



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

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April 15, 2020

Project ID: P156



Timeline and Budget

For Competitively Selected Projects:

(lab and non-lab projects)

- Project Start Date: 10/1/2017
- Project End Date: 12/31/2020
- Total Project Budget: \$1,111,110
 - Total Recipient Share: \$111,110
 - Total Federal Share: \$1,000,000
 - Total DOE Funds Spent*:
\$732,076

* As of 04/06/2020

Barriers

- Barriers addressed
 - F. Capital Cost
 - L. Operations and Maintenance

Partners

- University of Delaware
- Advent North America
- NREL
- LBNL
- SNL



Objective: To reduce the cost of anion-exchange membrane electrolysis systems through the development of new materials for these reactors and to gain a better understanding of the interaction between these materials and the electrolyte.

- Identify new catalysts for the oxygen evolution and hydrogen evolution reactions.
- Develop novel and robust ionomer membranes capable of sustained intermediate-temperature operation.
- Model the reactions of these reactors to inform optimum operating conditions

| Target | Units | Year 0 | Year 1 | Year 2 | Year 3 |
|--|-------------------|---------|--------|--------|--------|
| Cell voltage | V | 2 | 1.92 | 1.82 | 1.72 |
| Current density | A/cm ² | 0.5 | 0.8 | 1 | 1 |
| Operating temperature | °C | 80 | 80 | 90 | 90 |
| Membrane ASR | Ω·cm ² | | 0.15 | 0.12 | 0.08 |
| HER overvoltage @ 500 mA/cm ² | mV | 400-350 | 300 | 200 | 150 |
| OER overvoltage @ 500 mA/cm ² | mV | 200 | 150 | 125 | 100 |
| Model Voltage | mV | 1.65 | 1.74 | 1.69 | 1.62 |
| Unexplained voltage losses | mV | 0.35 | 0.18 | 0.13 | 0.10 |



- Focus exclusively on developing and testing PGM-free catalysts to significantly lower the cost of catalysts
- Reduce maintenance cost by using durable anion-exchange membranes
- Increase reaction kinetics by leveraging membrane durability to operate electrolysis cells at elevated temperatures
- Inform catalyst development and catalyst layer architecture through the modeling efforts of our collaborators

Northeastern:

- Catalyst development and characterization
- Cell testing

LBNL

- Electrochemical systems modeling
- Small angle X-ray scattering study of ionomer membranes

University of Delaware:

- Membrane development and characterization

SNL

- Modeling the electrolyte/catalyst interface

Advent North America:

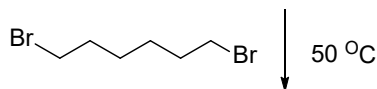
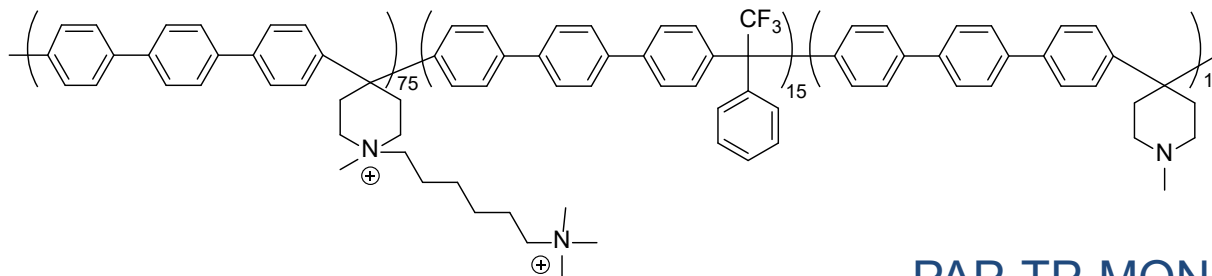
- Novel electrode architectures

NREL:

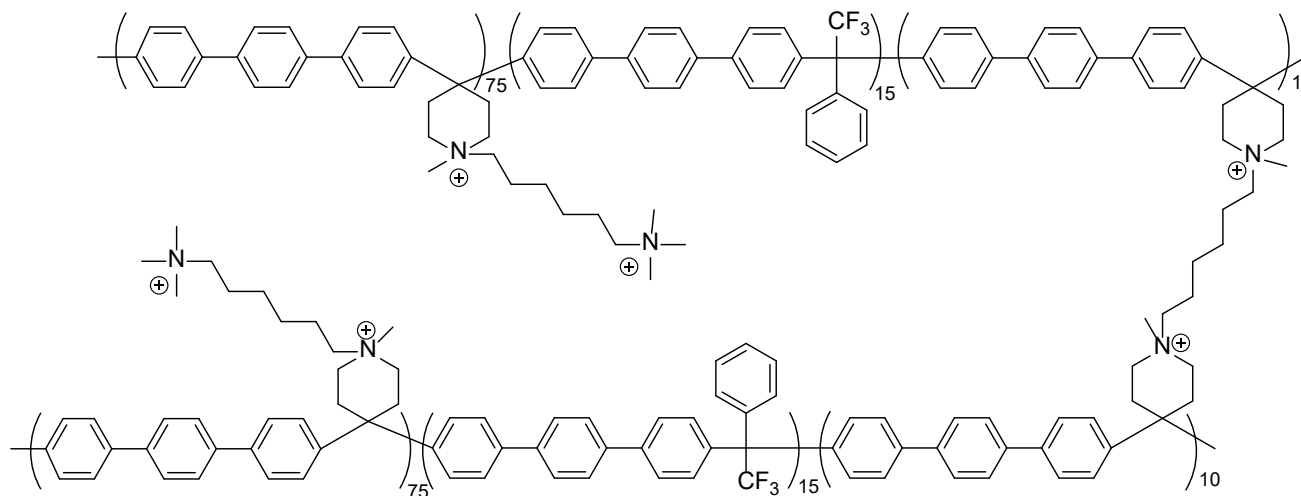
- Membrane durability testing and characterization



| Task Number | Task or Subtask | Milestone Description (Go/No-Go Decision Criteria) | Anticipated Quarter |
|---------------|------------------------------------|--|--|
| Task 4 | 4.1 | <p>4.1.1 Deliver one 5g batch of binary alloy HER catalyst for RDE and single cell tests. Demonstrate an $\eta \leq 250$ mV @ 500 mA/cm² in a hydrogen pump cell</p> <p>4.1.2: Deliver three 5 g batch samples of binary alloy HER catalysts for RDE and single cell tests.</p> | <p>Q5 Completed</p> <p>Q8 Completed</p> |
| | 4.2 | <p>4.2.1: Deliver three 5 g batch samples of ternary MMOx HER catalysts for RDE and single cell tests</p> <p>4.2.2: Demonstrate an $\eta \leq 250$ mV @ 500 mA/cm² in a hydrogen pump cell with one or more ternary MMOx HER catalyst .</p> | <p>Q8 Completed</p> <p>Completed</p> |
| | 4.3 | 4.3: Deliver three 10 g batch samples of optimized MMO OER catalysts for RDE and Single cell studies. | <p>Q8 Completed</p> |
| Task 5 | 5.4 | 5.4: Deliver reinforced PAP-MAC membrane samples (5 pieces, 12x12 cm each) with swelling ratio less than 10% at 20 °C and 20% at 80 °C. Demonstrate membrane ASR no higher than 0.12 Ω·cm ² and less than 20% IEC lost in 1M KOH at 90 °C for 500 h. | <p>Q7 Completed</p> |
| Task 6 | 6.2 | 6.2: Optimize porosity of cathode in a AEM electrolysis cell to accommodate 1 A/cm ² current density / H ₂ evolution with minimal transport resistance observed. | <p>Q6 Completed</p> |
| | 6.3 | 6.3: Demonstrate combination of optimized cathode layer and cathode current collector achieving 1 A/cm ² at 1.82V in a full electrolysis cell. | <p>Q8 Outstanding</p> |
| | BP2 Go/No-Go Decision Point | <p>HER Electrocatalysts: Using PGM-free HER electrocatalysts in an AEM MEA operating under H₂ pump mode at a current density of 500 mA/cm² achieve 200 mV or lower overvoltage.</p> <p>OER Electrocatalysts: Using PGM-free OER electrocatalysts in an AEM MEA operating under electrolysis conditions, at a current density of 500 mA/cm² achieve 125 mV or lower overvoltage.</p> <p>AEM Membranes and Ionomers: Achieve AEM membrane ASR of 0.12 Ω cm² measured in MEA and less than 15% loss of IEC in 1 M KOH at 90°C for 1000 hours.</p> <p>AEM MEA: Demonstrate PGM-free AEM MEA electrolyzer performance of 1 A/cm² at ≤1.82 V with less than 5 mV/hr decay at 90°C for 48 hrs.</p> | <p>Q8 Completed</p> <p>Completed</p> <p>Completed</p> <p>Completed</p> |



PAP-TP-MQN-10N
10N = % neutral N



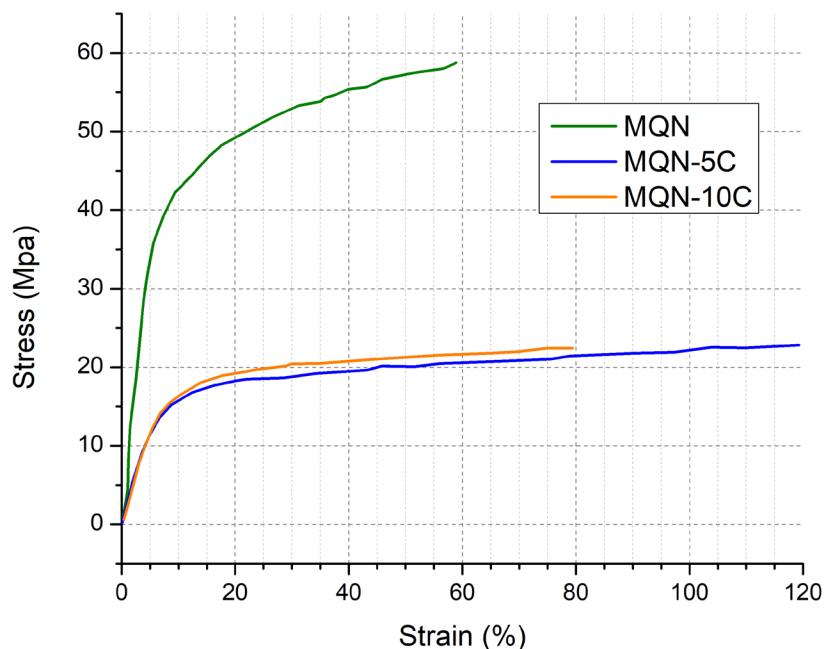
Cross-linking not only improves the mechanical properties but introduces additional ion-exchange sites

PAP-TP-MQN-10N-XC
X = % cross-linked sites

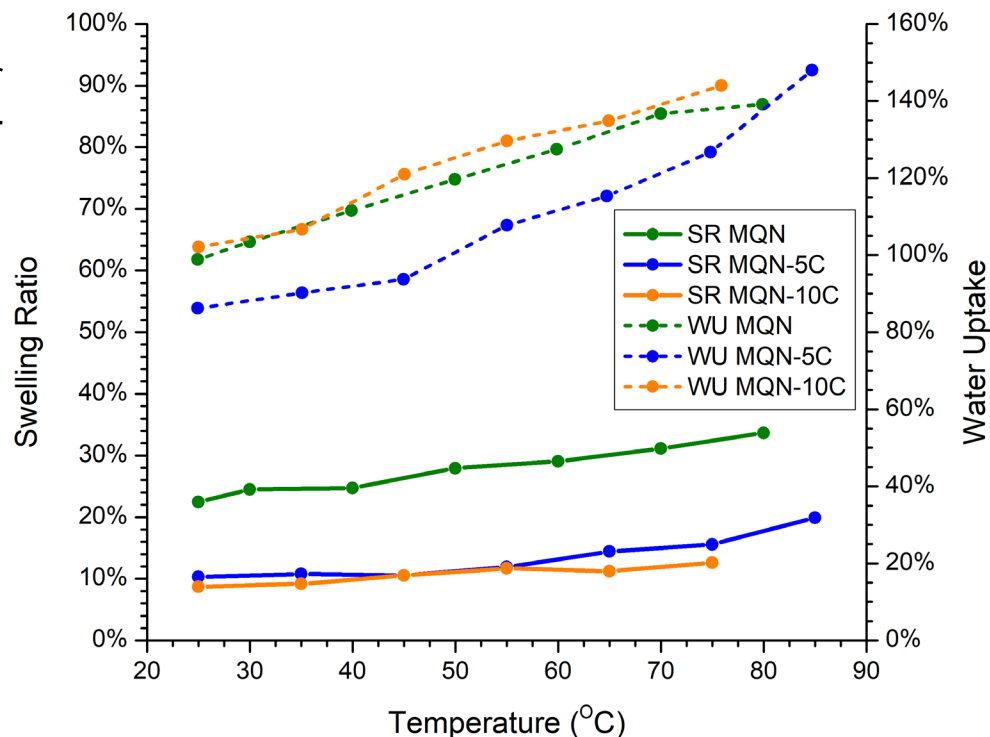


- The physical properties of University of Delaware's 2nd generation membrane (PAP-TP-MQN) were improved via cross-linking.
- Cross-linking and reinforcement reduces water swelling from 25% to 10.3% and 8.71% (MQN-5C and 10C, respectively) at 25 °C.
- Cross-linking does not result in a significant loss of ion-exchange capacity.
- Stress is reduced 3 times versus standard MQN ionomer

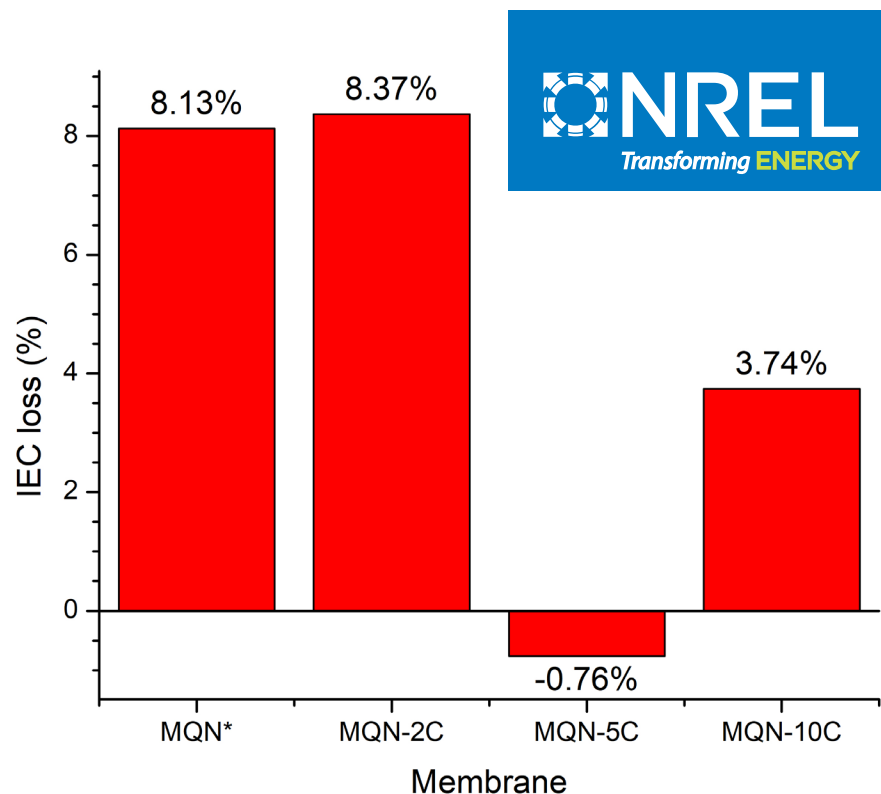
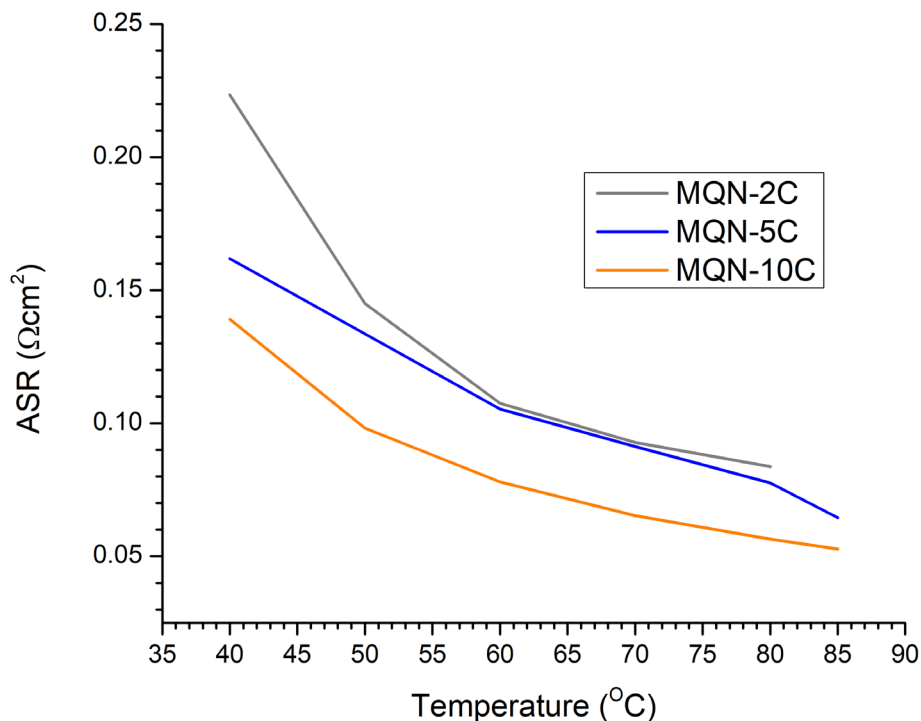
DMA of Crosslinked Membranes



Water Swelling and Uptake of Crosslinked Membranes

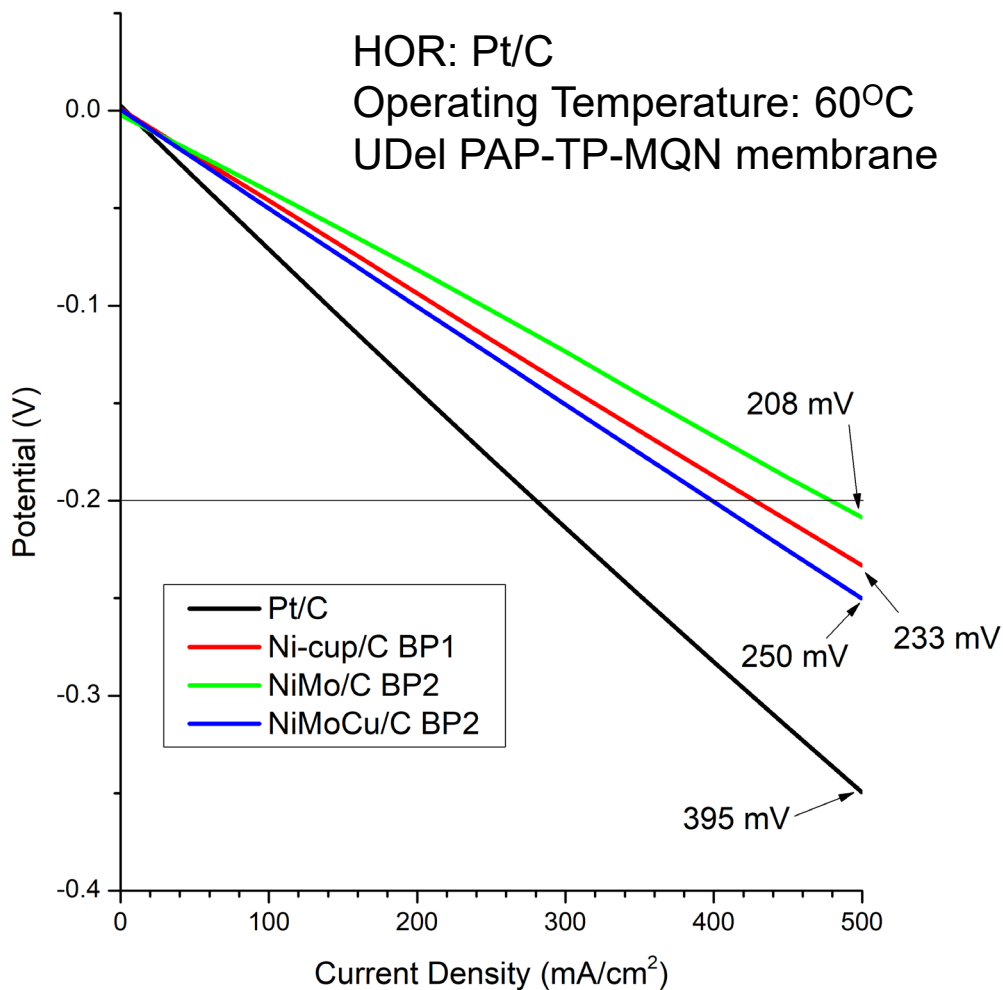


| Ionomer | IEC Theo (mequiv/g) | Udel IEC (mequiv/g) | NREL IEC (mequiv/g) |
|-------------|---------------------|---------------------|---------------------|
| MQN | 3.3 | 2.9 | 2.81 |
| MQN-10N-2C | 3.24 | | 2.32 |
| MQN-10N-5C | 3.29 | 2.5 | 2.37 |
| MQN-10N-10C | 3.38 | 2.7 | 2.4 |



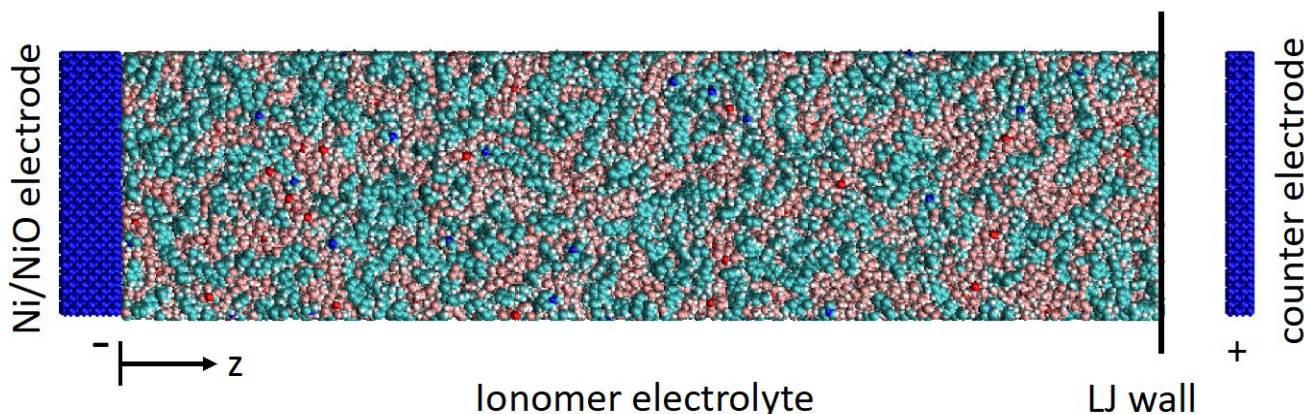
- All crosslinked membranes had area specific resistances (ASRs) of $< 0.12 \Omega \cdot \text{cm}^2$ at temperatures relevant to normal AEM/EI operating temperatures ($60^\circ\text{C} <$).
- All crosslinked membranes had an IEC loss of $< 10\%$ after a 1000-hour treatment in 90°C 1M KOH.

| Milestone # | Project Milestone | Progress |
|-------------|---|-----------|
| Go/No-Go | AEM Membranes and Ionomers: Achieve AEM membrane ASR of $0.12 \Omega \text{ cm}^2$ measured in MEA and less than 15% loss of IEC in 1 M KOH at 90°C for 1000 hours. | Completed |

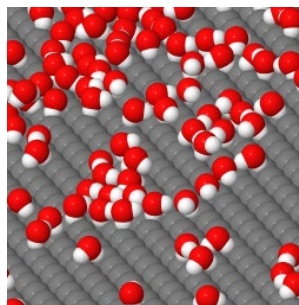
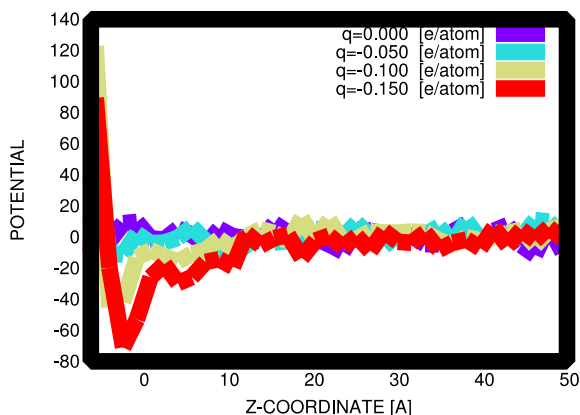


- Ni-cupferron/C: A functionalized monometallic catalyst prepared through the chelation technique reported in BP1.
- The NiMo/C H₂ pump required 208 mV to operate at 500 mA/cm₂, 25 mV below the HER catalyst from BP1.
- The ternary NiMoCu/C catalyst achieved a potential of 250 mV

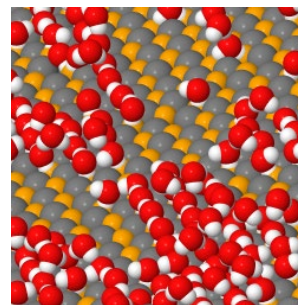
| Milestone # | Project Milestone | Progress |
|-------------|--|---|
| 4.3 | Demonstrate an $\eta \leq 250$ mV @ 500 mA/cm ² in a hydrogen pump cell with one or more ternary MMOx HER catalyst | Completed |
| Go/No-Go | HER Electrocatalysts: Using PGM-free HER electrocatalysts in an AEM MEA operating under H ₂ pump mode at a current density of 500 mA/cm ² achieve 200 mV or lower overvoltage. | Completed* (8mV above Go/No-go) |



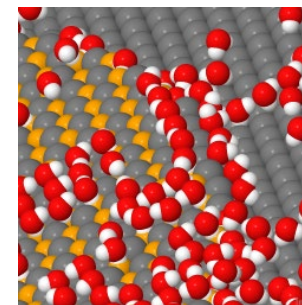
- Built a molecular model of a PAP ionomer and Ni HER electrode
- Charge distribution in the electrode from DFT, overall model was classical molecular dynamics
- Simulated the effects of charging the electrode on the ionomer and mobile species and observed surface coverage, near electrode distributions and other quantities tied to water splitting efficiency



(a) bare Ni



(b) NiO monolayer



(c) partial NiO coverage

Closeup views of water orientation on electrode surface

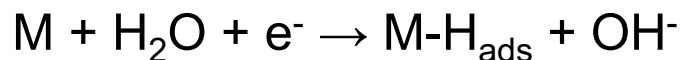
Potential as a function of surface charge

Reese E. Jones, William C. Tucker, Matthew J.L. Mills, Sanjeev Mukerjee, *Insight into hydrogen production through molecular simulation of an electrode-ionomer electrolyte system*, **Journal of Chemical Physics**, accepted 2019

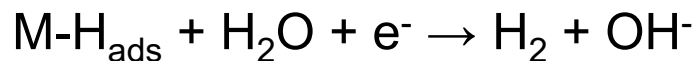


Alkaline HER Mechanism

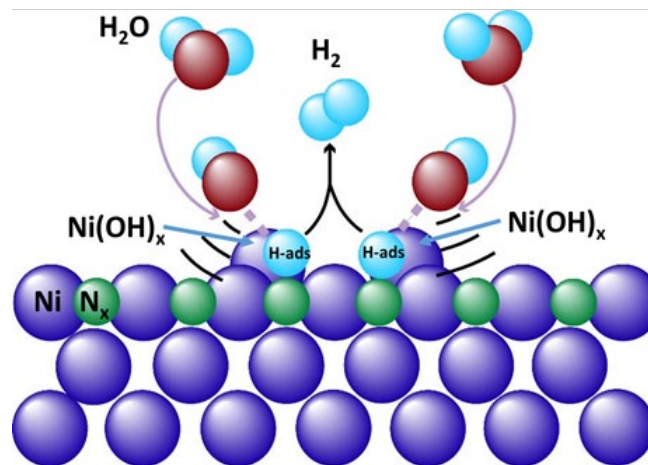
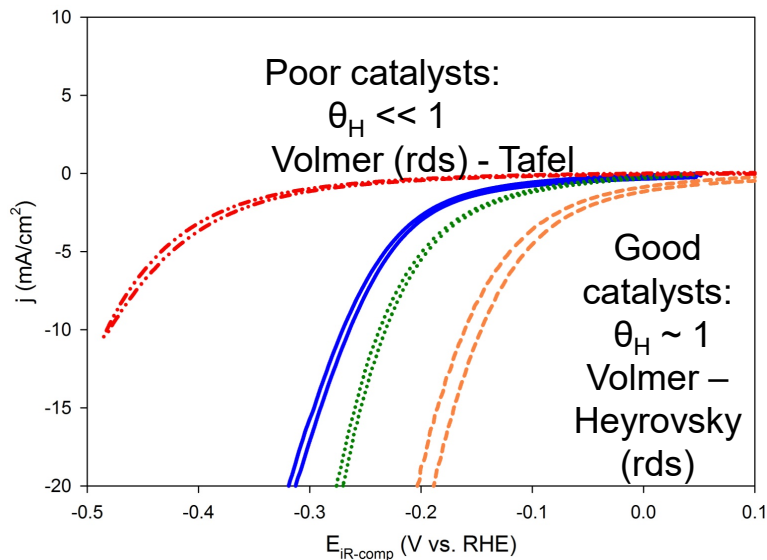
Volmer:



Heyrovsky:

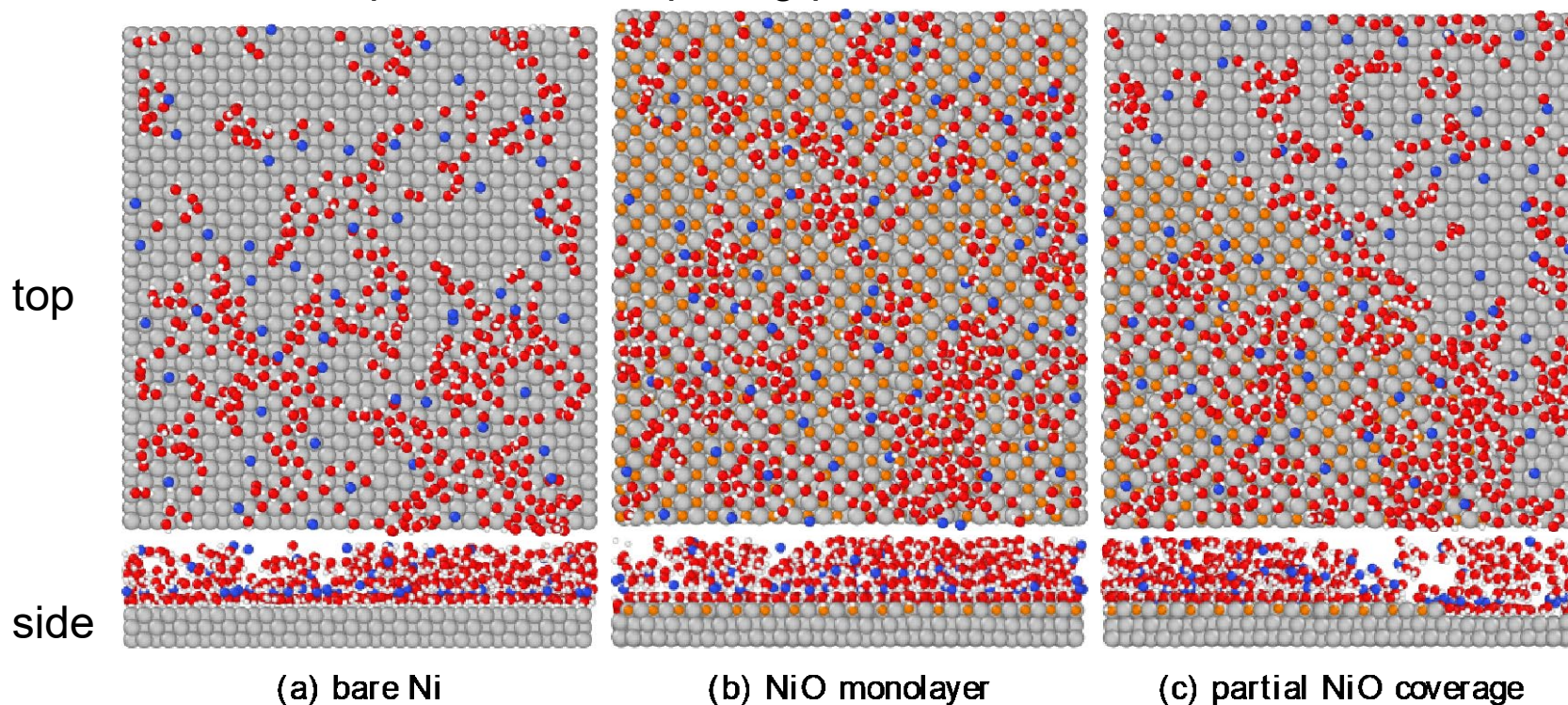


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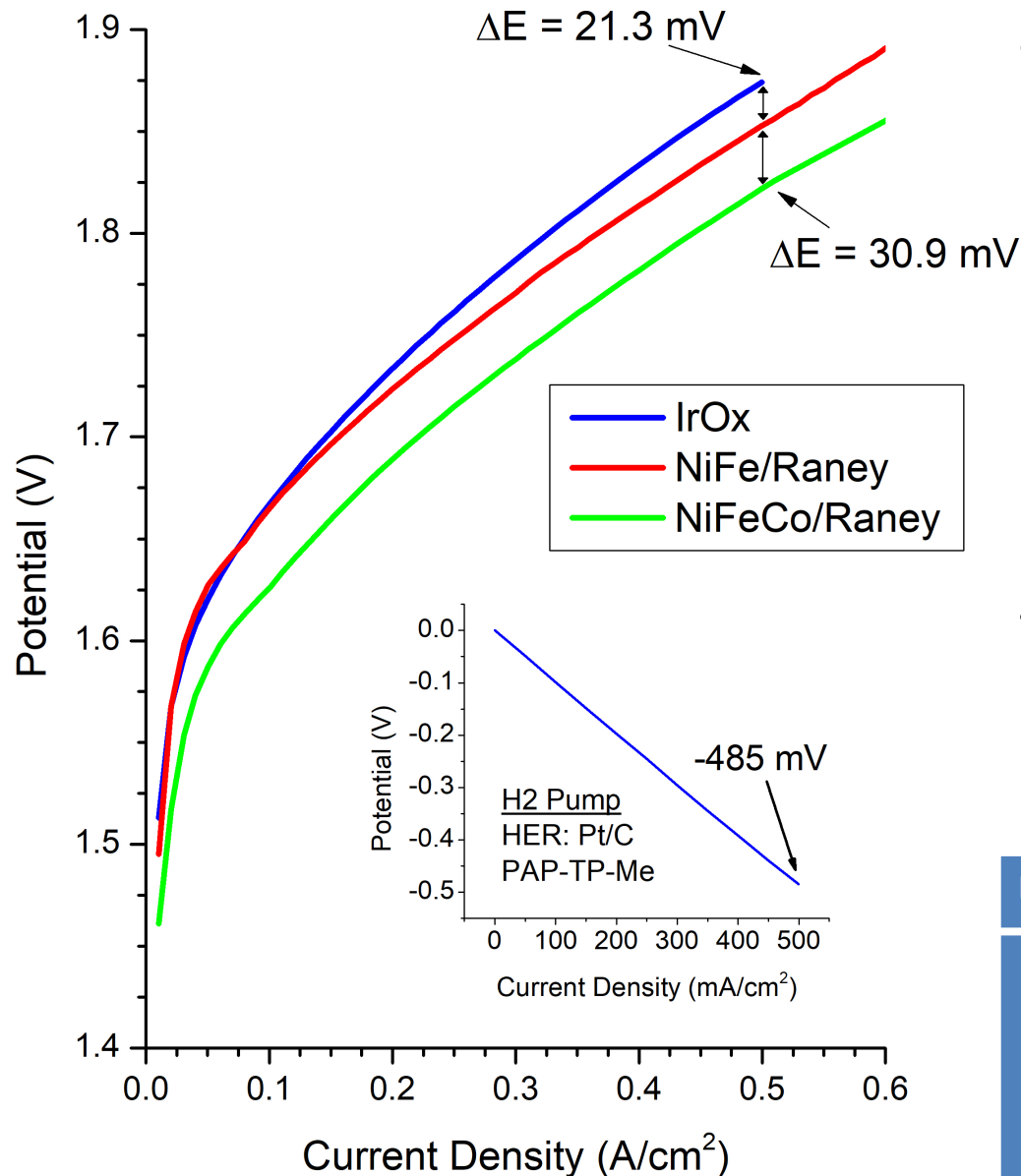




The negatively charged electrode water coverage strongly depends on the oxide layer. The results below illustrate the increased concentration of water molecules on an oxide monolayer and at the monolayer boundary (at comparable voltages). This enhancement at oxide sites is directly related to improved water-splitting performance.



Ni: gray, oxide O: orange, ionomer N+: blue, water O: red, H: white

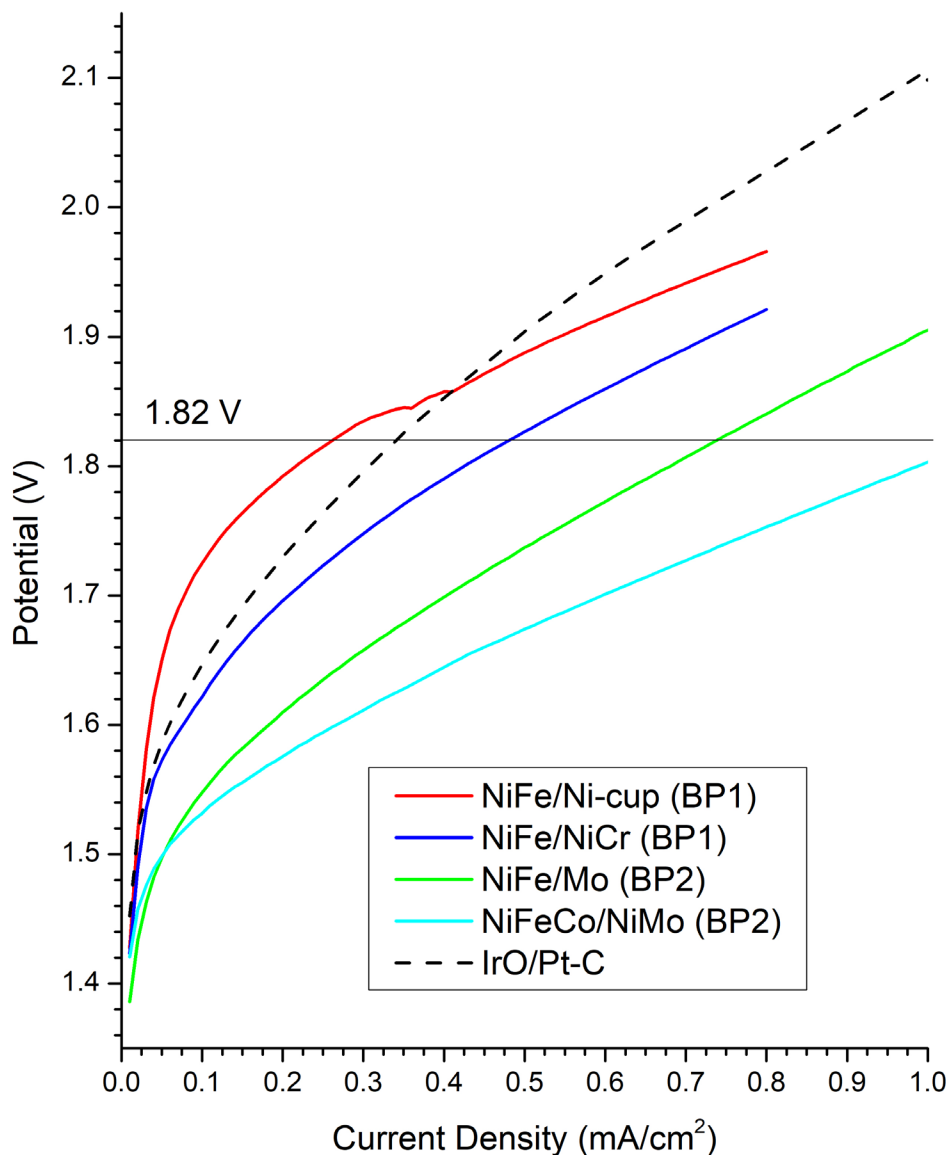


- A cell using an NiFeCo OER catalyst operated at 1.822 V @ 500 mA/cm², 31 mV lower than NiFe.

| | |
|---------|--------------------------------------|
| 1.230 V | E^0 |
| 0.075 V | Membrane Ω |
| 0.485 V | Pt η (From H ₂ pump) |
| 0.125 V | OER η (Go/No-go) |
| <hr/> | |
| 1.915 V | Total > 1.822 V |

- Operating conditions:
 - Pt/C (TKK 47.2 %) HER electrode
 - Baseline UDel membrane
 - T = 50°C
 - 1% K₂CO₃ electrolyte

| Milestone # | Project Milestone | Progress |
|-------------|--|---------------------|
| Go/No-Go | OER Electrocatalysts: Using PGM-free OER electrocatalysts in an AEM MEA operating under electrolysis conditions, at a current density of 500 mA/cm ² achieve 125 mV or lower overvoltage. | Completed 13 |



- A water-splitting cell using NiMo/C HER catalyst showed a 95 mV lower potential than any cell run in BP 1.
- When NiFeCo is used as the OER electrode the operating potential at 1A/cm² reaches 1.80 V, exceeding the BP2 goal by 20 mV.

OER: NiFeCo/Raney

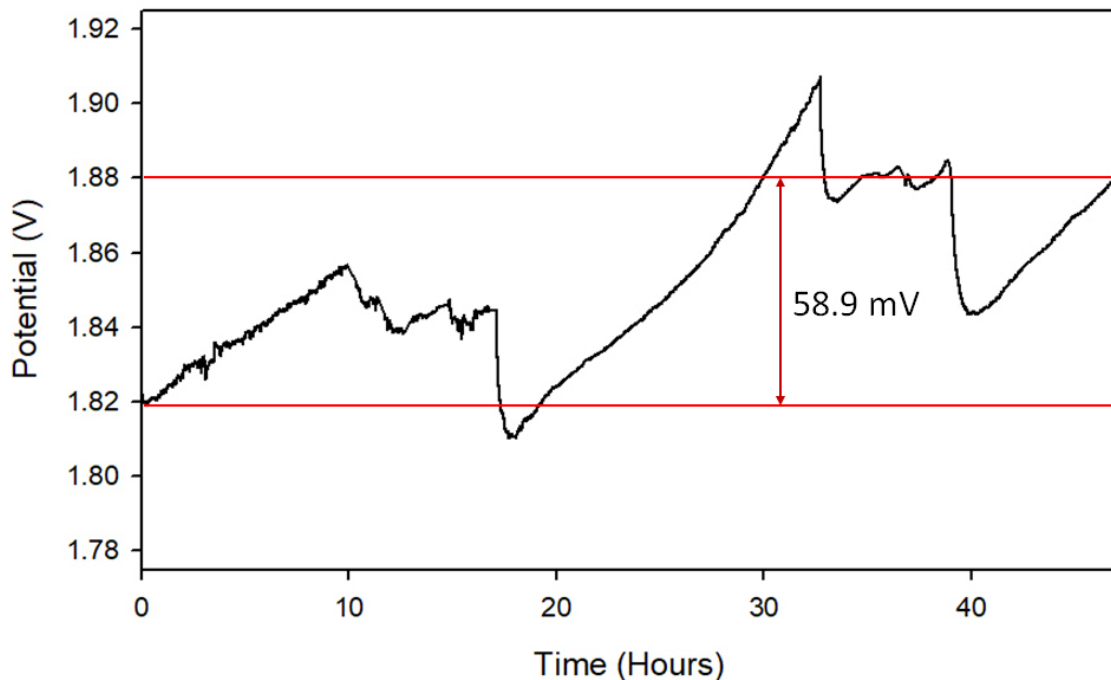
HER: NiMo/C

Operating Temperature: 85°C

UDeI PAP-TP-MQN-XC membrane

3% K₂CO₃ solution feed to OER electrode

| Milestone # | Project Milestone | Progress |
|-------------|--|-----------|
| Go/No-Go | AEM MEA: Demonstrate PGM-free <u>AEM MEA</u> electrolyzer performance of 1 A/cm ² at ≤1.82 V with less than 5 mV/hr decay at 90°C for 48 hrs. | Completed |



- Voltage increased only 58.9 mV over a 47.1-hour period, a rate of 1.25 mV/hr.

OER: NiFeCo/C
HER: NiMo/C
Electrolyte: 3% K_2CO_3 at OER electrode
PAP-TP-MQN-10C
Operating temp: 90°C

- Periodic decreases in potential correspond to instances where the electrolyte solution is replaced.
- The source of OH^- reactant for the OER reaction is from the equilibrium between CO_3^- and water, suggesting that CO_3^- is consumed at the OER electrode.

| Milestone # | Project Milestone | Progress |
|-------------|--|-----------|
| Go/No-Go | AEM MEA: Demonstrate PGM-free AEM MEA electrolyzer performance of 1 A/cm ² at ≤ 1.82 V <u>with less than 5 mV/hr decay at 90°C for 48 hrs.</u> | Completed |



“This project is strategically attacking challenges associated with both the catalyst and the membrane. The results are extremely encouraging.”







“The project has had difficulty in accessing a solid benchmark and has seen complex chemistry during in situ electrolysis testing. There is a challenge to overcome with membrane stability during in situ operation (>5000 hours), as well as a challenge in electrode and membrane integration (ionomer/binder concept).”

- We have demonstrated the *in-situ* durability via a 65-hour steady state experiment at 1 A/cm² wherein the operating potential increased at a rate of 1 mV/hr.

“It is not clear that the alkaline membrane will be effective. It is simply a very hard problem to develop a new membrane.”

- Crosslinking has gone a long way in addressing the issues with the membranes encountered in BP1. The mechanical strength has increased while water swelling and area specific resistance has decreased.



| Partner | Project Role |
|---|---|
|  Northeastern University | Northeastern University Project lead, catalyst development, and cell testing |
|  UNIVERSITY OF DELAWARE | University of Delaware Membrane development, synthesis, and characterization |
|  Advent | Advent North America Electrode fabrication |
|  BERKELEY LAB Lawrence Berkeley National Laboratory | LBNL Electrochemical systems modelling |
|  Sandia National Laboratories | SNL Modeling of the catalyst-ionomer and catalyst-electrolyte interfaces |
|  NREL NATIONAL RENEWABLE ENERGY LABORATORY | NREL Membrane characterization |



- Assess the performance of different NiFeX ternary OER catalysts (where X= Zn, Cr, etc.) and optimize the relative ratios of each metal.
- Develop methods for increasing the Mo content of the NiMo/C HER catalyst.
- Investigate the efficacy of different ionomer membrane backbone structures.
- Determine the feasibility of increasing the ionomer membrane crosslinking.
- Apply the understanding of alkaline electrolyzers gain from modeling efforts to practical reactors.
- Leverage modelling efforts to determine the benefits of metal nanoparticle encapsulation (BP1) and metal core-shell structures (BP2) in HER catalysts.



- One quarter through BP3 we have met all the milestones related to membrane development.
- The milestones for cell stability and OER catalyst performance have met.
- We are 50 mV from meeting the over cell performance requirement.

| | Target | Units | Current Status | Ultimate Target |
|----------------------|---|-------------------|----------------|-----------------|
| Operating conditions | Current density | A/cm ² | 1 | 1 |
| | Operating temperature | °C | 90 | 90 |
| | Model Voltage | V | 1.69 | 1.62 |
| | Unexplained voltage losses | V | 0.13 | 0.10 |
| Milestones | Cell voltage | V | 1.77 | 1.72 |
| | Cell performance decay (@90°C for 48 hours) | mV/hr | 1* | 1 |
| | Membrane ASR | Ω·cm ² | 0.05* | 0.08 |
| | HER overvoltage @ 500 mA/cm ² | mV | 208 | 100 |
| | OER overvoltage @ 500 mA/cm ² | mV | 32* | 100 |
| | Membrane IEC loss after 1000 hrs in 1M KOH at90°C | % | 3.74* | 10 |

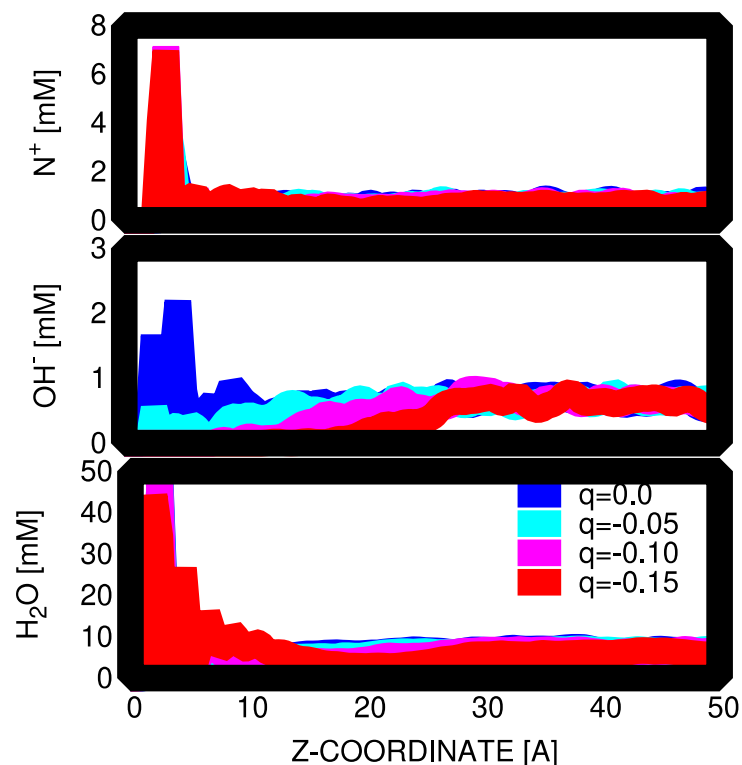
* Indicates end of project milestones that have already been met



Technical Backup Slides



- The electrical potential is significantly and **quantifiably altered by the ionomer**.
- The water molecules near the electrode surface orient with the electric field (with O further away from the surface); however, in the surfaces with an oxide layer one of the H legs of the **water molecule becomes embedded in the surface** leaving the other leg aligned along the electrode surface.
- The N^+ in the ionomer are **coordinated with both OH^- and H_2O** . A region depleted of OH^- forms near the electrode with electrical bias and grows with increased bias. Since the N^+ are **relatively immobile**, there are **significant N^+ atoms in the depletion region**, but these N^+ remain coordinated with water.
- Approximately **40% of the bare metal surface is coordinated with water molecules** and this **surface coverage almost doubles in areas covered by an oxide layer**.
- **Nanoscale heterogeneity** such as at the edge of a oxide region **provides local configurations favorable for water adsorption**.

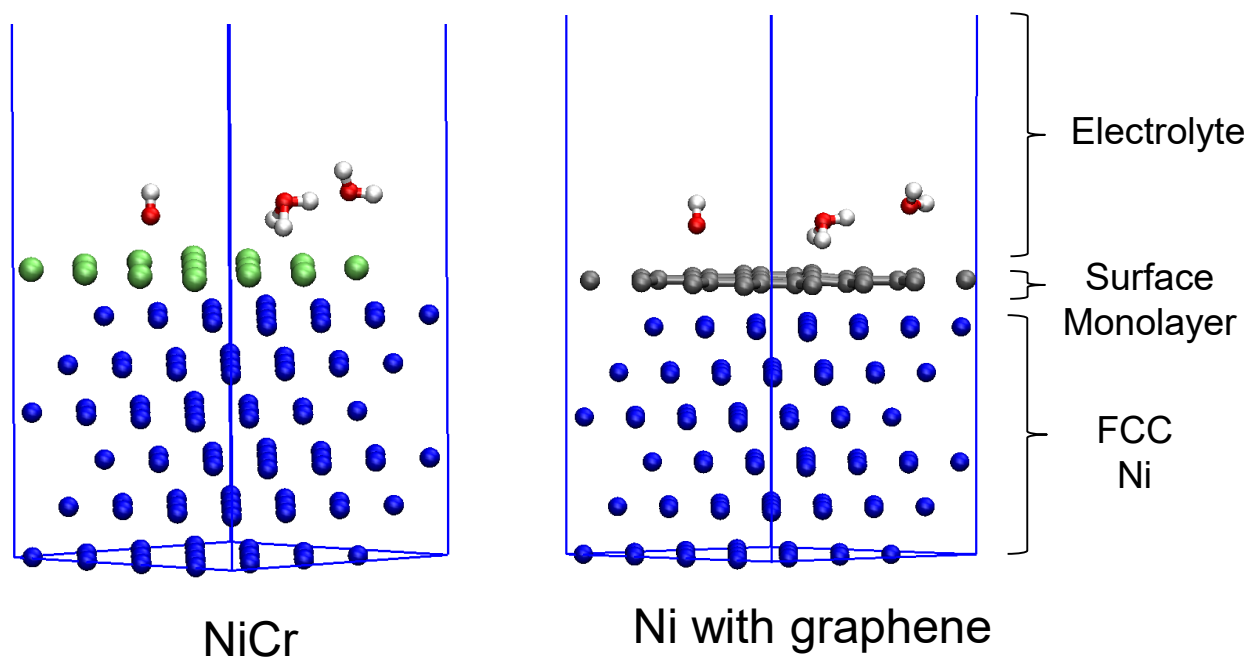


Species concentration profiles showing changes with negatively charging the HER electrode



The full molecular model has emphasized the importance of the oxide formation; however, classical molecular dynamics does not simulate reaction chemistry with fidelity. We are currently simulating the reaction chemistry for a variety of electrode compositions using *ab initio* DFT method.

| Electrode | Reacting species |
|-----------|-------------------------------|
| Ni | H ₂ O |
| NiCr | O ²⁻ |
| NiMo | OH ⁻ |
| Ni-C | H ₃ O ⁺ |

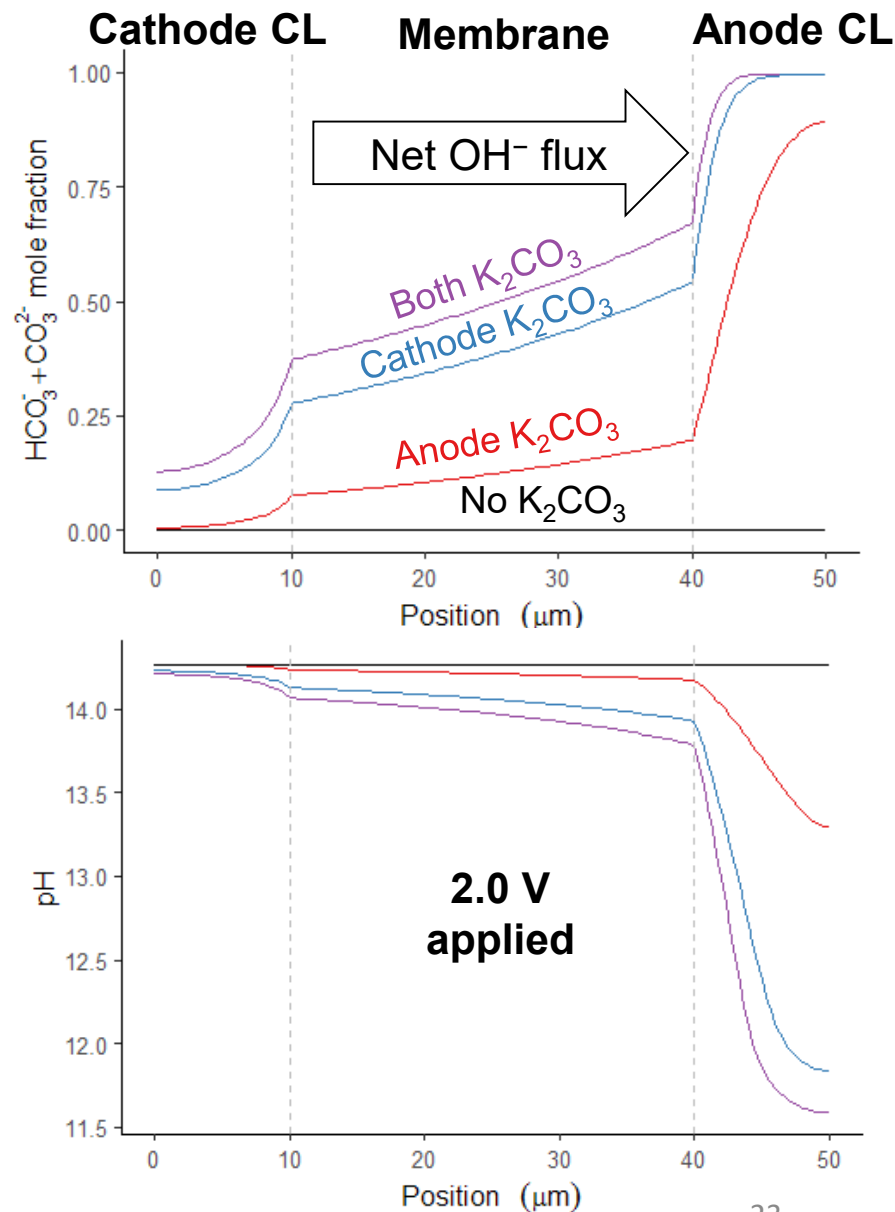
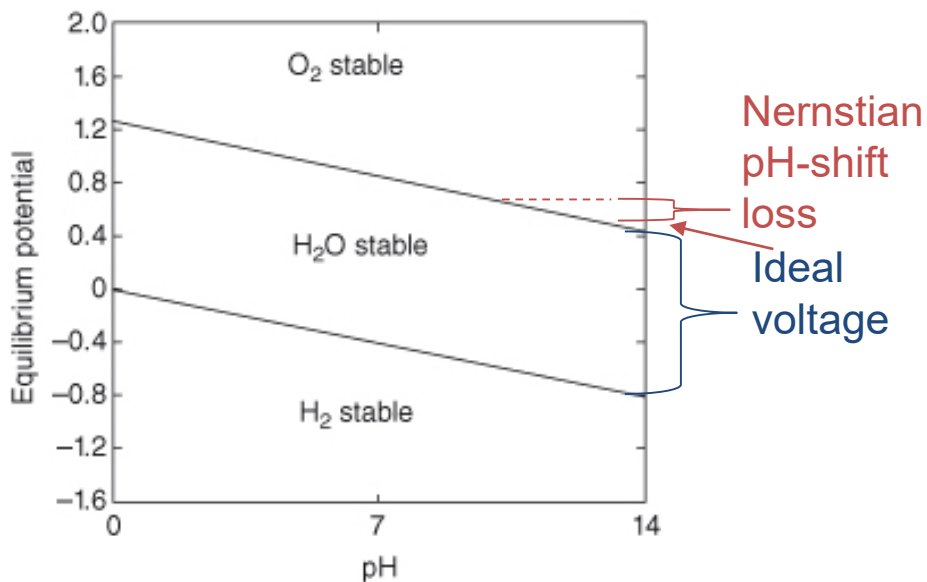


We are investigating the binding energies and the influence of surface oxides in order to better understand how Ni electrodes perform with voltage cycling / oxide buildup



Carbonate and pH gradients in cell

- Carbonate accumulates at anode due to electric field driving hydroxide flux from cathode to anode
- Accumulation of carbonate results in pH gradient
 - As anode acidifies, OER potential increases – higher voltage needed
- Anode acidifies less when carbonate is fed to anode

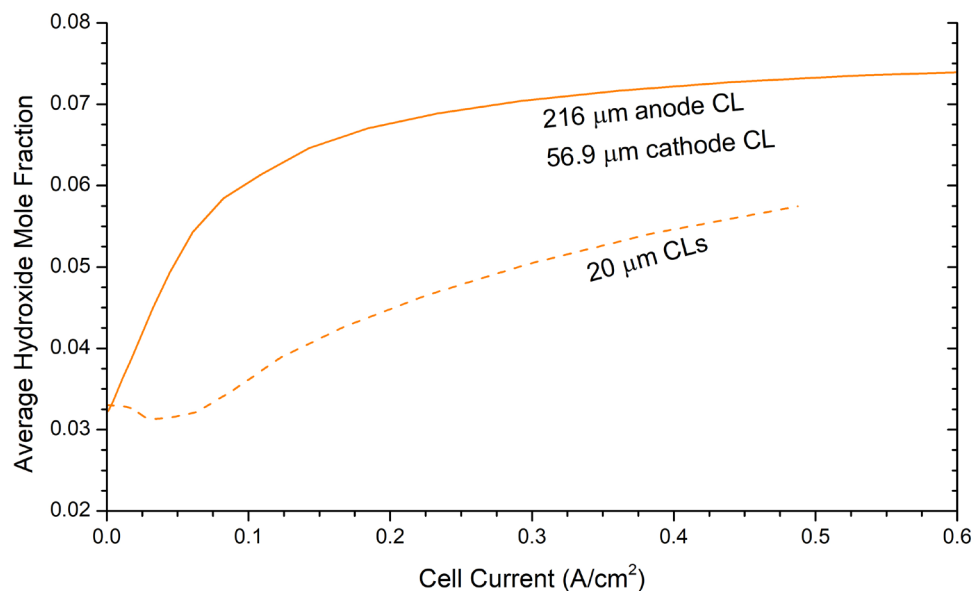
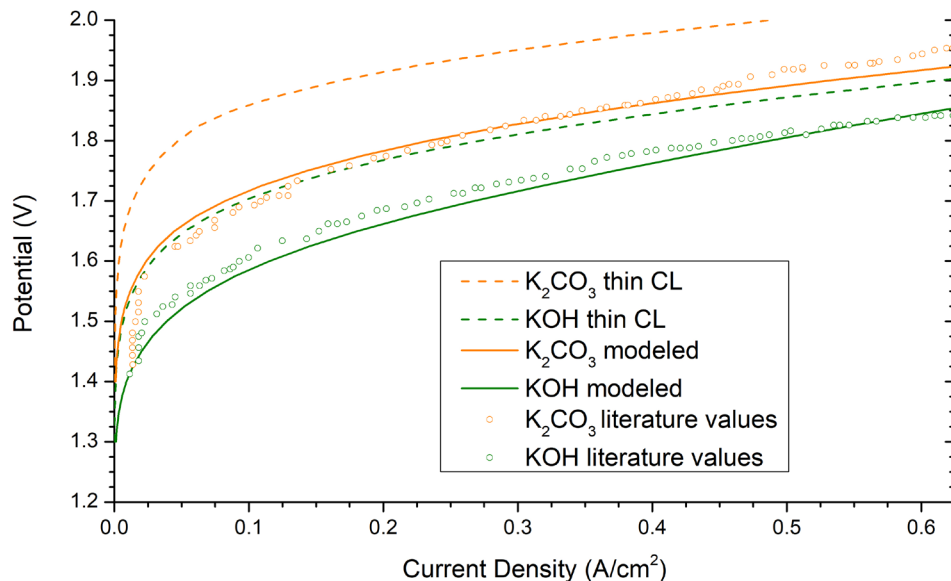




- Modeling data was used to estimate the dependence of catalyst layer (CL) thickness to performance.
- Thicknesses were estimated using the catalyst loading (L), estimated density (ρ_{solid}), and pore volume (V_{pore}):

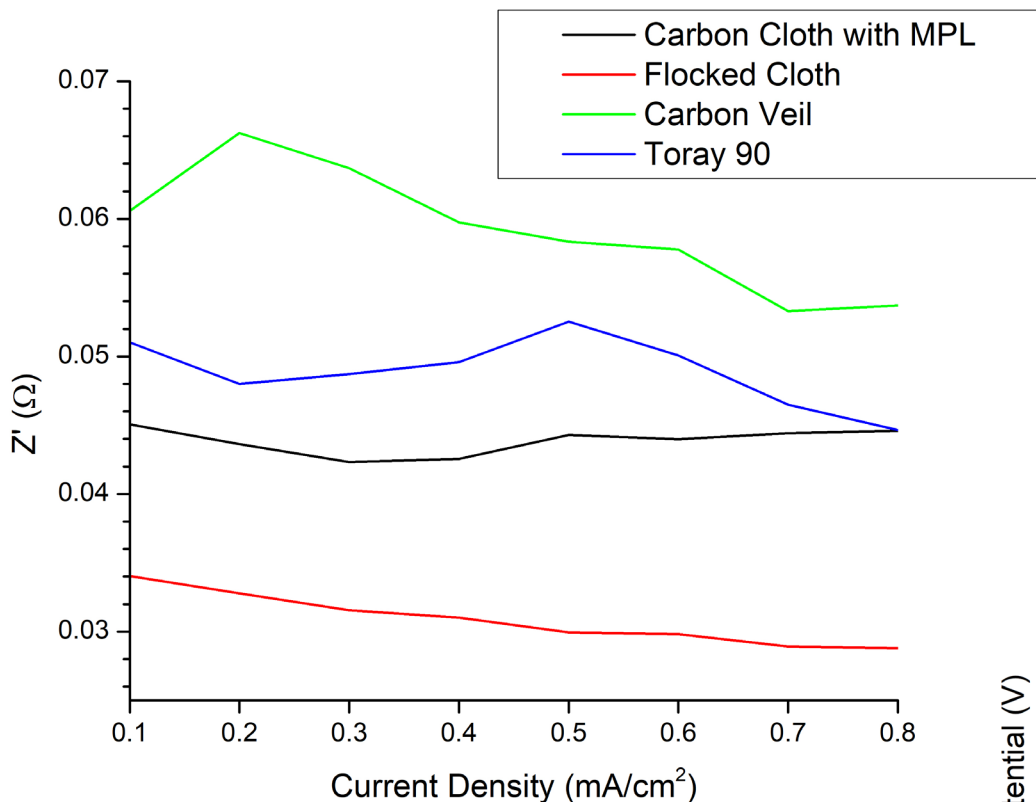
$$T_{CL} = L \left(\rho_{solid} + \frac{1}{V_{pore}} \right)$$

- Setting the catalyst layer thickness to 20 μm increased the potential.
- Thinner CLs results in decreased hydroxide content resulting in increased kinetic losses.





- Advent Technologies provided expertise in identification and preparation of unique HER electrode architectures.
- The goal was to reduce interfacial resistance by allowing hydrogen gas to clear the electrode more efficiently.
- The approach was to find a material with a porous surface that still allowed for an even deposition of a catalyst ink.
- The three proposed electrode architectures are:
 - Carbon cloth with microporous layer (MPL):
 - Proprietary Advent ink with PTFE and emulsifiers.
 - Highly hydrophobic
 - Deposited on carbon cloth and sintered
 - “Flocked” MPL
 - More concentrated version of Advent’s standard MPL ink
 - Intended to remain on the surface of the cloth and not penetrate the bulk
 - Carbon veil
 - Non-woven carbon mat
 - Highly porous ($3.4 \mu\text{g}/\text{cm}^2$)
- Interfacial resistance will be assessed by collecting the high-frequency resistance from impedance spectra taken at increasing current densities.



iR corrected polarization curves of water-splitting cells using carbon cloths with standard and flocked MPLs are nearly identical, suggesting these two data sets are the most comparable. The surface of the carbon veil is too uneven to perform well.

Current density-dependent high frequency impedance measurements show that the flocked carbon cloth has the least interfacial resistance

