2018 DOE Hydrogen and Fuel Cells Program Review

Developing Novel Platinum Group Metal-Free Catalysts for Alkaline Hydrogen and Oxygen Evolution Reactions

(DE-EE0008082)

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Project ID#: pd156

Project Overview

Award #	EE0008082
Start Date Year 1 End Date Project End Date	10/1/2017 9/30/2018 9/30/2020
Total DOE Share Total Cost Share Year 1 DOE Funding	$1.0M $0.1M $0.25M

Project Partners

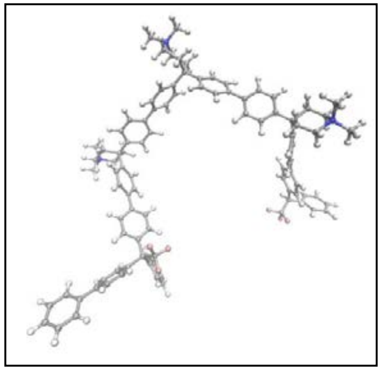
PI: Sanjeev Mukerjee - Northeastern University

Partner organizations:

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

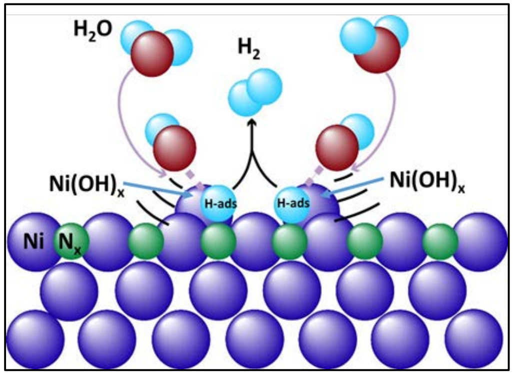
Project Vision

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.



Approach - Summary

Project Motivation

The focus of this project is on durable, high-performance materials advanced water splitting, enabling a pathway for achieving $<\$2/\text{Kg}_{H2}$ 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	Baseline	Year 1
Cell voltage	V	2	1.92
Current density	A/cm^2	0.5	0.8
Operating temp	^{O}C	80	80
Membrane ASR	Ω cm^2	.13/.08	0.15
HER volumetric + overvoltage @500 mA/cm^2, 25 ^{O}C	A/cm^3 mV	1.7/3.46 350-400	2 300
OER volumetric activity @1.47V_{RHE}, and overvoltage @500 mA/cm^2, 25 ^{O}C	A/cm^3 mV	18.7/6.45 200	6 150
Model voltage	V	1.65	1.74
Unexplained voltage loss	V	0.35	0.18

Approach - Summary

Partnerships and Roles

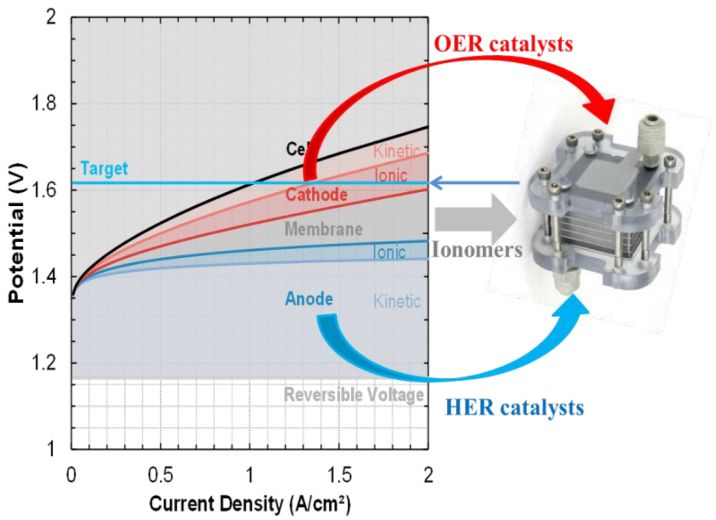
- *Northeastern Univ*., (Prime) Boston, MA: S. Mukerjee (P.I):
  - **Novel HER catalysts:**
    - Metal-Metal Oxides
    - Functionalized mono-metallic
    - Embedded Metal-N-C Systems
  - **Novel OER Catalysts:**
    - Double layer metal oxides on Raney Ni (strategies for increasing active site density)
  - **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^{o}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

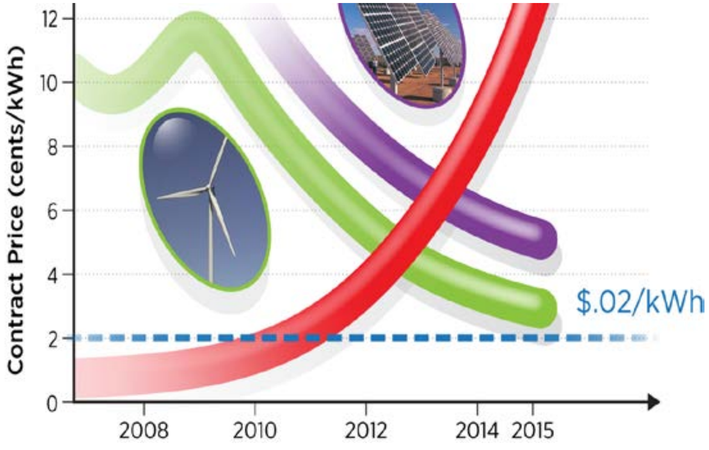
Relevance and Impact

- 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:

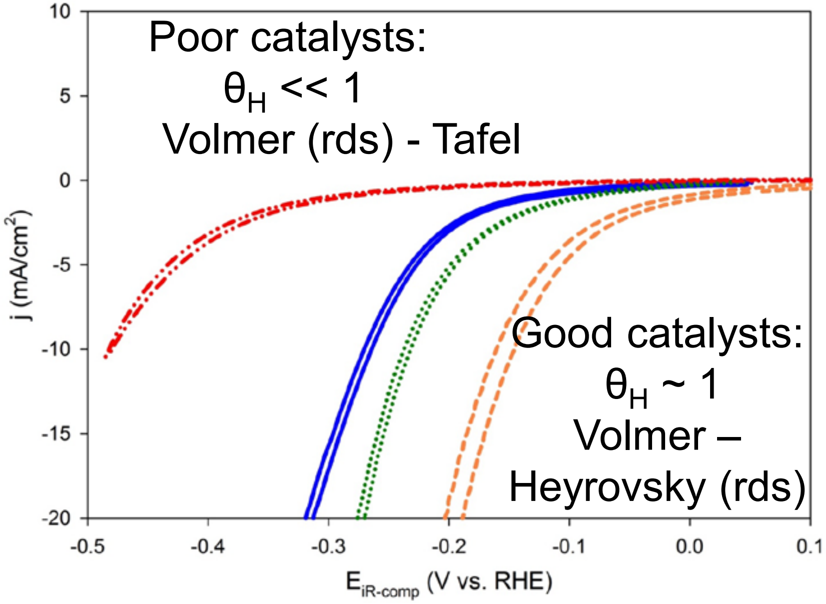
$M + H_2O + e^- \rightarrow M\text{-}H_{ads} + OH^-$

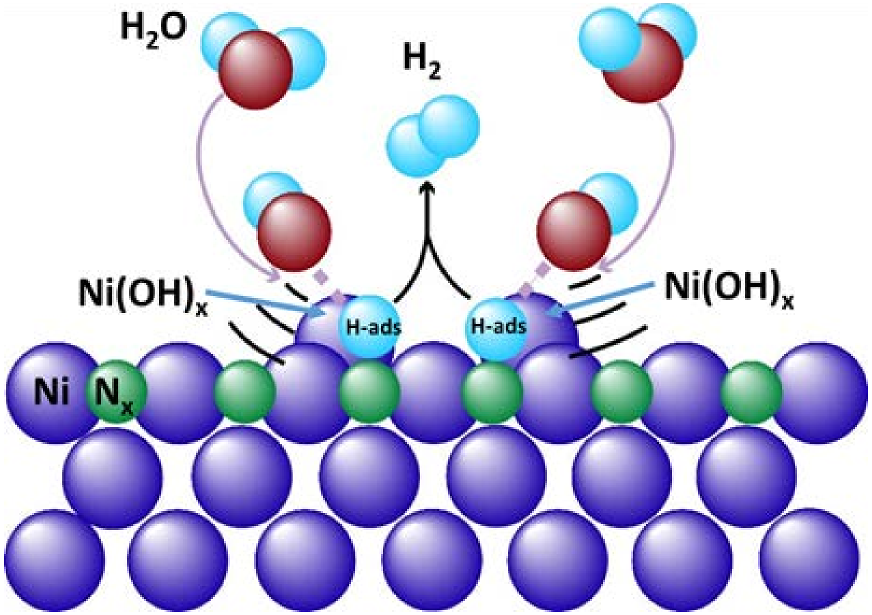
Heyrovsky:

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

Tafel:

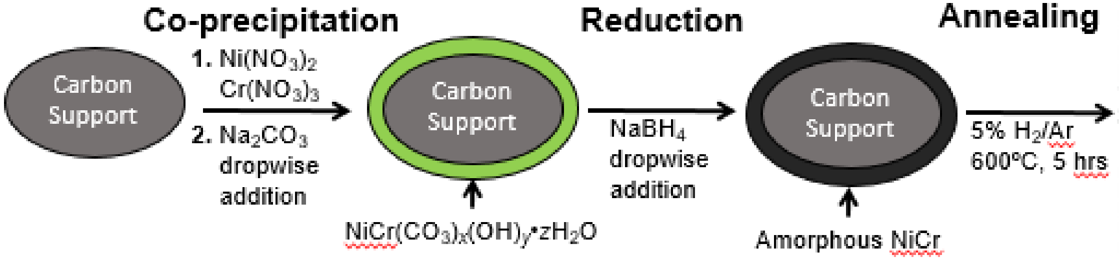
$2\ Pt\text{-}H_{ads} \rightarrow H_2$





Approach - Materials Design Strategy: Non-PGM HER Electrocatalysts

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



Co-precipitation

Carbon Support

1. $Ni(NO_3)_2$ $Cr(NO_3)_3$
2. Na_2CO_3 dropwise addition

Carbon Support

$NiCr(CO_3)_x(OH)_y{\bullet}zH_2O$

Reduction

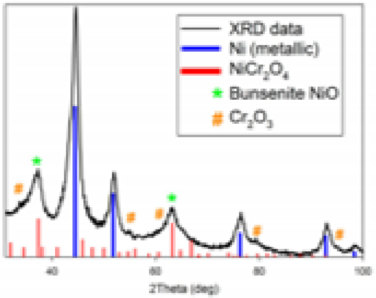
$NaBH_4$ dropwise addition

Carbon Support

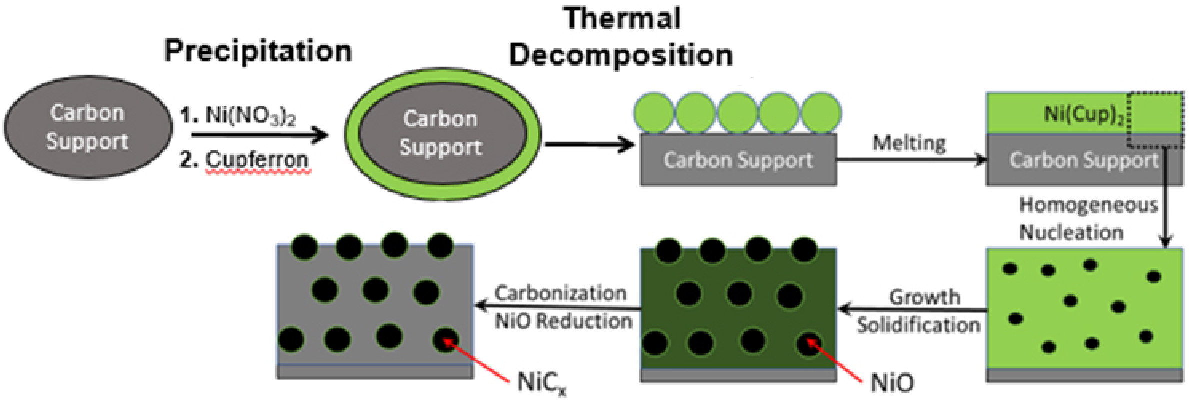
Amorphous NiCr

Annealing

5% H_2/Ar
600°C, 5 hrs



❖ Strategy 2: Functionalized mono-metalic electrocatalysts



Precipitation

Carbon Support

1. $Ni(NO_3)_2$
2. Cupferron

Carbon Support

Thermal Decomposition

Carbon Support

Melting

$Ni(Cup)_2$

Carbon Support

Homogeneous Nucleation

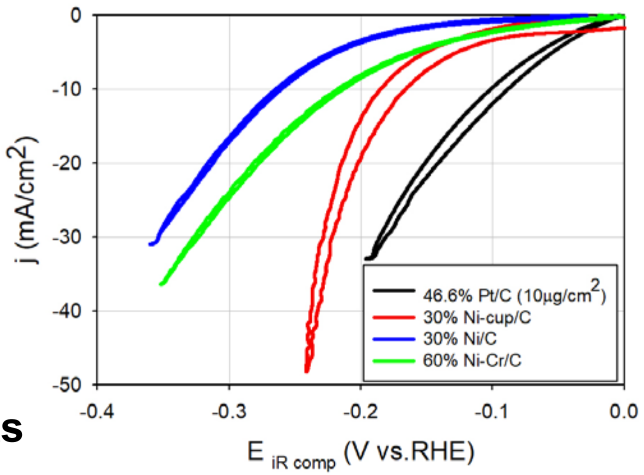
Growth Solidification

NiO

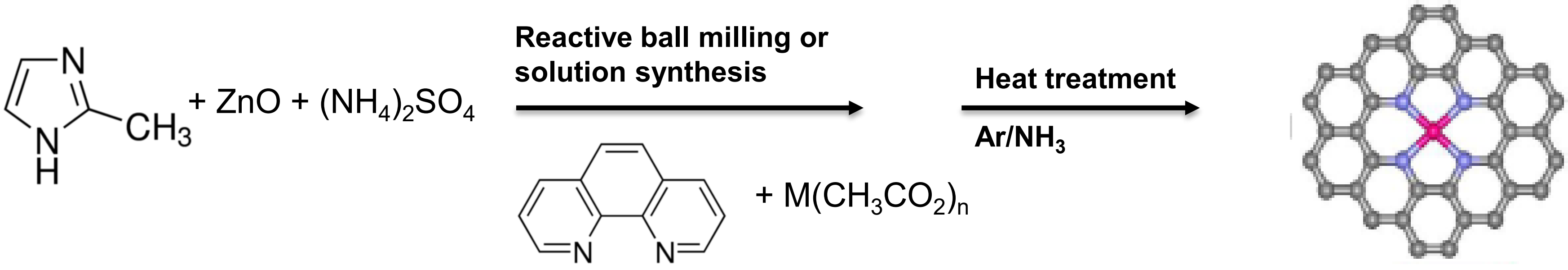
Carbonization NiO Reduction

NiC_x

Comparison of HER activity of non-PGM catalysts
50 µg/cm2 - 0.1M KOH (H2 purged) -rpm, 50°C



❖ Strategy 3: Embedded metal nanoparticle electrocatalysts



+ ZnO + $(NH_4)_2SO_4$

Reactive ball milling or solution synthesis

+ $M(CH_3CO_2)_n$

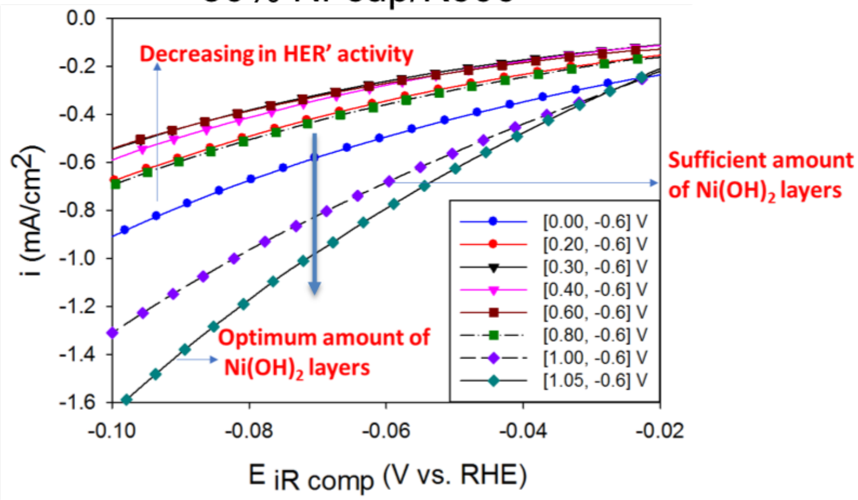
Heat treatment

Ar/NH_3

High Voltage Stability

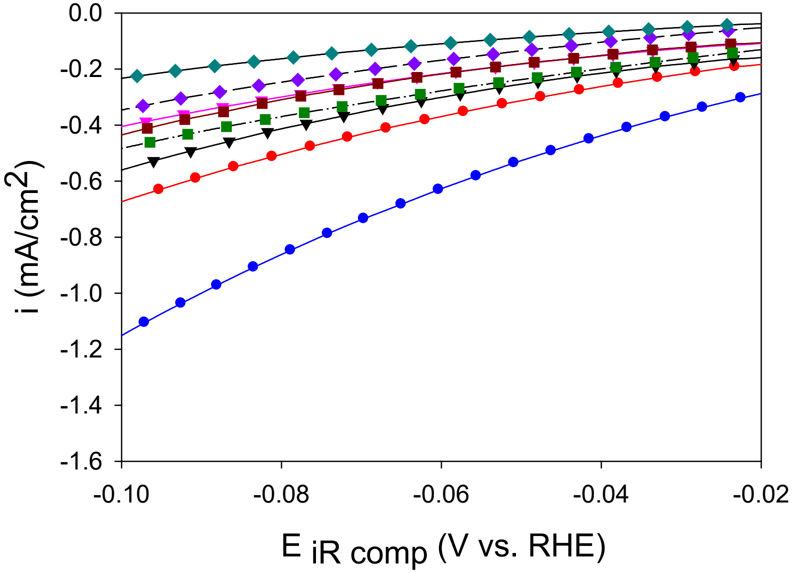
Improved HER function

30% Ni-cup/K600

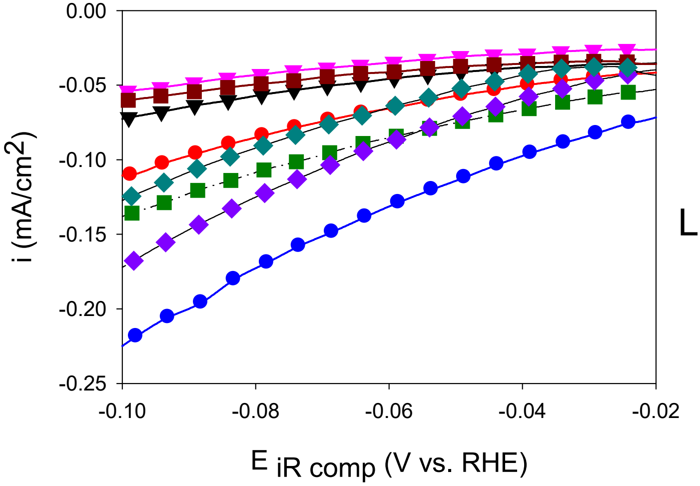


Lowered HER function

60% Ni-Cr/K600



25% Ni/K600



Lowered HER function

Approach - Cathodic Stability

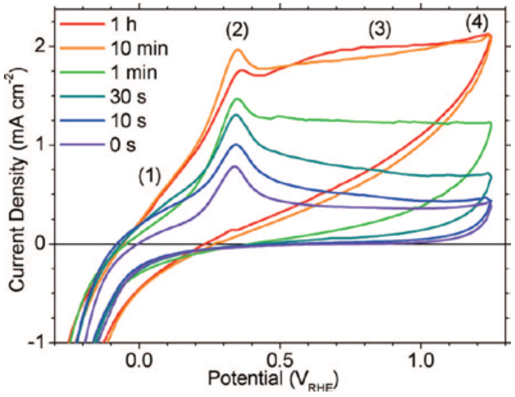
Reaction Reference to CV regions

(2) Ni(s) +xH_2O(l)+ x e− → ß − NiHx(s) + x OH^-(aq), x = 0.60 − 0.65 @ -0.12/-0.13 V vs. RHE

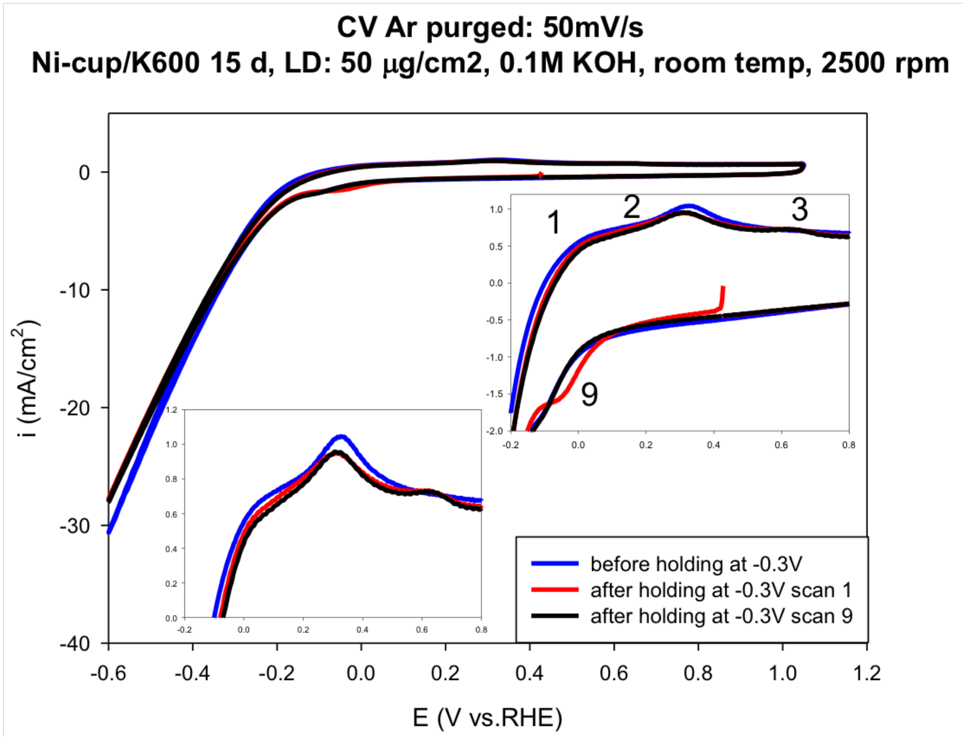
Ni(s) + x H_2O(l) + x e− → α − NiHx(s) + x OH−(aq), x = 0.01 − 0.03 @ -0.075/-0.095 V vs. RHE

(9) ß-Ni$(OH)_2$(s) + 2 e− → Ni(s) + 2OH^-(aq) @ 0.108 V vs. RHE

NiO (s) + H_2O(l) + 2 e− → Ni(s) + 2OH−(aq) @ 0.132 V vs. RHE



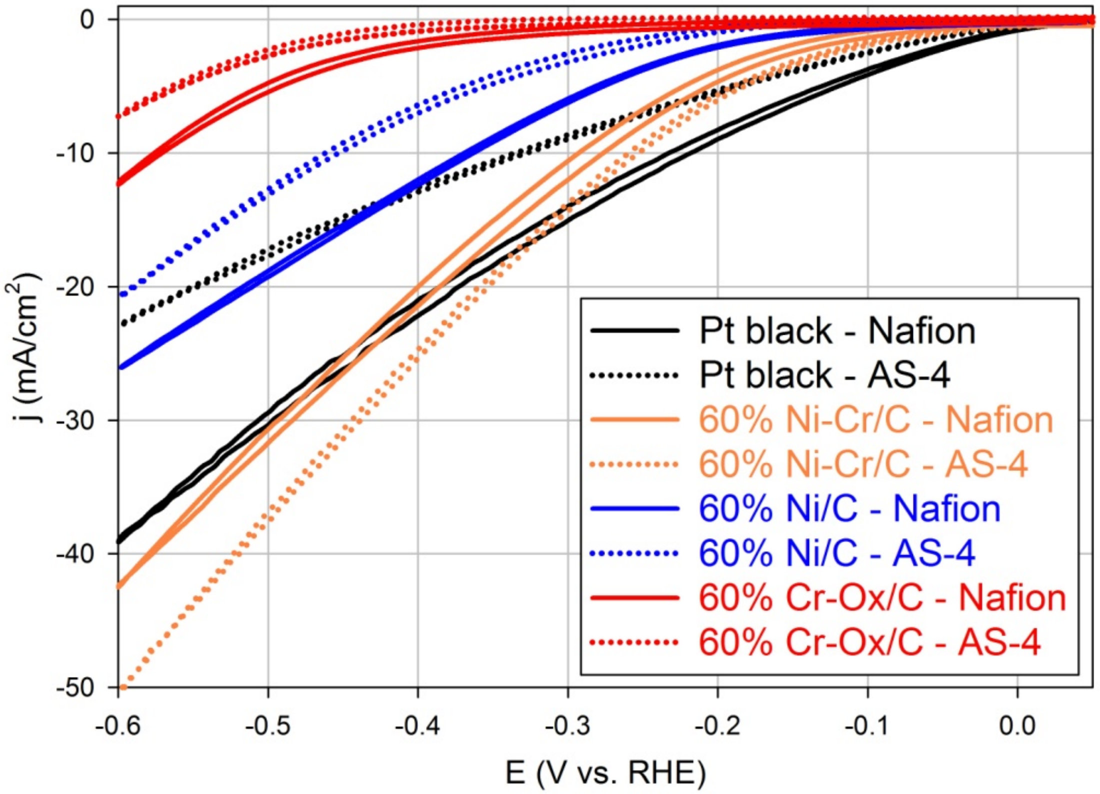
Freshly polished Ni electrodes were held at −300 mVRHE for various periods then scanned at 100 mV s−1 in Ar-purged 0.1 M KOH.(Hall 2013)


CV Ar purged: 50mV/s
Ni-cup/K600 15 d, LD: 50 µg/cm2, 0.1M KOH, room temp, 2500 rpm

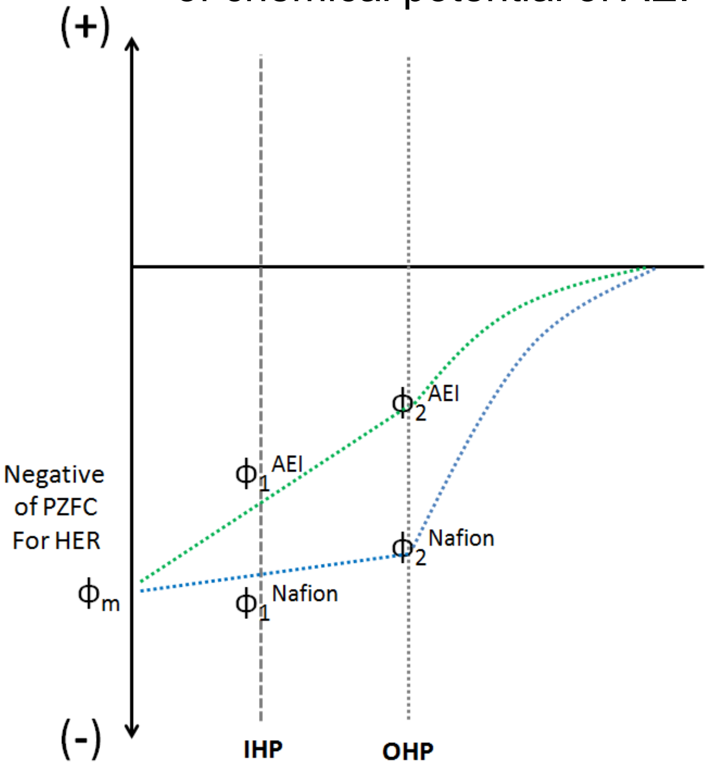
Irreversible process for Ni bulk material.

- Before and after holding at -0.3V, the HER's activity mostly remain the same.
- The structure of Ni-cup/K600 changed after holding at -0.3 V. The peak at 0.6 V indicates the more Hx was incorporated in the Ni lattice after holding at -0.3 V for 1 h.

Approach - Ionomer effects

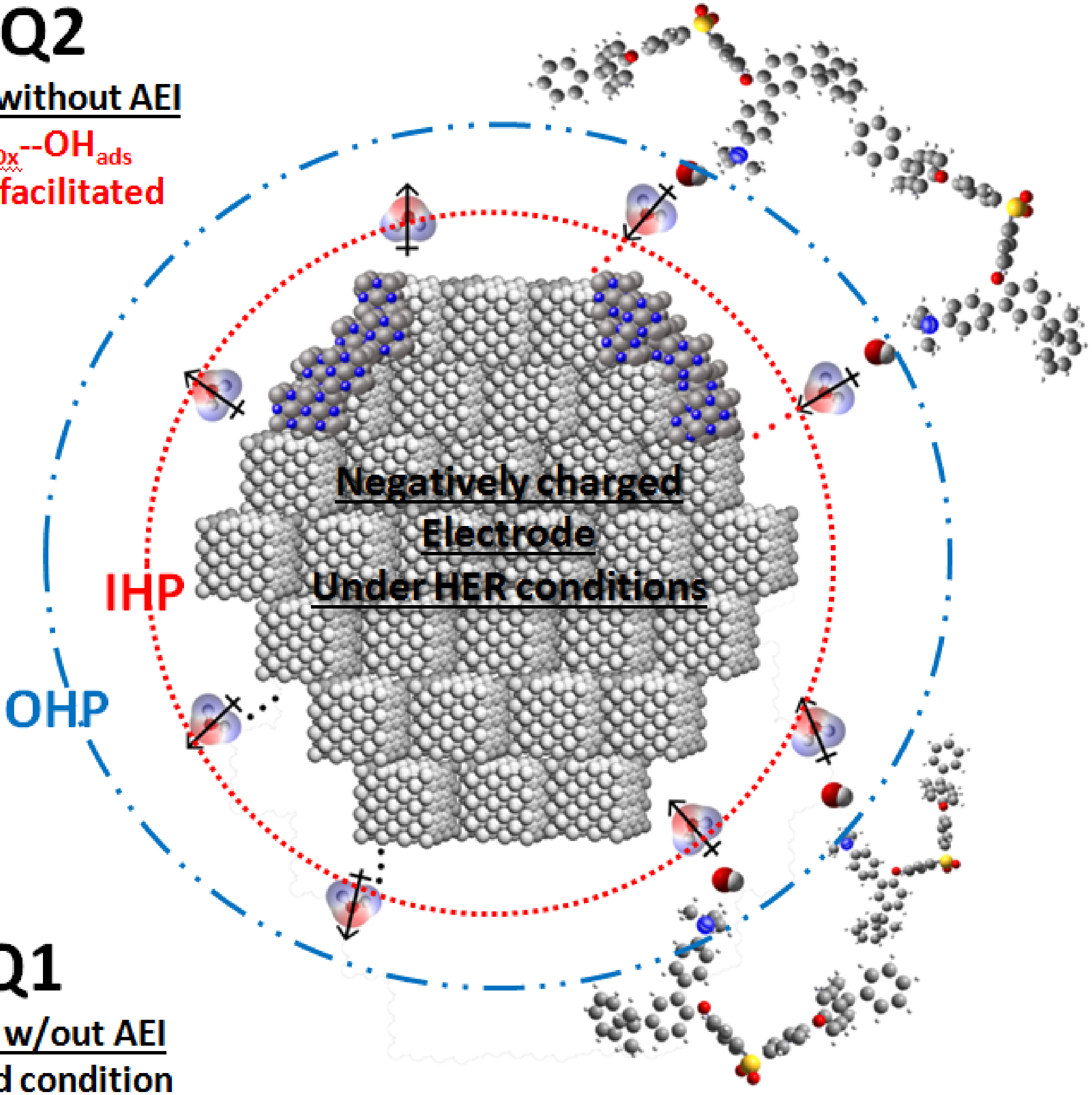


H_2O at interface experiences smaller magnitude of η because of chemical potential of AEI



- Pt, Ni/C and Cr/C exhibit *decreased* HER in presence of AEI
- Ni-Cr/C exhibits ***increased*** HER in presence of AEI
- Electrostatic model doesn’t explain enhanced HER on Ni-Cr

Approach – Interface Model



Q2

Ni-Cr without AEI

M_{Ox}--OH_{ads}
NOT facilitated

Q3

Ni-Cr/C with AEI

M_{Ox}--OH_{ads}
facilitated.
(Best non-PGM HER kinetics)

Q4

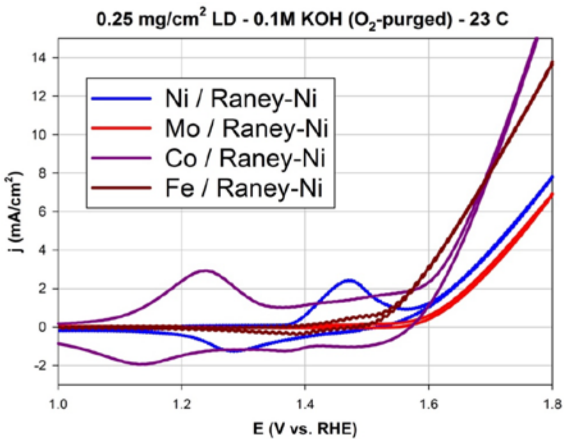
Ni or Pt with AEI

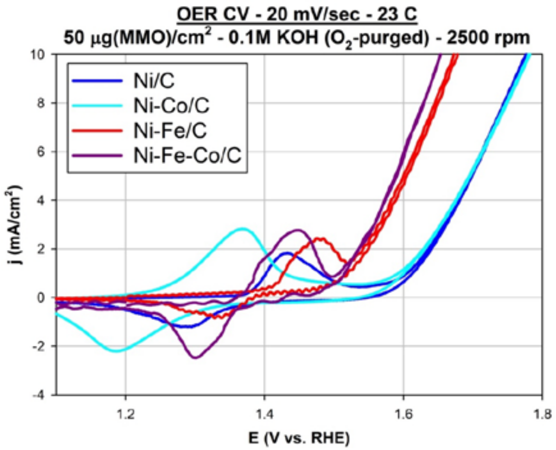
M_{Ox}--OH_{ads}
NOT facilitated
M-H_{ads}
NOT facilitated
(Worst HER kinetics)

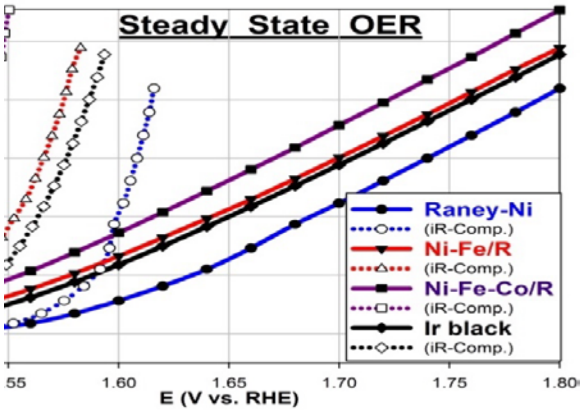
Q1

Ni or Pt w/out AEI
Standard condition

Approach - OER on Mixed-metal oxides







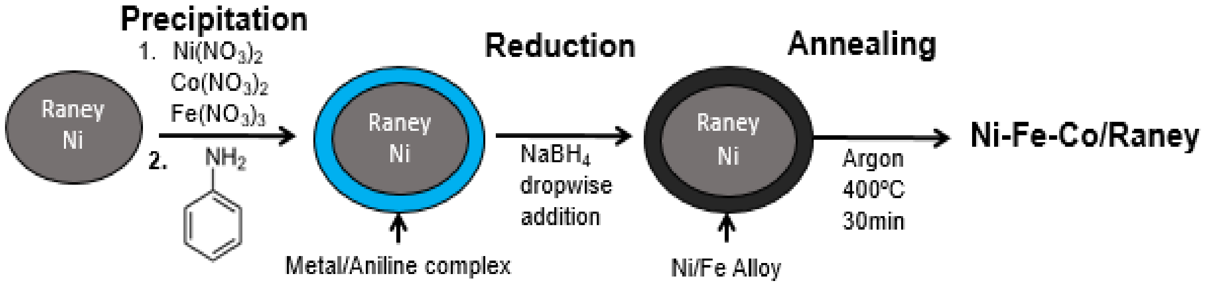
Mono-metallic films on Raney-Ni substrate:

Fe ~ Co > Ni > Mo

Model MMOs on Carbon-support:

- Shift in $Ni^{2+/3+}$ peaks
- Co: lower voltage
- Fe: higher voltage

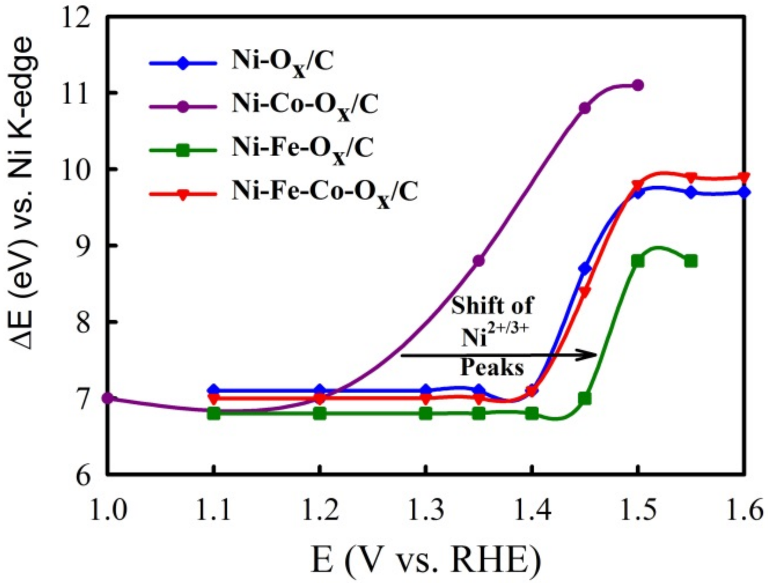
Materials Synthesis Strategy



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

Approach - Mechanistic Aspects

- Potential-dependent XAS:
  - Shift in Ni-edge energy different for each MMO
- XANES at 1.45 V most descriptive
- ΔE (eV, XAS) vs E_{appl}:
  - 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:

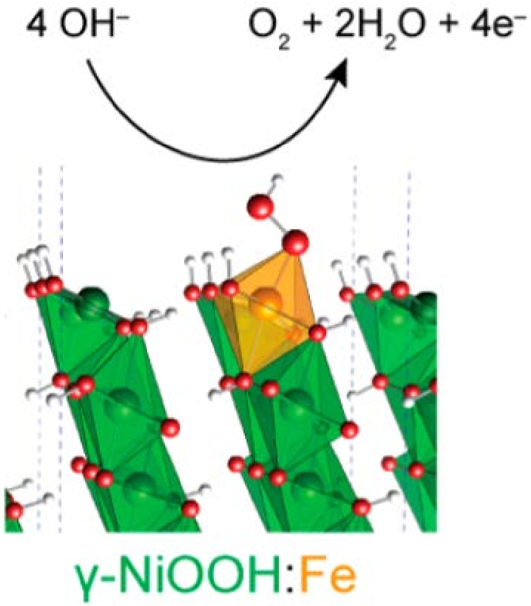
  Fe^{3+} sites exhibit optimized binding of -OH & -OOH intermediates

Fe^{3+} binding sites

&

Proton-transfer from

Ni^{3+} redox shuttles



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

Milestone Summary Table

Recipient Name:	**Northeastern University**
Project Title:	**Enabling Efficient Water Splitting with Advanced Materials Designed for High pH Membrane Interface**

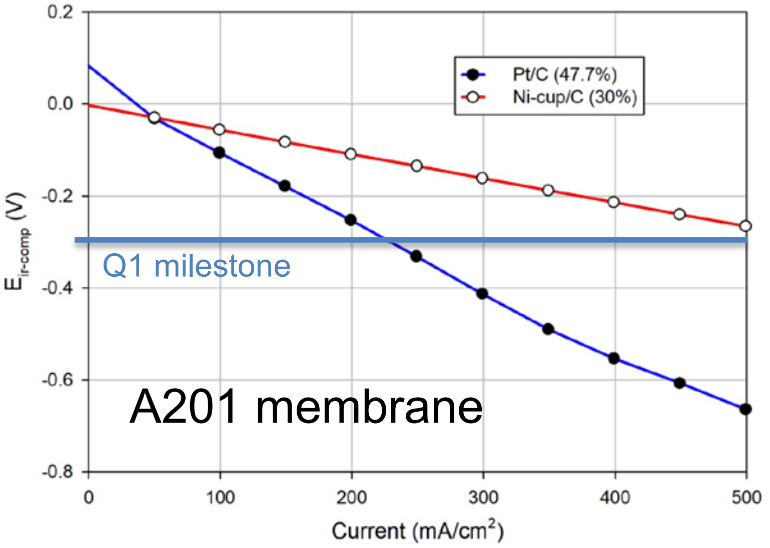
Task Number	Task or Subtask (if applicable) Title	Milestone Type (Milestone or Go/No-Go Decision Point)	Milestone Description (Go/No-Go Decision Criteria)	Anticipated Quarter (Quarters from Start of the Project)
Task 1	1.1	Milestone	M1.1: Deliver three 5 gm batch samples of Ni-MOx/C HER catalysts for RDE and Single Cell tests with η of 300 mV @ 500 mA/cm^2 and 2 A/cm^3 (HER)	Q1 100% Completed
	1.2	Milestone	M1.2: Deliver one 5 gm batch of Ni-N$_x$/C HER catalysts for RDE and Single cell studies η of 300 mV @ 500 mA/cm^2 and 2 A/cm^3 (HER)	Q2 100% Completed
	1.3	Milestone	M1.3: 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/cm^2 and 2 A/cm^3 (HER)	Q3
	1.4	Milestone	M1.4: Deliver three 5 gm batches of MMO$_x$ OER catalysts for RDE and single cell tests	Q2 100% Completed
Task 2	2.3	Milestone	M2.3: Deliver at least 5 grams of PAP-TQN ionomers and cast membranes that have less than 20% loss of IEC in 1 M KOH at 90 °C for 100 hours (Q3).	Q3
		BP1 Go/No Go Decision Point	HER Electrocatalysts: Using PGM-free HER electrocatalsyts in an AEM MEA operating under electrolysis conditions, at a current density of 500 mA/cm^2 achieve 300 mV or lower overvoltage and volumetric current density (VCD) of 2 A/cm^3 . OER Electrocatalysts: Using PGM-free OER electrocatalsyts in an AEM MEA operating under electrolysis conditions, at a current density of 500 mA/cm^2 achieve 150 mV or lower over-voltage and 6 A/cm^3 (VCD). AEM Membranes and Ionomers: Achieve AEM membrane ASR of 0.15 Ω cm^2 measured in MEA and less than 20% loss of IEC in 1 M KOH at 95°C for 1000 hours. AEM MEA: Demonstrate PGM-free AEM MEA electrolyzer performance of 0.8 A/cm2 at ≤1.92 V .	Q4

Main Takeaways

- Ni-MOx outperforms Pt as HER catalyst
- Ni-Nx is a viable alternative to Pt as an HER catalyst
- UDel PAP-TP-Me membrane is stable at high temperatures

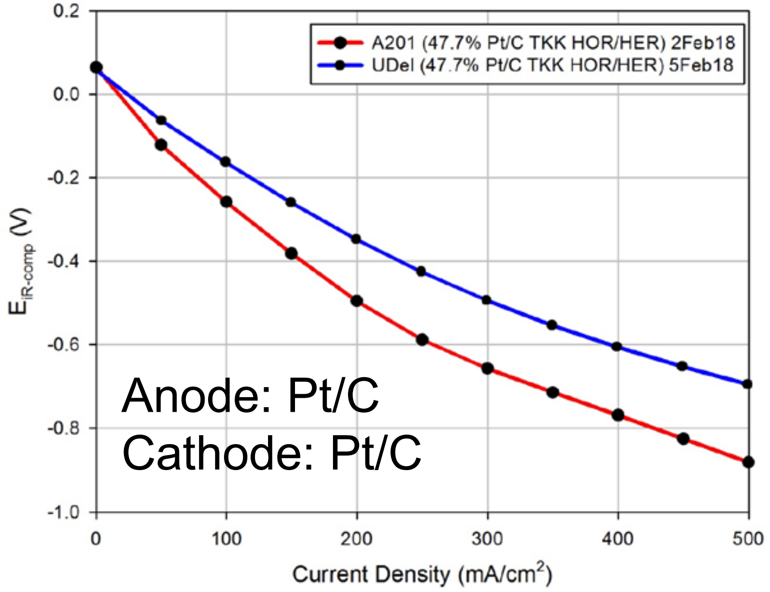
H_2 Pump Cell

H$_2$ Pump - Polarization Curve



- H_2 pump experiments measure the HER activity directly by decoupling the overall cell potential from OER.
- Ni-cup/C exceeds the Q1 milestone of 300mV at 500mA/cm^2
- Ni-cup/C out performs Pt by 400 mV at 500 mA/cm^2.
- UDel membrane out performs A201 in a Pt/C H_2 pump

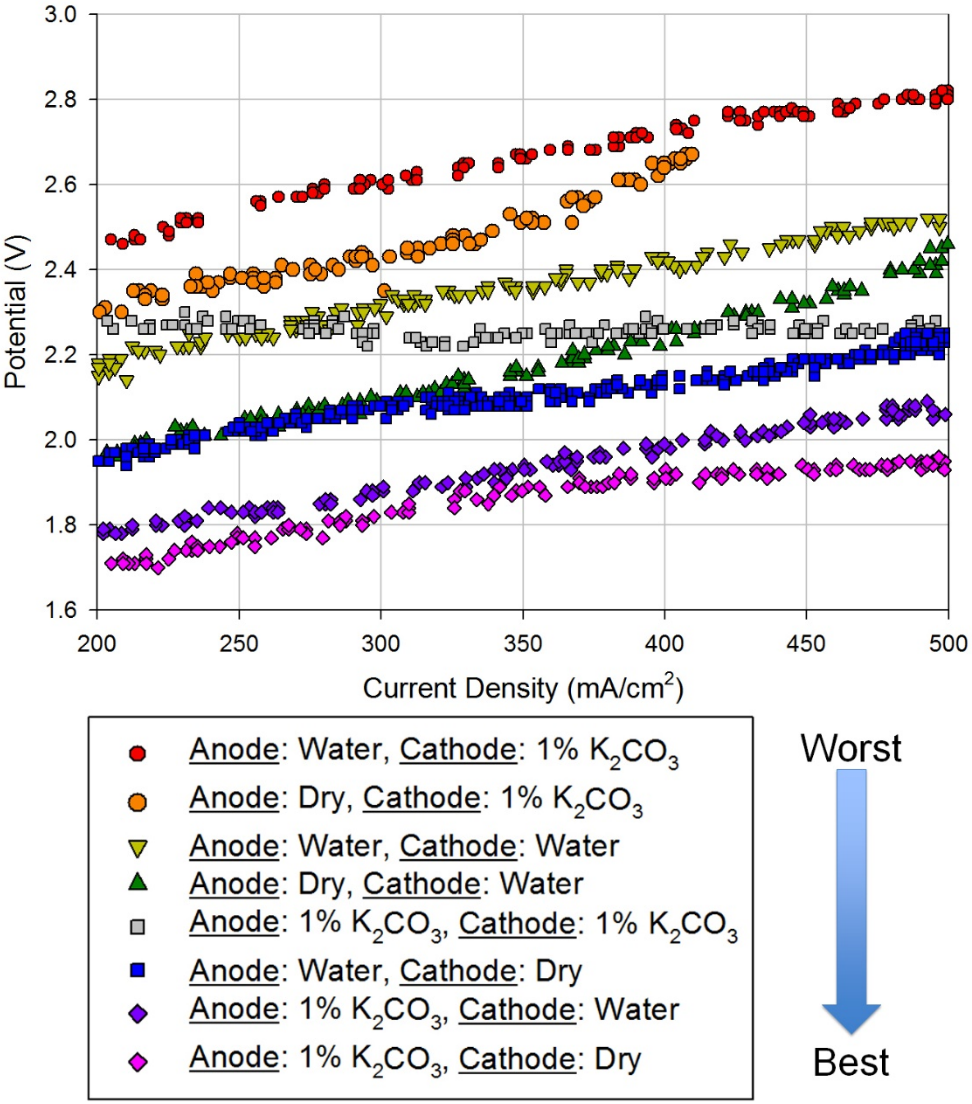
H$_2$ Pump - Polarization Curve



HER Summary

- Metal / Metal-oxides weaken H-OH bond in H_2O to facilitate Volmer reaction
  - Enhance formation of M-H$_{ads}$ intermediate
- Metal / Metal-oxides benefit from enhanced HER in presence of AEI
  - Poisoning adsorbate for PGM catalysts
- Further optimization of M/M-Ox surfaces
  - Composition & Morphology

Electrolysis cell performance trends

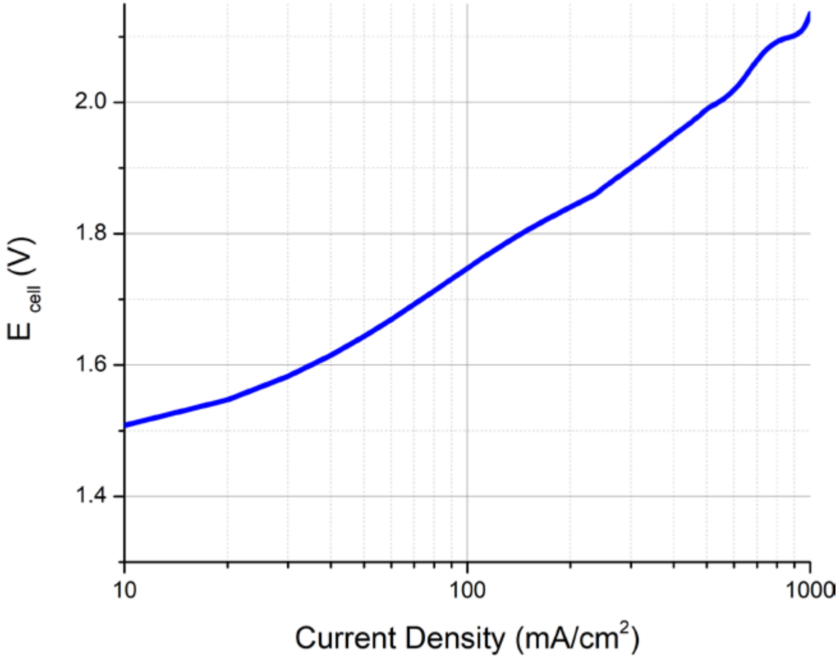


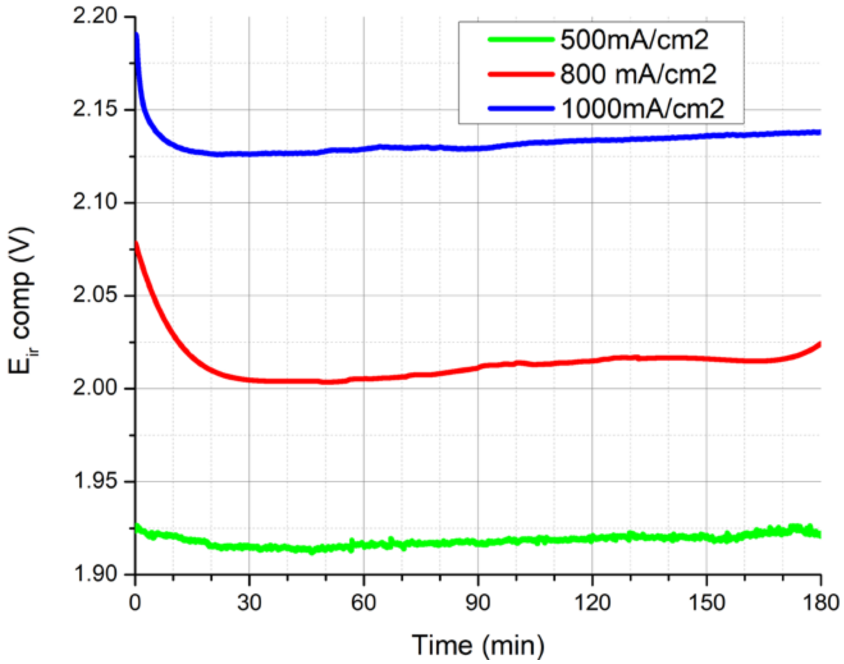
- K_2CO_3 at the cathode poisons the membrane via electro-osmotic drag.
- Large amounts of water at either electrode floods the electrode and reduces performance.
- Water is delivered to "dry" anodes via water molecules solvating the OH^- crossing the membrane.
- Water is delivered to dry cathodes by back diffusion of water.
- The best results are obtained with K_2CO_3 solution at the anode.

- Cell temp 50^{o}C
  Anode: Ir-O_x (3mg/cm^2)
  Cathode: Pt (3mg/cm^2)

Collected data at Proton On-Site

Water Splitting: Non-PGM Testing





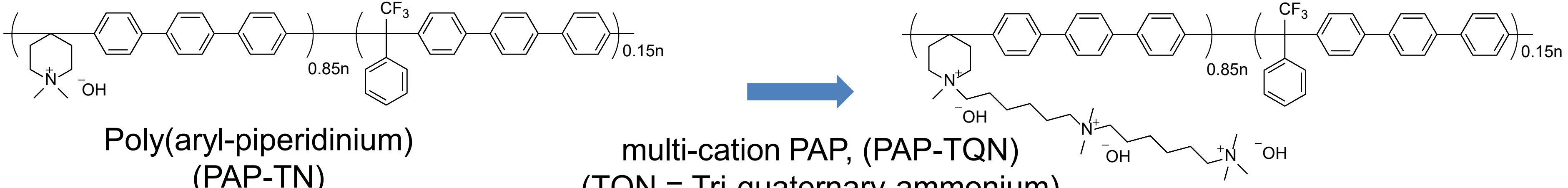
- OER catalyst: 3.08 mg/cm^2 NiFe/Raney
- HER catalyst: 2.94 mg/cm^2 Ni-cup/C
- Operating temperature: 90 ^{O}C
- Anolyte: 1% K_2CO_3 at 300mL/min
- Membrane: Baseline: Udel PAP-TN

BP 1 Target

- 1.92 V, 80^{0}C, 800 mA/cm^2

Membrane: Milestones and Approach

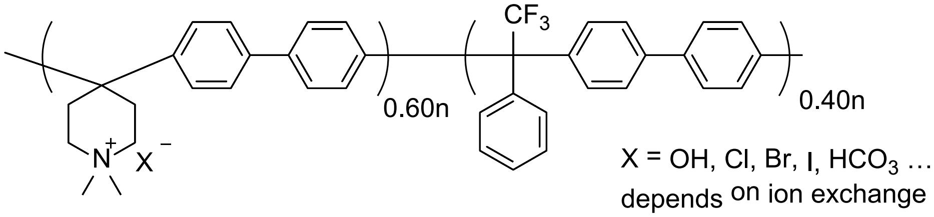
Quarter	**Task 2:** Preparation of PAP-TQN polymer	Description	Milestone
Q1-4	**Subtask 2.1:** Synthesis of PAP-TN polymers	PAP-TN is synthesized by polyhydroxyalkylation of N-methyl-4-piperidone, trifluoro-acetophenone and terphenyl. Reaction and polymerization conditions, i.e., temperature, solvent and reaction time, will be optimized.	Q1 Completed
	Subtask 2.2: Synthesis of two-ammonium-cations iodo-alky side-chain (DQN-I)	DQN-I is synthesized in two steps by Menshutkin reactions between a diamine, methyl iodide, and 1,6-diiodohexane. Reaction conditions, i.e., reactant ratios, temperature, solvent and reaction time, will be optimized.	Q2
	Subtask 2.3: Synthesis of PAP-TQN polymers	PAP-TQN is synthesized by Menshutkin reaction of PAP-TN and DQN-I. Reaction conditions, i.e., temperature, solvent and reaction time, will be optimized.	**Milestone 2.3:** Deliver 5 grams of PAP-TQN ionomers and cast membranes that have less than 20% loss of IEC in 1 M KOH at 90 °C for 100 hours (Q3).
	Subtask 2.4: Preparation and evaluation of PAP-TQN membrane	Reliable procedures of membrane; Screening of solvent, co-solvent, temp. and casting condition; evaluation of IEC, OH^- conductivity, water uptake, mechanical properties, alkaline stability, gas permeation and microstructure	Q4
	Go/No Go Decision: Achieve AEM membrane ASR of 0.15 Ω cm^2 measured in MEA and less than 20% loss of IEC in 1 M KOH at 95°C for 1000 hours.		



Poly(aryl-piperidinium)
(PAP-TN)

multi-cation PAP, (PAP-TQN)
(TQN = Tri-quaternary-ammonium)

Accomplishments - Membrane Properties



X = OH, Cl, Br, I, HCO$_3$ …
depends on ion exchange

* X = OH

Temp. (°C)	Conductivity (mS/cm)	Water uptake (wt%)	Swelling ratio (%)
20	60.5	25	8
30	65.8	25	8
40	76.5	26	8.5
50	90	27	9
60	104.1	28	10
70	116.5	29	11
80	130.9	30	12
90	142.4	33	13
95	150.5	35	14

Mechanical properties:

Strain at break = 9% (elongation),
Stress at break = 160 Mpa
(X = I, room temperature, average number)

IEC (ion exchange capacity) = 2.00 mmol/g (X = OH, theoretical)

Crystallinity: will be measured with wide angle x-ray scattering

Collaboration: Effectiveness

- Models provided by Sandia National Labs have shed light on the response of the ionomer active site to charge. Specifically, the distance between cationic sites and solvation of the anion were examined. This study will be useful to determine the optimal side-chain length and ion-exchange capacity of future ionomer materials.

- Small angle X-ray scattering studies were performed at LBNL to gain insight on the morphology of the anion exchange membrane in different states of hydration.

- LBNL has also modeled the interaction of carbonate ions at the interface of the catalyst layer and the anion exchange membrane. The model has provided insight into how and where the ion accumulates in an electrolysis cell when different amounts of current are applied.

- Modeling of the ionomer structure at the interface has begun and is showing the effect of metal charge and its effect on the ionomer morphology

- The efforts of our EMN partners are described in detail in the Technical Back-Up Slides

Proposed Future Work

1. **Materials Discovery**: (NEU & Udel) FY2 (Q1-Q4)
   - HER Catalysts: Ni-Nx catalyst optimization, stability tests, structure function determination. Preparation of MOF derived catalysts.
   - OER catalyst: Enhance active site density of Ni-Fe-Co/Raney Ni
   - 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) FY2 (Q2-Q4)
   - Accurate determination of OER overvoltage
   - Optimization of Full Cell for long duration tests
3. **In situ XAS and Raman Measurements**: (NEU): FY2 (Q2-Q3)
4. **Detailed modeling of transport processes** for deciphering carbonate effect (LBNL) FY2 (Q2)
5. **SAXS measurement** for membrane structure and morphology as a function of temperature, ion exchange and humidity (LBNL) FY2 (Q2-Q4)
6. **Interfacial modeling** to understand ionomer effects (Sandia) FY2 (Q2-Q4)
7. **Durability measurements** on PAP-TQN membranes (NREL) FY2 (Q3-Q4)
8. **MEA optimization and testing** (NREL) FY2 (Q3-Q4)

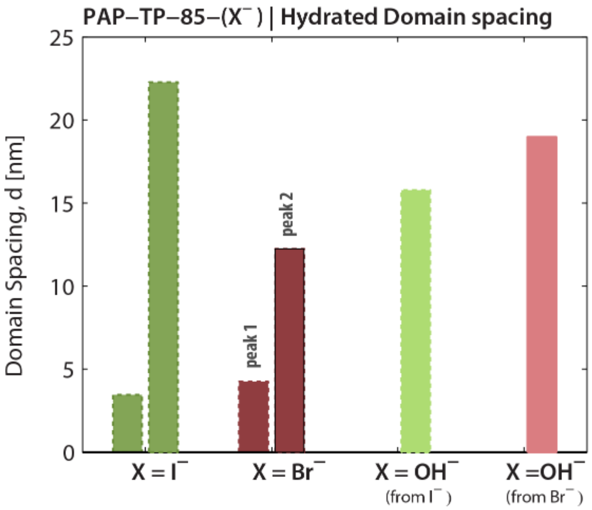
Technical Backup Slides

SAXS Measurements-LBNL (A Kusoglu)

- **Key findings**
  - 2D Scattering Spectra (images, not shown here) indicates isotropic structure
    - No preferential orientation
  - There is weak degree of phase-separation
    - Very broad, less apparent peak
  - Not a significant difference among the 4 samples tested
  - Structure does not appear to change much from ambient to liquid (full hydration) state
    - The polymer exhibits a more or less a “gel”-like or amorphous state

Interpretation and future Efforts

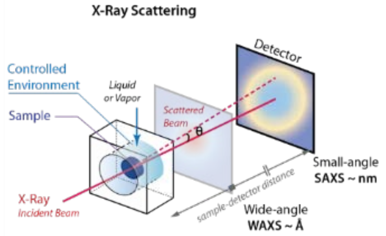
- Need to correlate this with the water uptake capacity of the samples
  - How much water does the membrane uptake from dry to liquid state?
- Spectroscopic analysis to help interpret the morphology from SAXS
- Possible effects of carbonate formation?
  - May need to prepare samples for SAXS in controlled environment
- Next experiment:
  - Controlled heating in liquid water

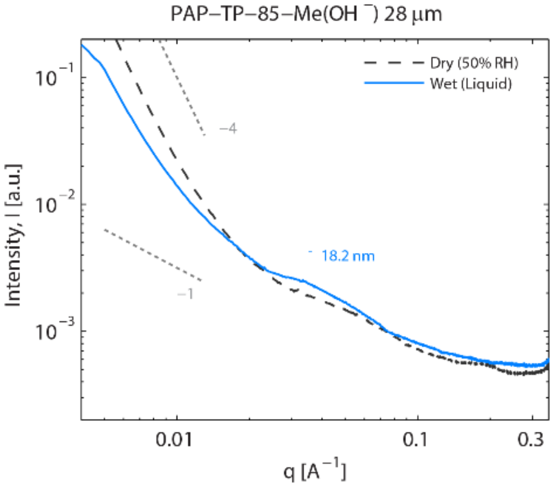


Low-q slope:

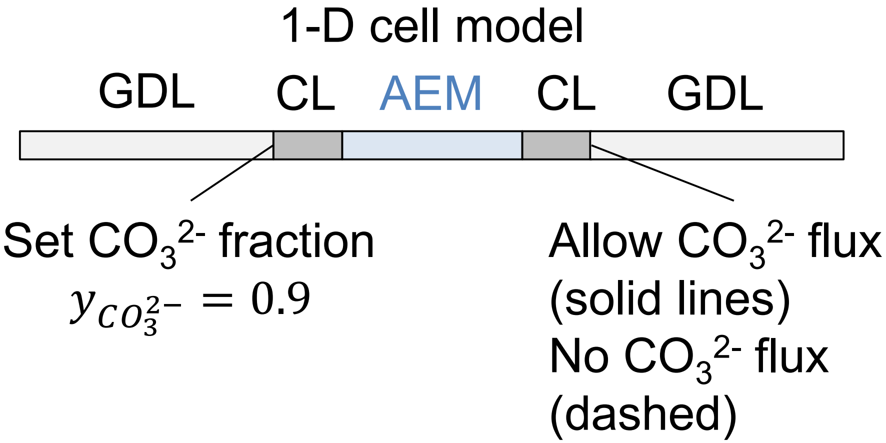
-1 → cylindrical aggregates

-4 → spherical aggregates





Effects of carbonate in AEM electrolyzers



1-D cell model

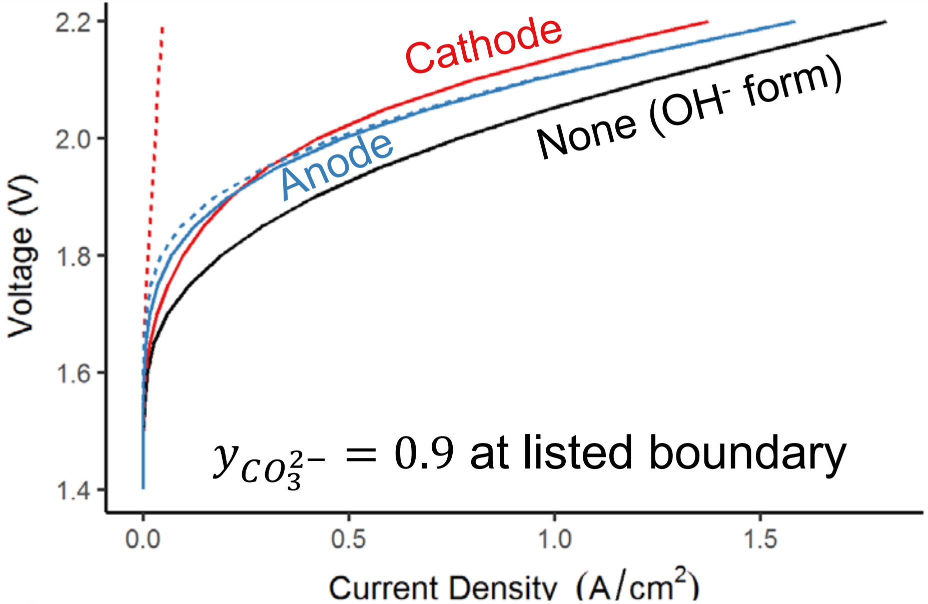
GDL CL AEM CL GDL

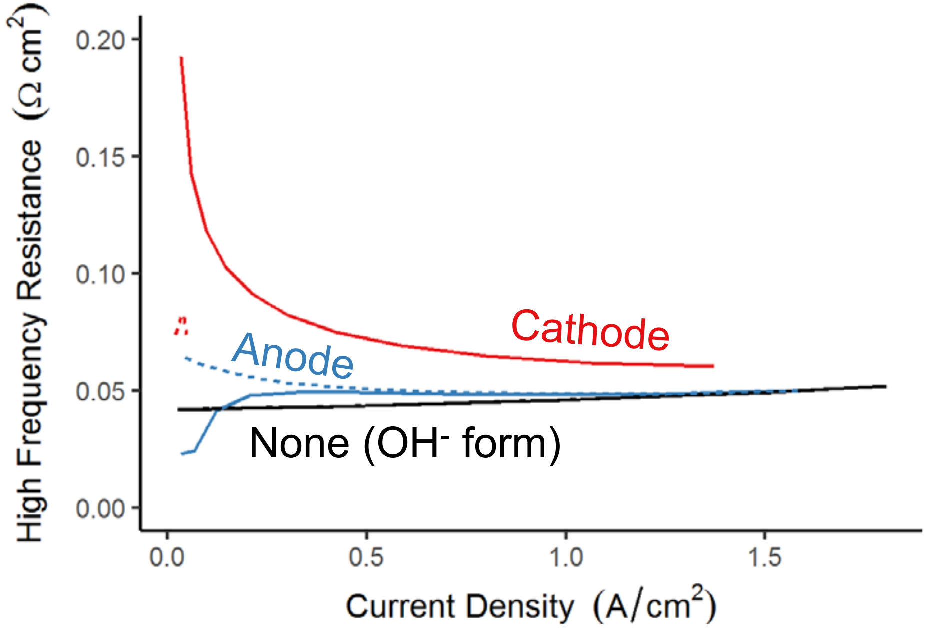
Set CO_3^{2-} fraction

$y_{CO_3^{2-}} = 0.9$

Allow CO_3^{2-} flux (solid lines)

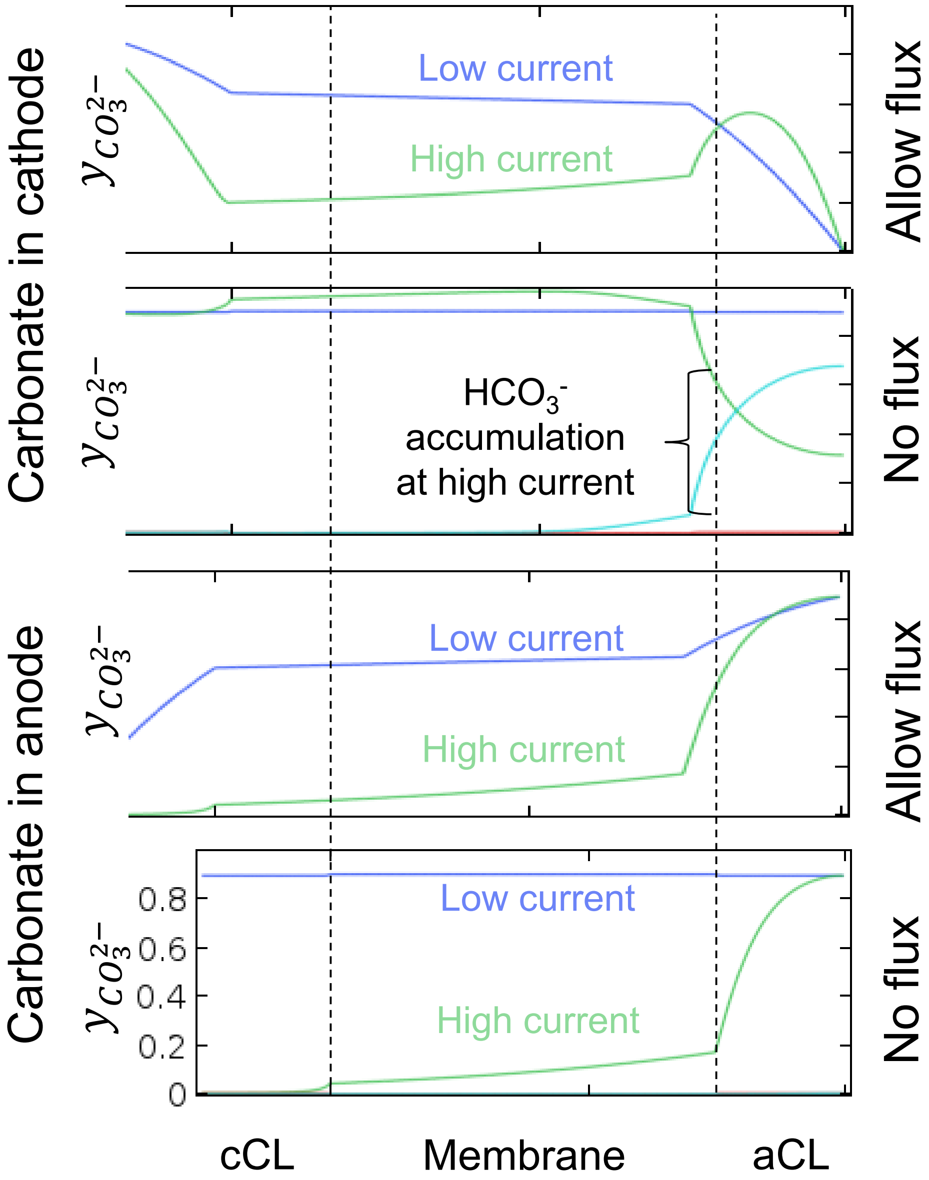
No CO_3^{2-} flux (dashed)





- System appears more tolerant of CO_3^{2-} in anode than in cathode.
- HFR suggests CO_3^{2-} at cathode interferes with self-purging.
- CO_3^{2-} desorption as CO_2 (g) isn't fast enough to clear away CO_3^{2-} introduced at cathode.

Carbonate distribution in MEA

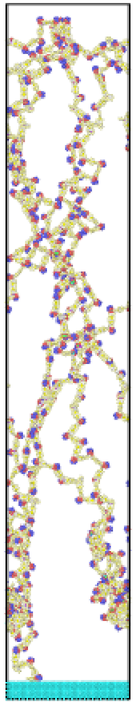


- **Carbonate accumulates in anode in all cases**
- **Lack of CO_3^{2-} in cathode feed allows OH^- production to clear out CO_3^{2-} in membrane**
- **Next steps:**
  - Modeling of ion-exchange process between membrane and liquid electrolyte
  - Incorporate additional carbonate effects on HER/OER kinetics as observed by NU
  - Explore sensitivity to material properties to identify performance limitations

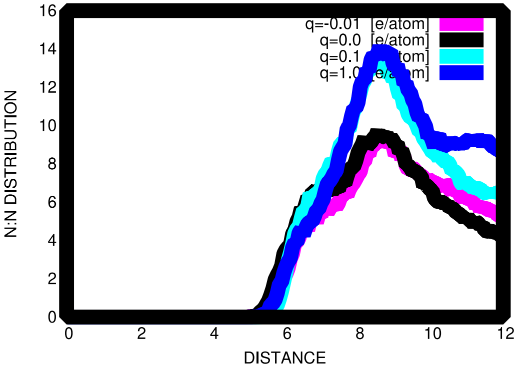
Interfacial Modeling: Sandia (Reese Jones)

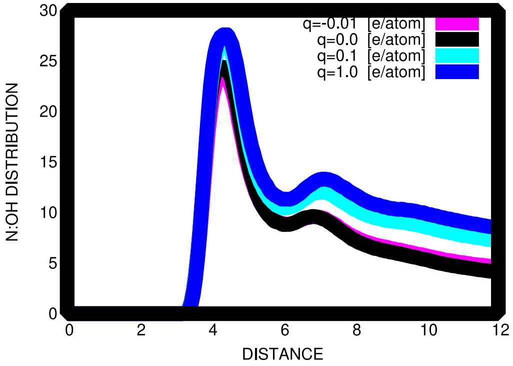
Structure response to electrode charge

4 ionomer chains of length: 100 units, with water and OH interacting with a metal surface



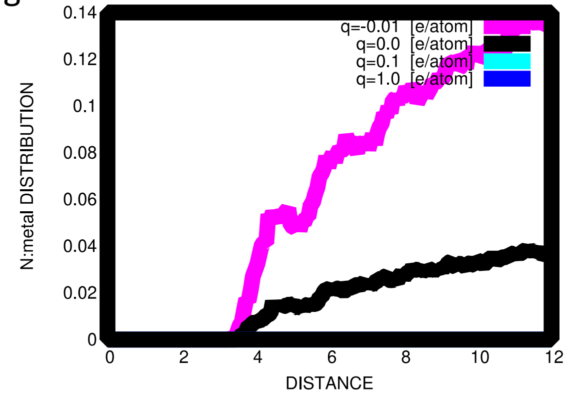
Water omitted for clarity





In this **preliminary** data we see

- The N+ charge centers are attracted by negatively charged metal surface and greatly repelled by positively charged metal surface
- The N:N distance peaks at ~9A and the peak increases with positive charge, which implies compaction of the ionomer chains
- The average number of OH solvating the N charge centers on the ionomer chains increase with positive surface charge

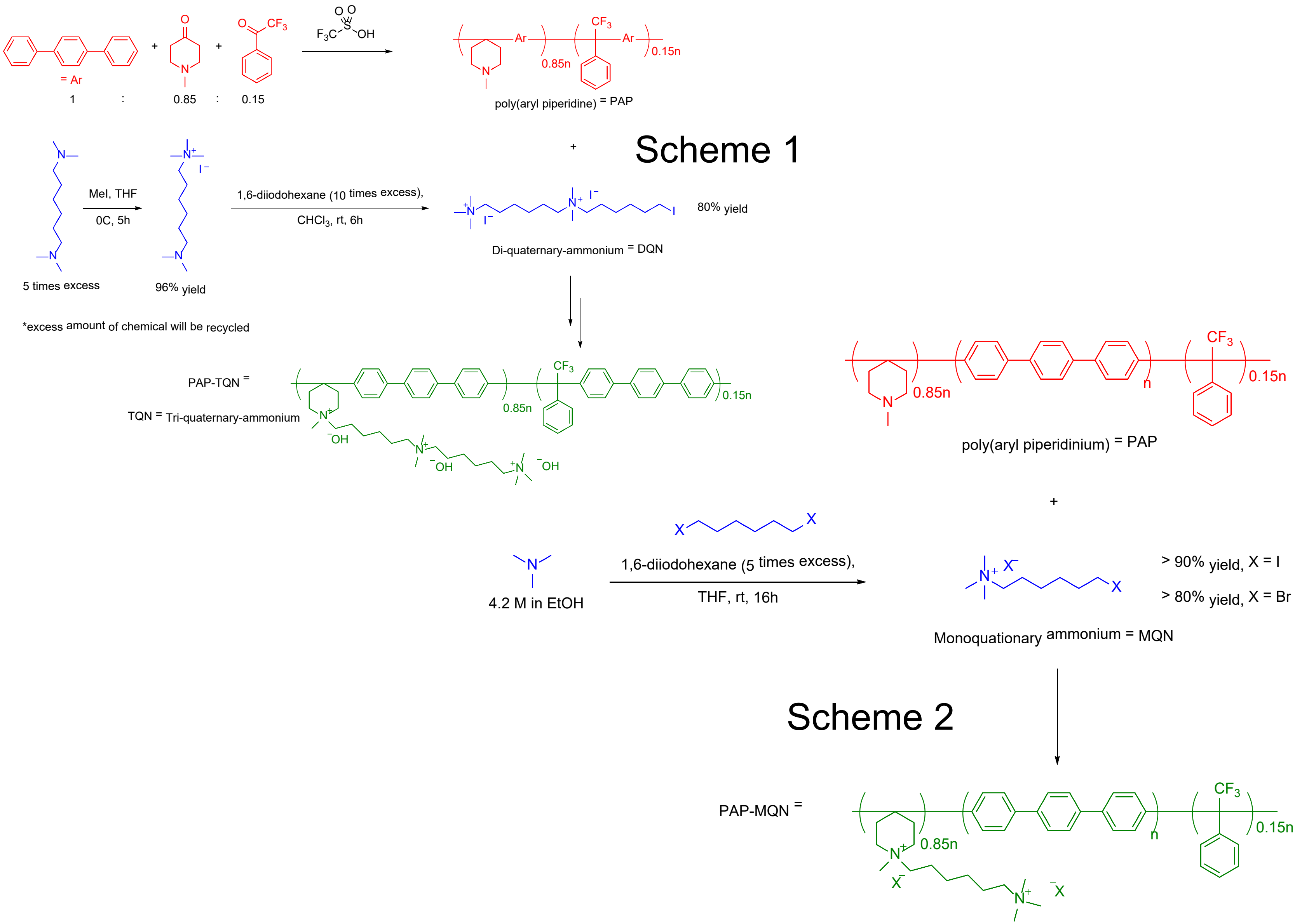


Current and Future Work

- Obtain experimental mass density and use this and the water percentage to build system with the correct species concentrations
- Investigate the structure plausibility of the resulting systems
- Add H+ (and compensating OH-) to explore pH effects on the structural response to metal surface charge.

Ultimately, use representative subconfigurations to investigate charge transfer with *ab initio* methods

Ionomer membrane synthetic scheme



*excess amount of chemical will be recycled