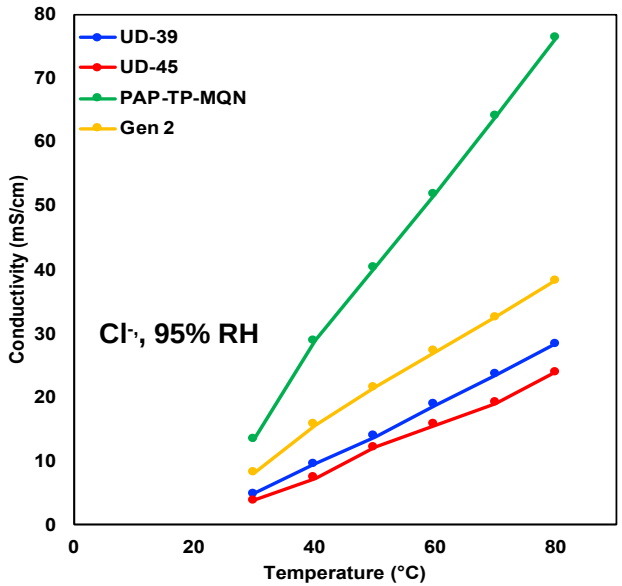


Milestone #	Project Milestone	Progress
2.1	Synthesis of PAP-TP polymers	**Completed**
2.2	Synthesis of two-ammonium-cations iodo-alky side-chain (DQN-I)	**Completed**
2.3	Synthesis of PAP-TQN polymers:	**Completed** (MQN-X side chain was found to be more suitable for synthesis rout and membrane properties)

Northeastern University
Center for Renewable Energy Technology

Accomplishments – Membrane stability and characterization

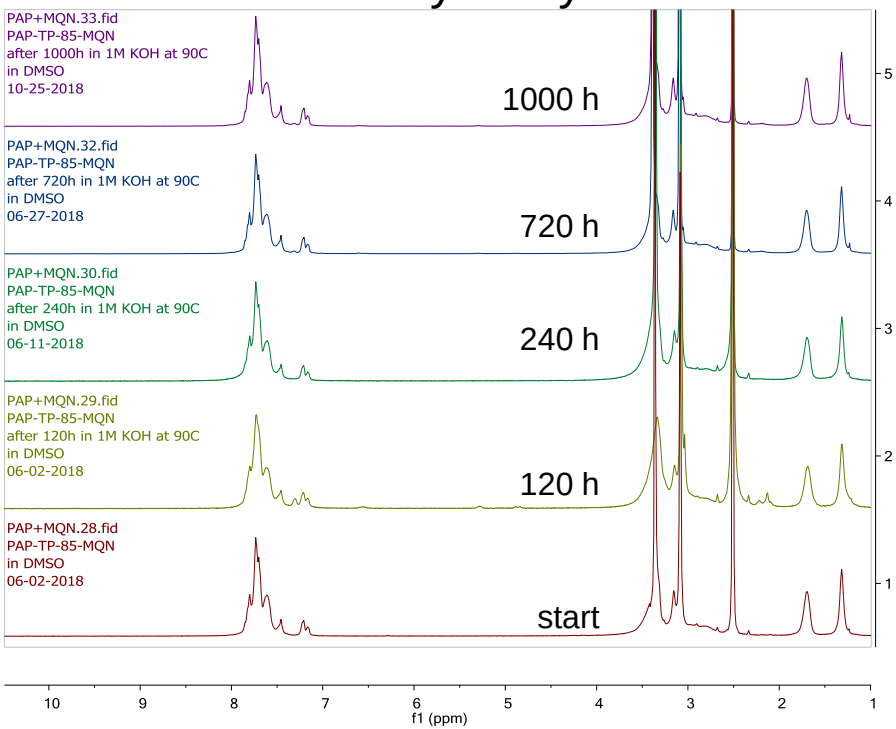
NREL Characterization



PAP-TP-MQN (UD-PAP)	24.3	No strip; melted
PAP-TP-85 (1) UD 39	17.6	16.5
PAP-TP-85 (2) (UD 45)	13	8

Milestone #	Project Milestone	Progress
Go/No Go	Achieve AEM membrane ASR of 0.15 Ω cm^2	**Completed**

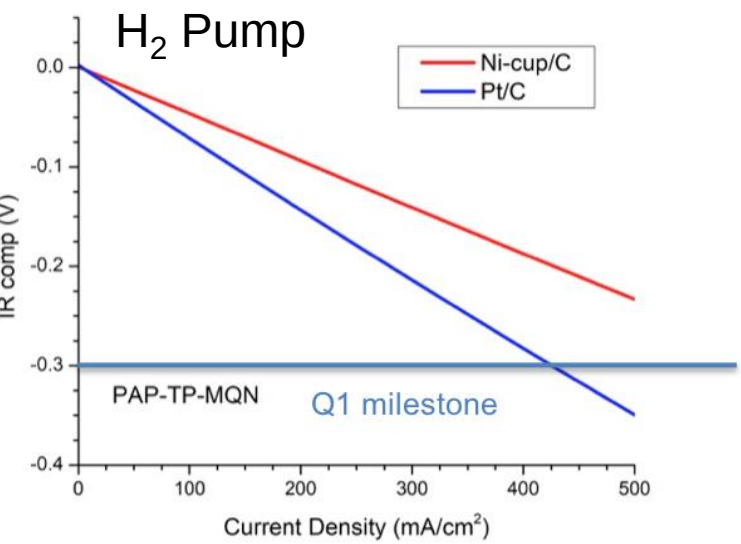
Stability study-U-Del



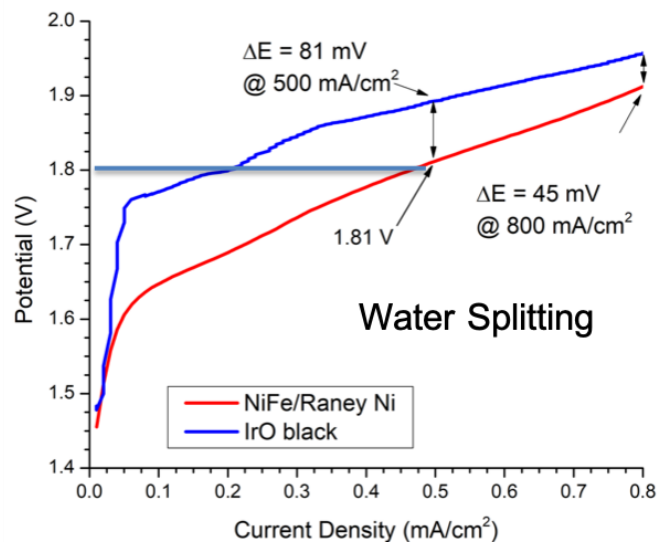
- $IEC_{titration}$: 2.9 mmol/g (Cl)
  IEC_{theory}: 3.1 mmol/g (Cl)
- Almost no change over 1000 h at 90 ^{O}C in 1M KOH solution observed by ^{1}H-NMR
- After 1000 hour in KOH: 0.025 ÷ 1 ÷ (85 %) ~ 2 % (decomposition yield)

Accomplishments – OER/HER catalysts

Temp: 60°C, HOR: Pt/C (TKK 47.2%),
Anode: Humidified H_2; Cathode: Humidified N_2,.

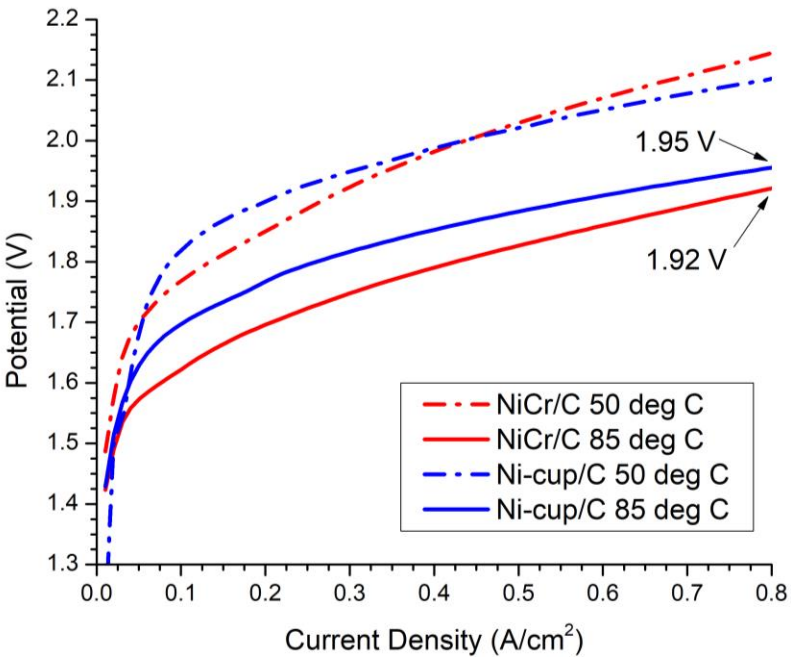


Milestone #	Project Milestone	Progress
1.1	Deliver three 5 gm batch samples of Ni-MOx/C HER catalysts for RDE and Single Cell tests with η of 300 mV @ 500 mA/cm2 and 2 A/cm3 (HER)	**Completed (did not meet overvoltage target)**
1.2	Deliver one 5 gm batch of Ni-Nx/C HER catalysts for RDE and Single cell studies η of 300 mV @ 500 mA/cm2 and 2 A/cm3 (HER)	**Completed**
1.3	Deliver one 5 gm batch of M-N(S)-C MOF HER catalysts for RDE and Single cell studies η of 300 mV @ 500 mA/cm2 and 2 A/cm3 (HER)	Catalyst was synthesized but <u>did not meet</u> performance milestone.
1.4	Deliver three 5 gm batches of MMOx OER catalysts for RDE and single cell tests	**Completed**
Go/No Go	**OER Electrocatalysts:** Using PGM-free OER electrocatalsyts in an AEM MEA operating under electrolysis conditions, at a current density of 500 mA/cm2 achieve 150 mV or lower over-voltage and 6 A/cm3 (VCD).	**Completed**



Water splitting cell equipped with at non-PGM OER electrode (NiFe/Raney) out performed a cell with an iridium oxide electrode. 1.8 V constitutes ~ 150 mV (η), Temp: 50°C.

Accomplishments - non-PGM MEA

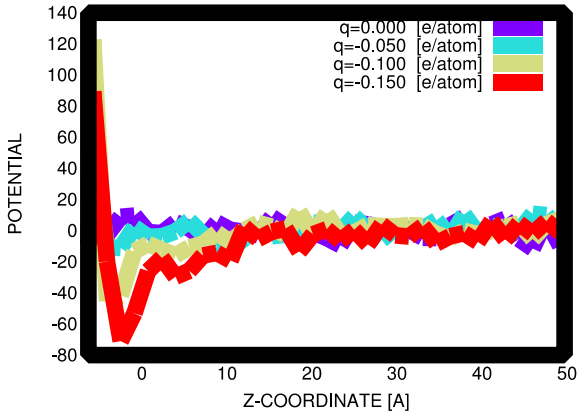


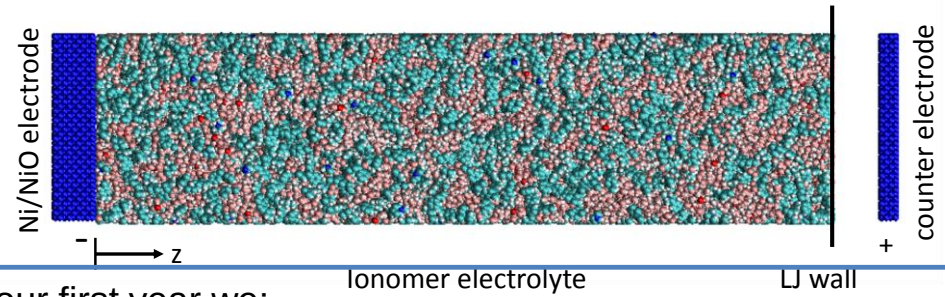
- NiFe/Raney Ni was used as the OER catalyst
- NiCr/C and Ni-cup/C required 1.92 and 1.95 V, respectively, to achieve a current density of 800 mA/cm^2
- High temperature stability of University of Delaware's ionomer materials enable this performance.
- Ni-cup/C and NiCr/C both showed similar stability in a water electrolysis cell.
- H_2 studies and RDE data suggests that over time, NiCr/C is less stable.

Milestone #	Project Milestone	Progress
Go/No Go		

Collaboration – SNL modeling

Potential as a function of surface charge

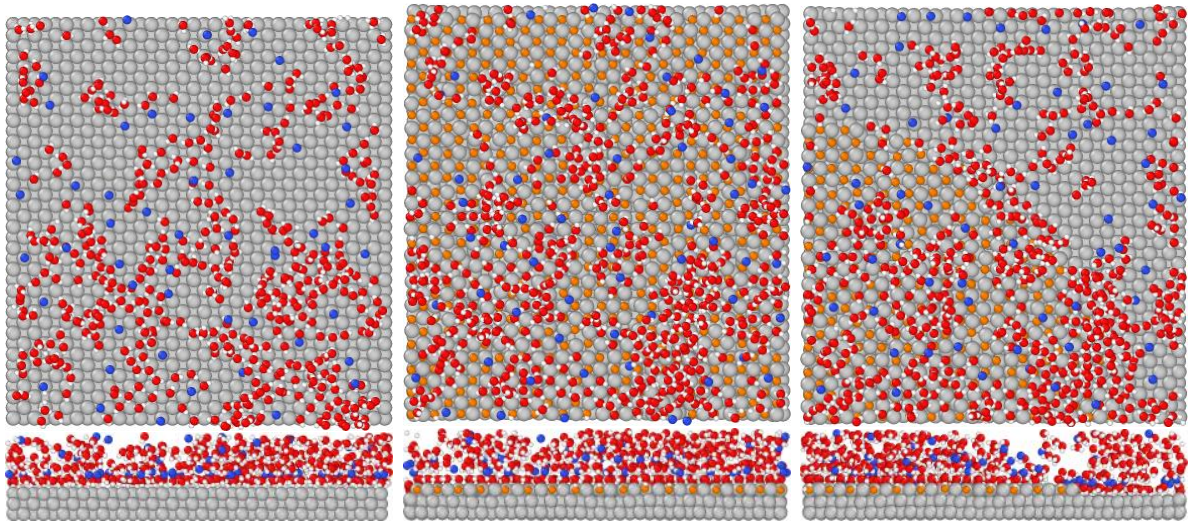




In our first year we:

- Built a molecular model of a standard PAP ionomer and Ni electrode using DFT and MD simulations
- Simulated the effects of charging the electrode on the ionomer and mobile species to tie local pH and other resolved quantities to water splitting efficiency

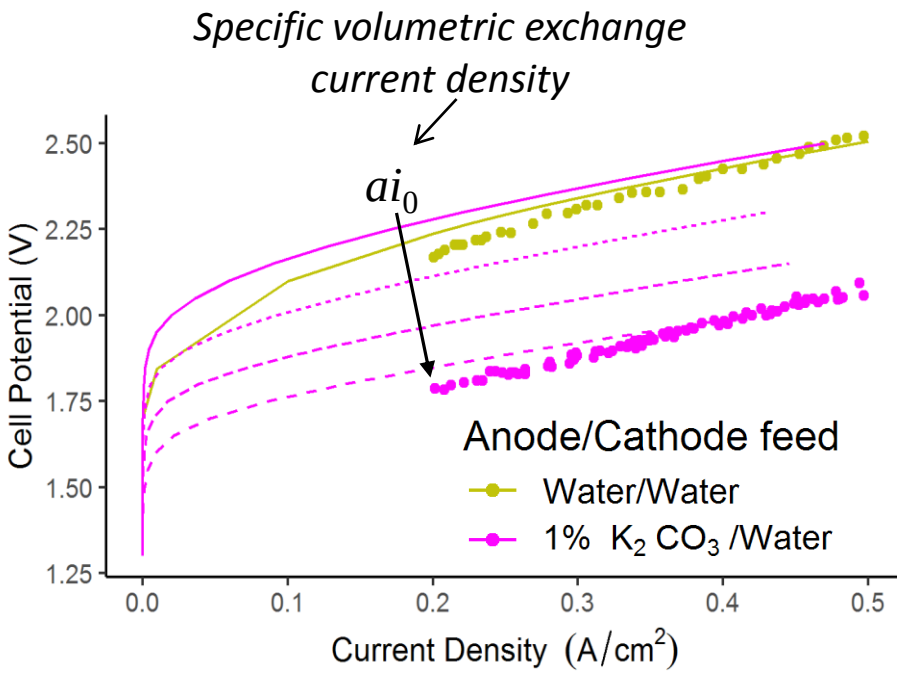
Water surface coverage for increase oxide coverage

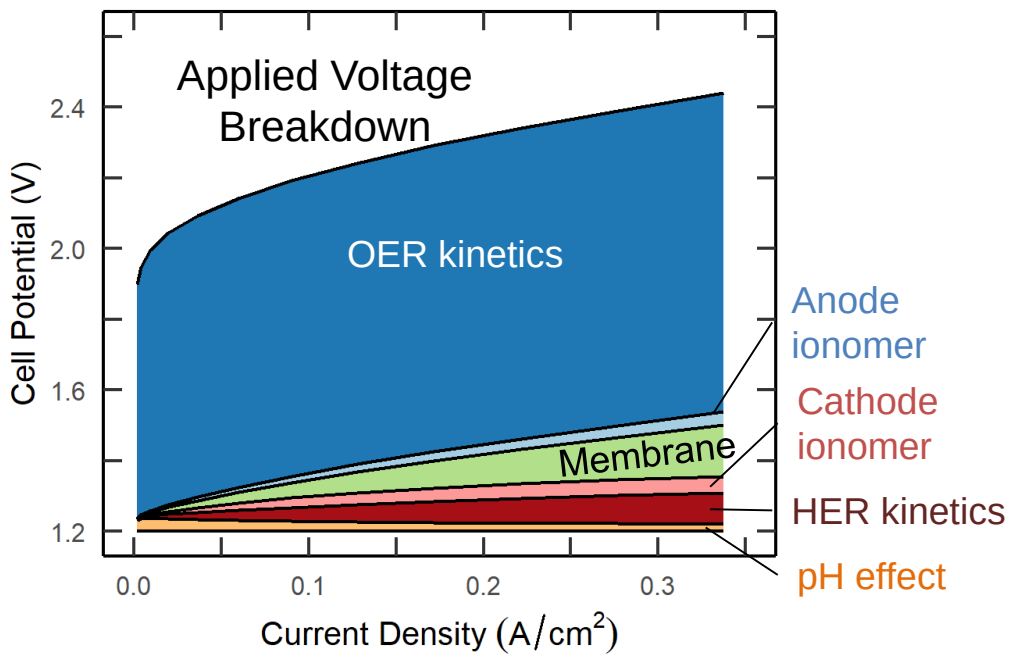


(a) bare Ni (b) NiO monolayer (c) partial NiO coverage
Quarter circle centered on lower left corner

Ni: gray, N+: blue, O: red, H: white

Collaboration – LBNL modeling



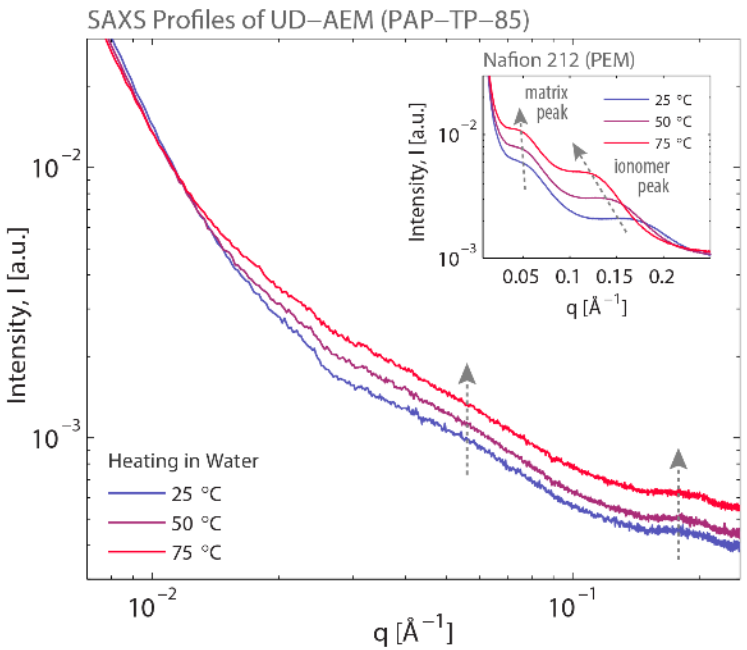


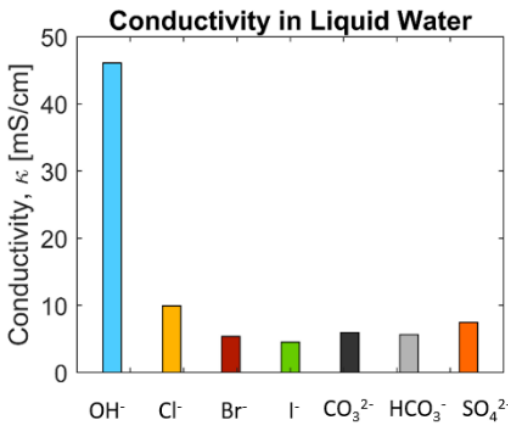
- Model fit to DI water-fed electrolyzer data from NEU
- Carbonate feed at the anode performs significantly better *despite* the predicted Nernstian voltage loss
  - Observed difference between feeding water and carbonate at anode equivalent to 1,000x increase in product of *active surface area* and *exchange current density*
    - Carbonate increases ionic pathways (decreased tortuosity) and maybe impacts kinetics

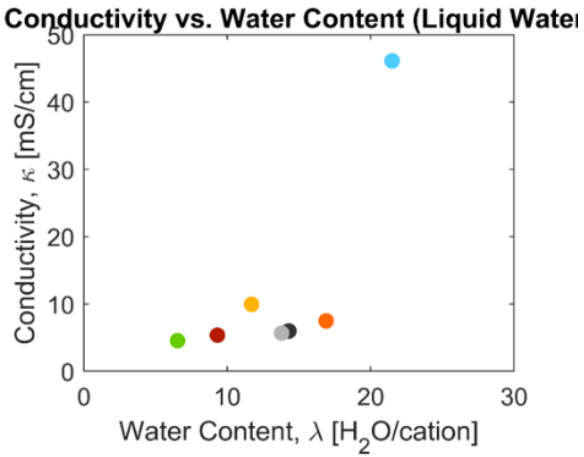
Collaboration – LBNL characterization

- AEM does not a strong phase-separation and structural features
  - Do not change with hydration
  - Do not change with <u>temperature</u>
    - AEM does not respond to environment the way other PEMs (e.g., Nafion) do. Indicates a set morphology that swells macroscopically without affecting nano-phase separation

- Conductivity in liquid water correlates with hydration (upon anion-exchange)
  - In OH form, conductivity is slightly lower than that of Nafion in proton form (~ 60-80 mS/cm)
  - OH form showing the highest uptake and conductivity
  - Reveals critical role of anion form and water content despite lack of a phase-separated nanostructure
  - Large shift in conductivity in OH form is in accord with the mixed, gel-like morphology facilitating hopping







Summary FY1

Catalyst development:

- HER Electrocatalysts: An overvoltage of 300 mV or lower was achieved at a current density of 500 mA/cm^2 using PGM-free HER electrocatalysts in an AEM MEA operating under electrolysis conditions.
- OER Electrocatalysts: At a current density of 500 mA/cm2 achieved at 150 mV using PGM-free OER electrocatalysts in an AEM MEA operating under electrolysis conditions,
- AEM MEA: Demonstrated a PGM-free AEM MEA electrolyzer performance of 0.8 A/cm2 at ≤1.92 V.

Membrane development:

- Reliable methods for preparing single and multi-cation polyaryl piperidinyl triphenyl AEM membranes were devised.
    - Physical properties of these materials such as ion-exchange capacity, physical stress, water uptake, swelling, and conductivity were obtained.
- University of Delaware materials showed an area-specific resistance of 0.048 $\Omega \cdot cm^2$
- Materials showed a loss of <2% of ion-exchange capacity after a 1000 hour treatment in 95 ^{O}C 1M KOH

Additional Activities

- Mathematical modelling of AEM electrolysis systems showed a decreased pH at the electrode/solution interface resulting in voltage loss. (LBNL)
- Modelling of the electrode/ionomer interface demonstrate the importance of the presence of surface metal oxides in facilitating the adsorption of water molecules. (SNL)
- SAXS profiles elucidate the microstructure of the UDel baseline membrane, showing its nanoscopic features remain consistent under various hydration conditions. (LBNL)

Proposed Future Work FY 2

1. **Materials Discovery**: (NEU & Udel) Q5-Q8
   - HER Catalysts: Ni-MOx-Nx catalyst optimization, stability tests, structure function determination.
   - OER catalyst: Enhance active site density of Ni-Fe-Co/Raney Ni.
   - Reinforced PAP-MQN membranes leading to PAP-TQN system for FY3.
   - Membrane and Ionomer: Extensive durability tests, Full Cell Testing at elevated temperatures
   - Electrodes and Ink Composition: New electrode design with novel ink compositions
2. **Cell Tests**: (NEU) Q6-Q8
   - Accurate determination of OER overvoltage
   - Optimization of Full Cell for long duration tests
3. **Detailed modeling of transport processe**s for deciphering carbonate effect (LBNL) Q6-Q8
4. **SAXS measurement** for membrane structure and morphology as a function of temperature, ion exchange and humidity (LBNL) Q6-Q8
5. **Interfacial modeling** to understand ionomer effects (Sandia) Q6-Q8
6. **Durability measurements** on PAP-MAC membranes (NREL) Q7-Q8
7. **MEA optimization and testing** (NREL) Q5-Q8

Publications and Presentations

Publications:

- Unifying Alkaline Hydrogen Evolution/Oxidation Reaction Kinetics by Identifying the Role of Hydroxy-Water-Cation Adducts. Ershuhai Liu, Li Jiao, Huong Doan, Zeyan Liu, Yu Huang, Kuzhikalail M. Abraham, and Sanjeev Mukerjee, *J. Amer. Chem. Soc.* **2019,** *141,* 3232-3239.
- Current Understanding of Sluggish Kinetics of Hydrogen Evolution and Oxidation reactions in Base. Qingying Jia, Ershuhai Liu, Li Jiao, and Sanjeev Mukerjee, *Current Opinion in Electrochemistry*. **2018,** *12,* 209-217.

Presentations:

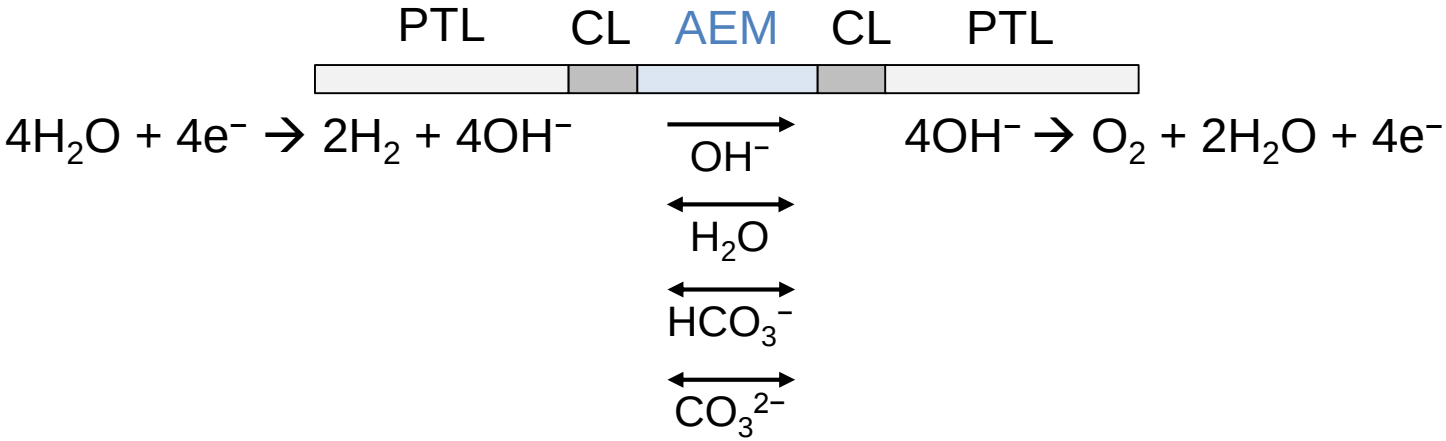
- Mukerjee, Sanjeev, and Qingying Jia. "Fundamental aspects of regenerative hydrogen electrocatalysis in alkaline pH." In *ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY*, vol. 256. 1155 16TH ST, NW, WASHINGTON, DC 20036 USA: AMER CHEMICAL SOC, 2018.
- Mukerjee, Sanjeev, Jingkun Li, and Qingying Jia. "Current Understandings of the Slow Kinetics of the Hydrogen Evolution Reaction in Alkaline Media." In *Meeting Abstracts*, no. 29, pp. 1703-1703. The Electrochemical Society, 2018.
- Qingying Jia, Jingkun Li and Sanjeev Mukerjee. “Understanding the Improved Kinetics of the Hydrigen Evolution/Oxidation Reactions on Pt-Oxophilic Metal Systems in Alkaline Media.” In Meeting Abstracts, no 29, pp 1710-1710. The Electrochemical Society, 2018.
- Ian Kendrick, Michael Bates, Qingying Jia, Huong Doan, Wentao Liang and Sanjeev Mukerjee. “Tuning Ni Surfaces for Enhanced Oxygen Evolution Reaction.” In *Meeting Abstracts*, no 29, pp 1702-1702. The Electrochemical Society, 2018.

Technical Backup Slides

Mathematical Model

- **Model overview**

1-D cell model



- **Model physics**

Thermodynamics

Standard cell potential
Equilibrium H_2O content
membrane, liquid, vapor

Kinetics

Butler-Volmer for HER and OER
H_2O phase change

Transport

Stefan-Maxwell diffusion
for gas-phase components
Darcy's law for liquid, gas phases
Ohm's law for e^- current
Modified Ohm's law for ion current
H_2O transport by ion drag
H_2O diffusion in membrane
Enthalpy balance for energy

Conserved quantities

Mass; Charge; Energy

Constitutive relations

Faraday's law
Ideal-gas law

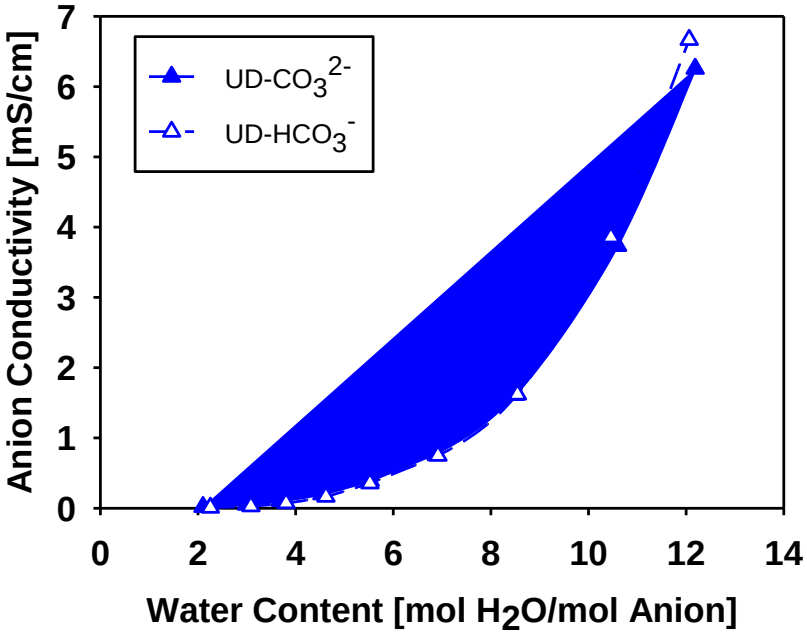
Properties

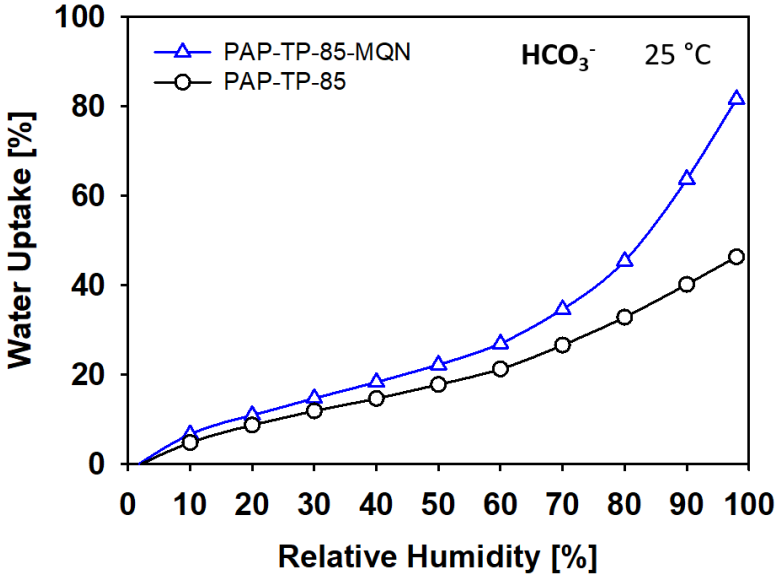
Function of *T*
and H_2O content

Equations (12): 7 2nd-order PDEs; 5 Algebraic equations

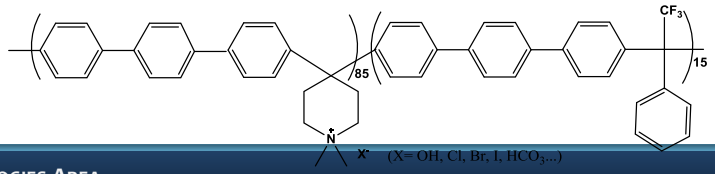
Anion Conductivity (κ) of PAP-TP-85 in Water Vapor

- PAP-TP-85: HCO_3^- form possesses slightly greater κ than CO_3^{2-} counter ion for given hydration number
- PAP-TP-85-MQN exhibits greater water uptake than PAP-TP-85 for a given RH, which could be due its higher IEC value (3.0 VS. 2.1 mmol/g)
  - MQN has also higher conductivity



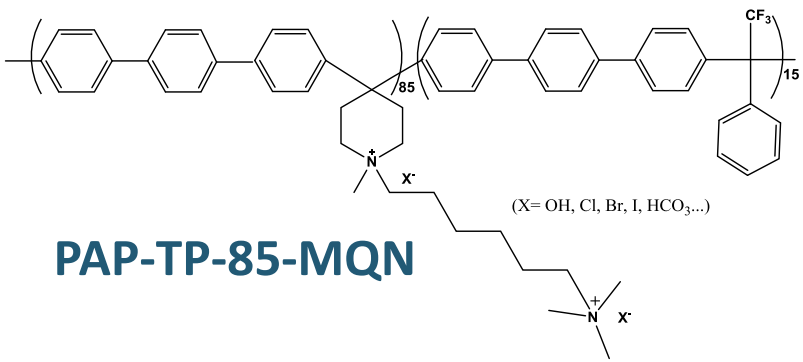


PAP-TP-85

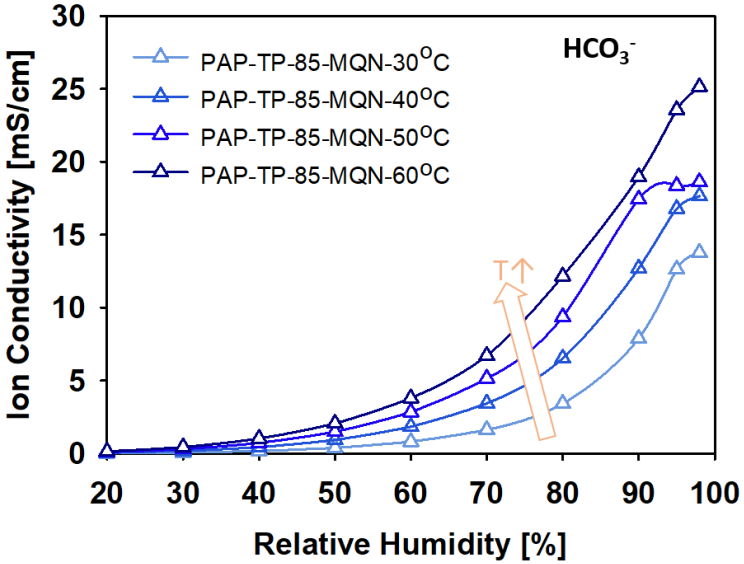


Anion Conductivity: Temperature Impact

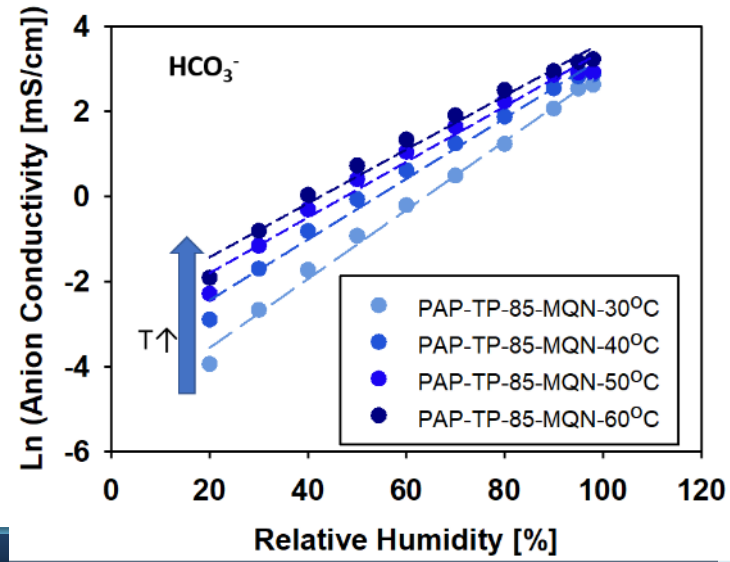
Optional slide on conductivity-temperature of new chemistry



PAP-TP-85-MQN



- **The anion conductivity of PAP-TP-85-MQN increases with temperature**
- **Activation energy of anion conduction decreased from 56.5 to 15.5 kJ/mol, when increasing the RH from 20 to 98%**
  - The plotting of Ea as a function of RH is in progress

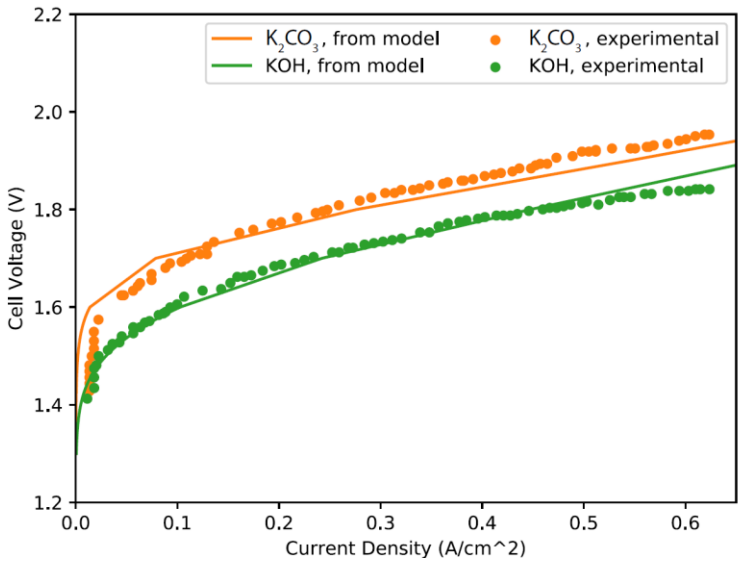


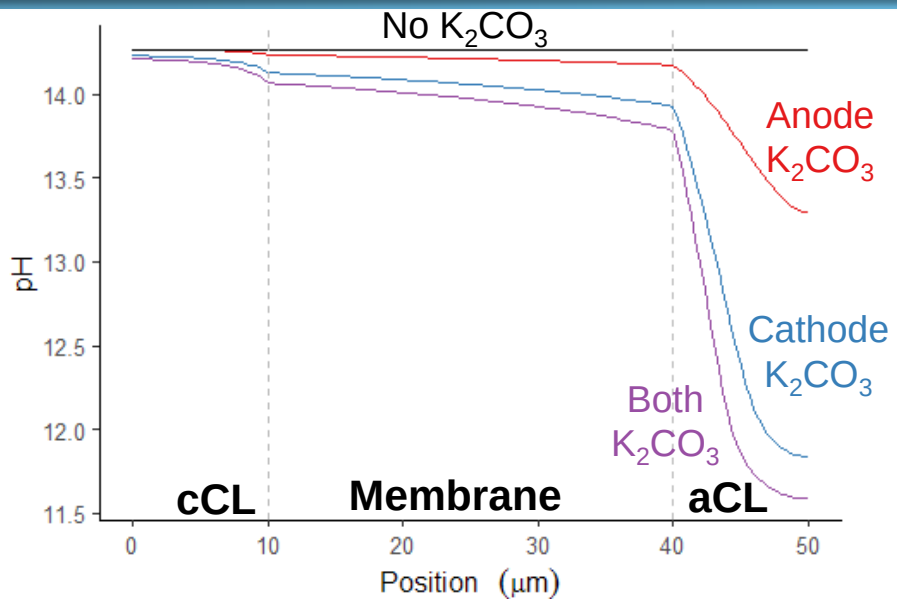
Notes and Comments

Not for AMR – this slide provides a status update and comments

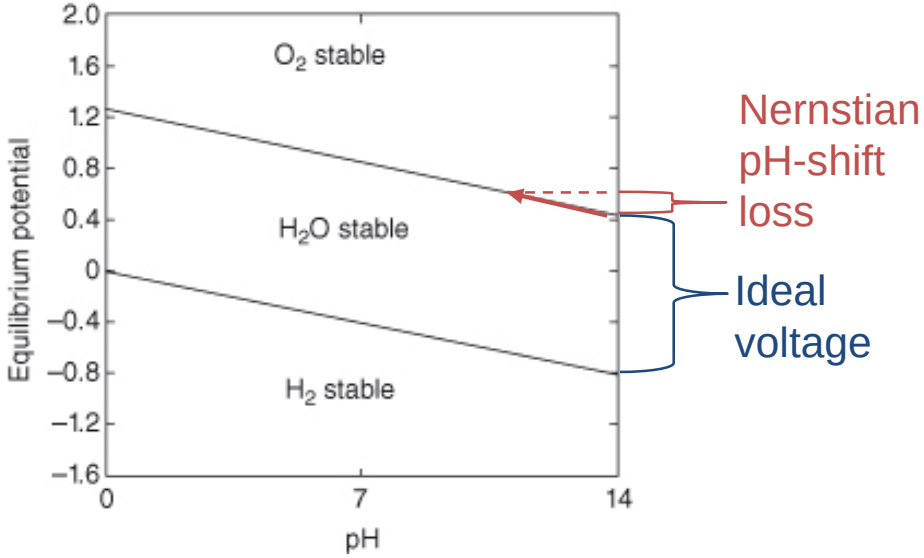
- **Slide -1: Summary (self-contained)**
  - New results showing temperature-**in**dependent morphology in water
- **Slide -2: Comparison of New (MQN) AEM**
  - It exhibits higher uptake and conductivity than the previous set
- **Key overall findings:**
  - Lack of a strong phase-separated morphology indicates a gel-like structure with strong ion concentration which cause a big shift in OH conductivity due to effective facilitation of hopping
  - For the same reason activation energy for conductivity shows a strong dependence on hydration (RH)
  - In hydrated state, lack of morphological changes with heating agrees with the low activation energy for conductivity
- **Our data analysis will continue this year to draft a paper summarizing these results**

Collaboration – LBNL modeling





- **Electrolyzer model matches literature data[1] for KOH vs K_2CO_3 electrolytes**
- **pH gradient results in Nernstian voltage loss for K_2CO_3 electrolytes**



[1] C. C. Pavel *et al.*, *Angew. Chemie - Int. Ed.*, vol. 53, no. 5, pp. 1378–1381, 2014.