2018 DOE H_2 and Fuel Cell Annual Merit Review Meeting

Advanced Catalysts and MEAs for Reversible Alkaline Membrane Fuel Cells

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Newton, MA

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Project #
FC 129

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Project Overview

Timeline

- Project Start Date: June 1, 2015
- Project End Date: June 30, 2018

Budget

- Total $1,200,496
  - DOE share $959,334
  - Contractors share $241,162
- Spent $1, 182,565 (by April. 2018)

Giner Researchers

Shuai Zhao and Tom McCallum

Subcontractors

- SUNY-Buffalo: Prof. Gang Wu and Shiva Gupta
- NREL: Drs. Bryan Pivovar and Shaun Alia, Andrew Park

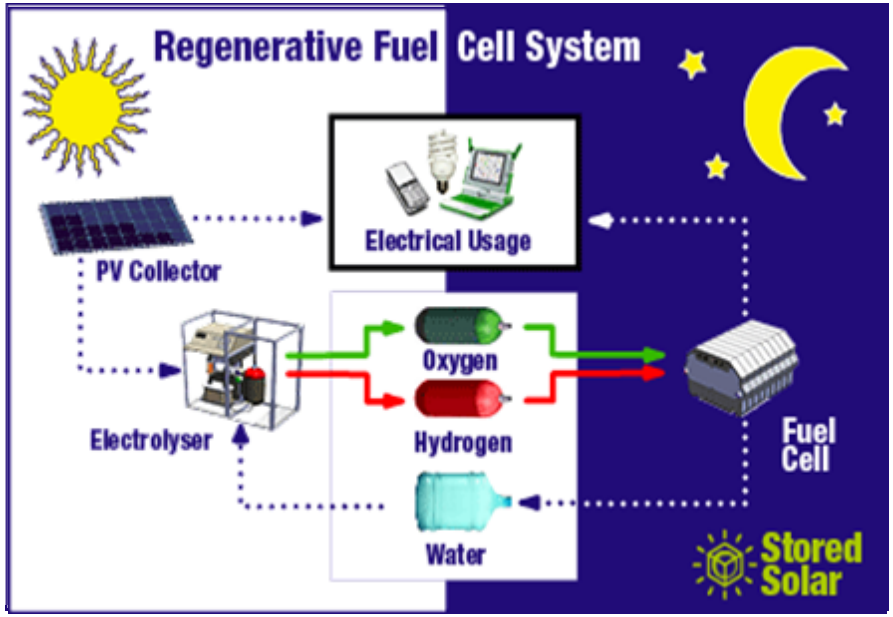
Barriers Addressed

- Activity (catalyst; MEA)
- Durability (catalyst; MEA)
- Cost (catalyst; MEA)

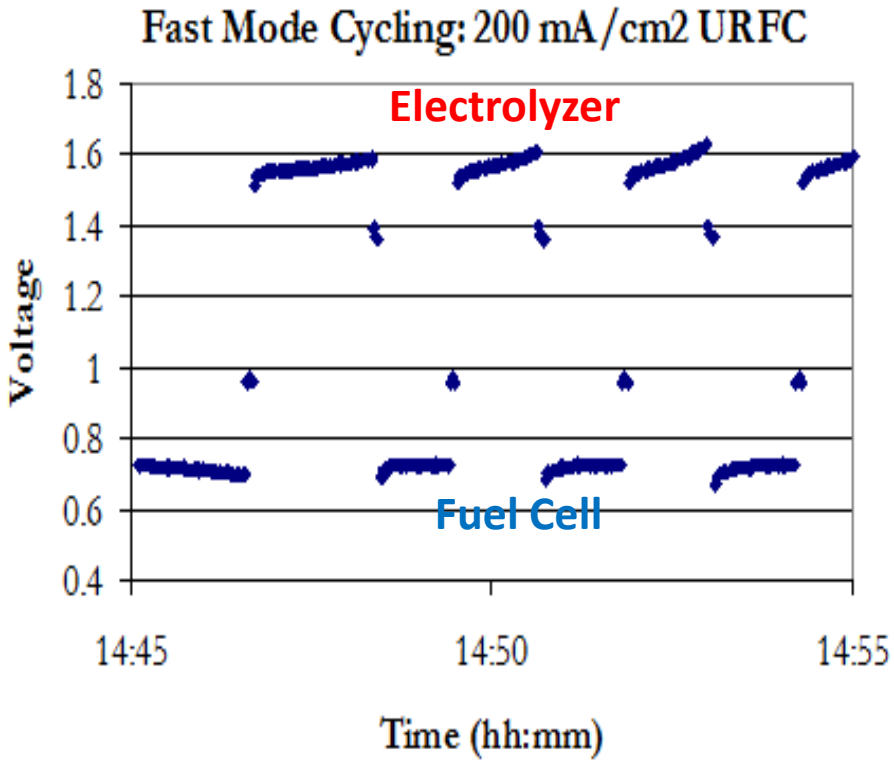
Technical Targets

- Design and develop ORR/OER bi-functional oxide catalysts
- Integrate ORR/OER bifunctional oxide catalysts and alkaline membranes to develop highly efficient reversible alkaline membrane fuel cells (AMFCs) for stationary energy storage

Reversible Fuel Cells

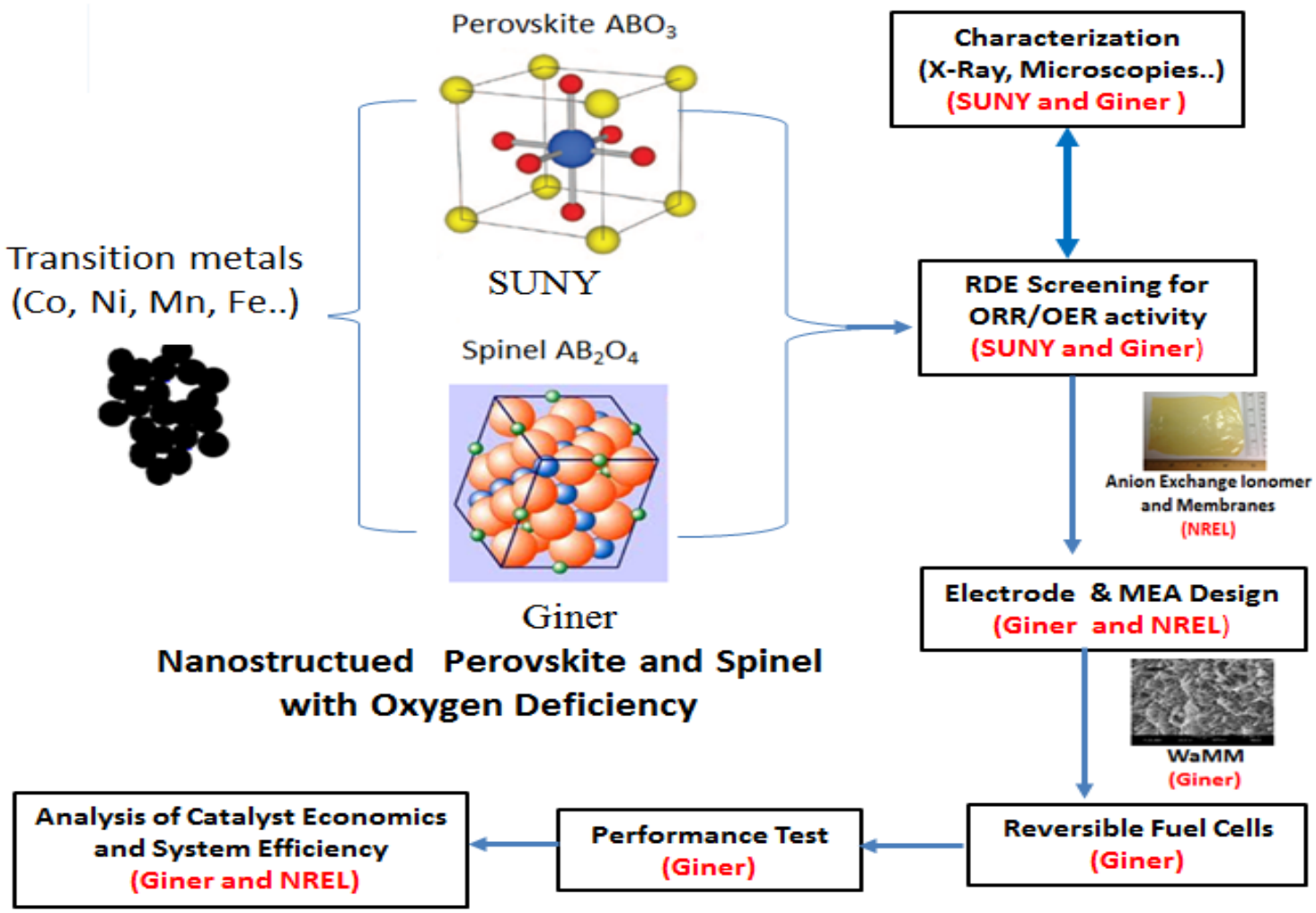


Giner unitized reversible PEM fuel cell



- Water electrolyzer is an ideal device to store energy from wind mills and solar farms, where surplus (off peak) energy is nearly free
- Stored H_2 can be used for fuel cells to generate electricity in peak time

Technical Approaches



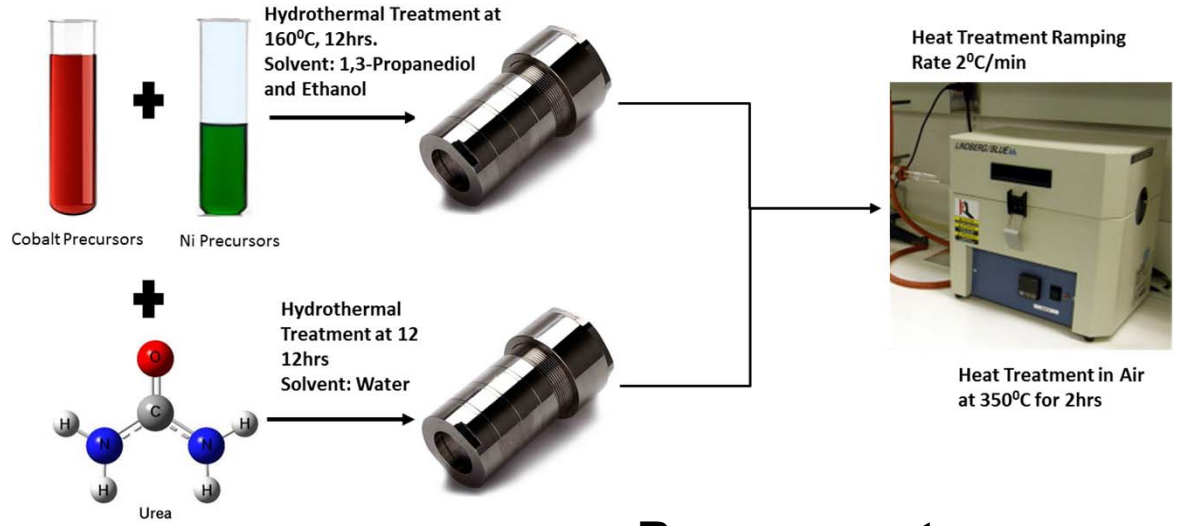
- **Catalyst Long-term Stability;**
- **MEA Fabrication Technology**

Technical Milestones

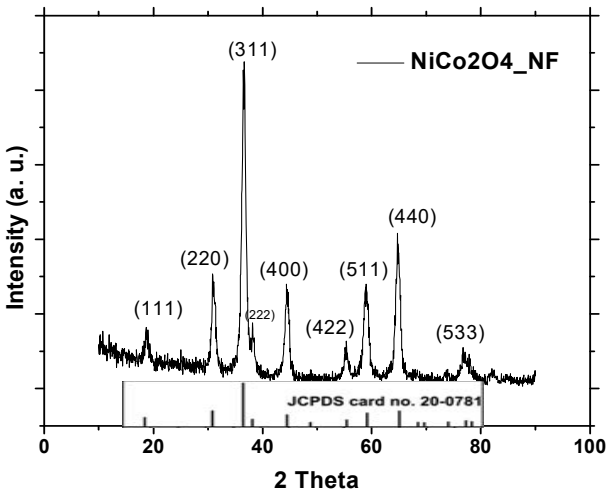
Time	Milestone Description	Completion
Q1	Synthesize $BaTiO_{3-x}$ perovskites with 3 different oxygen vacancy concentrations	100%
Q2	Prepare 3 other oxygen-deficient $AA'BB'O_{3-x}$ multiple perovskite catalysts (e.g., $BaSrCoFeO_{3-x}$ or $BaSrMnCrO_{3-x}$) with optimized defect structures	100%
Q3	Reduce perovskite particle size to nanoscale (<10 nm) with much increased surface areas (>20 m^2/g)	100%
Q3	Prepare 3 $A_xB_{1-x}C_2O_4$ spinel catalysts (A, B and C represent Co, Mn, Fe or other Metals) with particle size <10nm	100%
Q4 (go/no-go point)	In RDE, demonstrate ORR activity > 1 mA/mg oxide at IR-free 0.9 V; and OER activity > 15 mA/mg oxide at IR free 1.6 V.	100%
Q4	Provide 20g of PF AEM material in membrane/ ionomer form Membrane conductivity >0.05 S/cm at 60°C and 100% RH; H_2 permeability: 10^{-12} mol/(kPa.s.cm)	100%
Q5	3 AEI ionomer categories and 5 ionomer loadings will be evaluated to identify the best electrode composition	100%
Q6	Achieve RFC performance 0.55V for fuel cell and 2.0V for electrolyzer, both at 600mA/cm^2	100%
Q7	Achieve fuel cell and electrolyzer life of 500 hours with less than 10% performance decay	60%
Q8	Generate a full report of catalyst and reversible fuel cell economics	50%

Accomplishment 1: Carbon-free Metal Oxide Catalysts (UB)

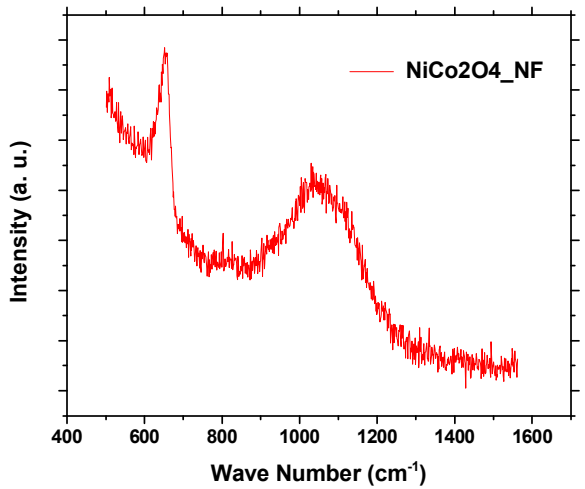
Low-cost and scalable hydrothermal synthesis



XRD Patterns

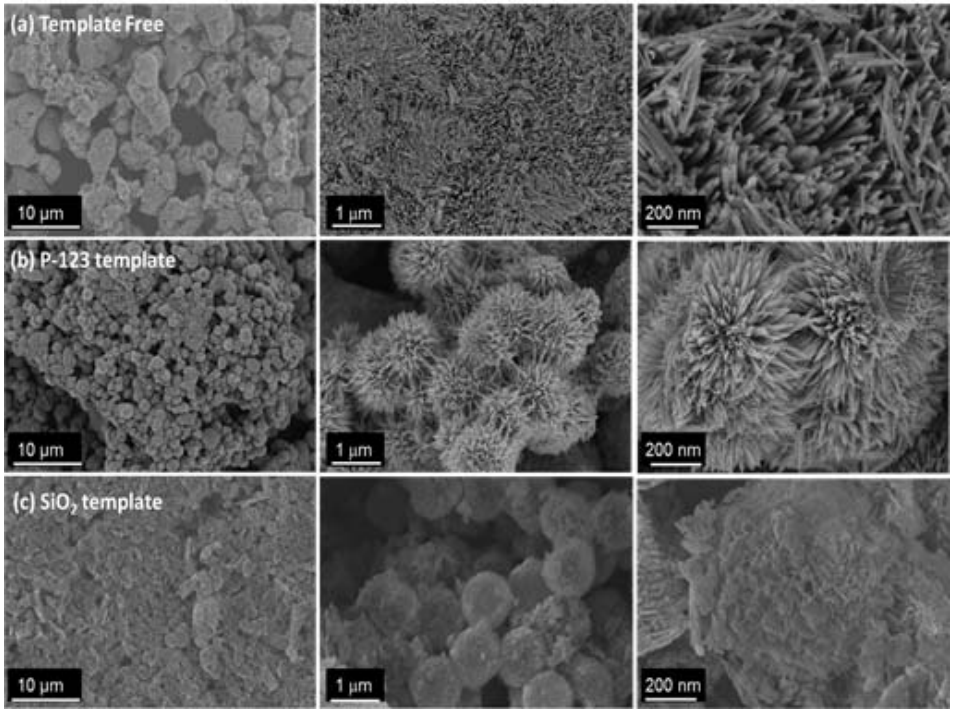


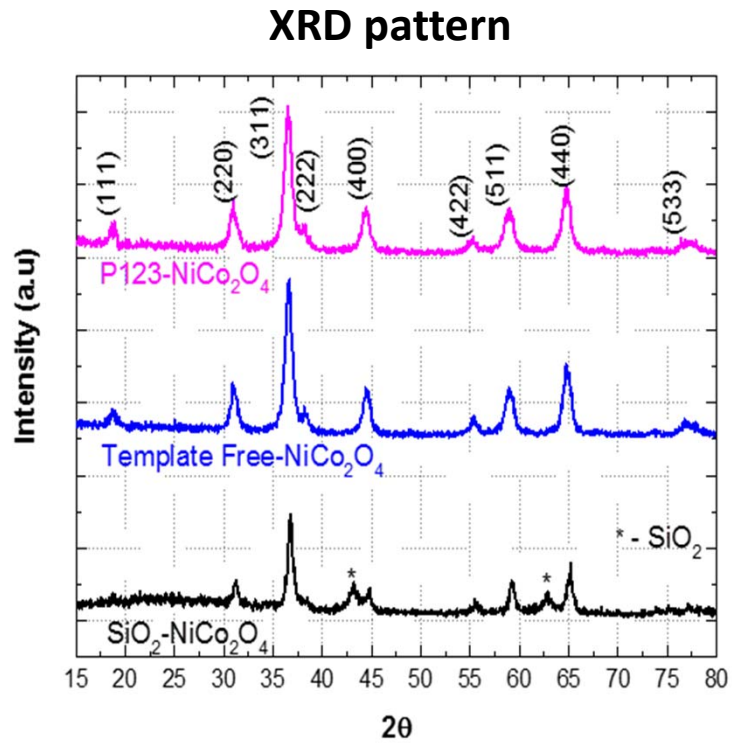
Raman spectroscopy



The XRD and Raman confirmed $NiCo_2O_4$ phase and peaks for Nickel-Cobalt Oxide are well in agreement confirmation the formation of $NiCo_2O_4$ phase.

Accomplishment 2: Carbon-free Metal Oxide Catalysts (UB)



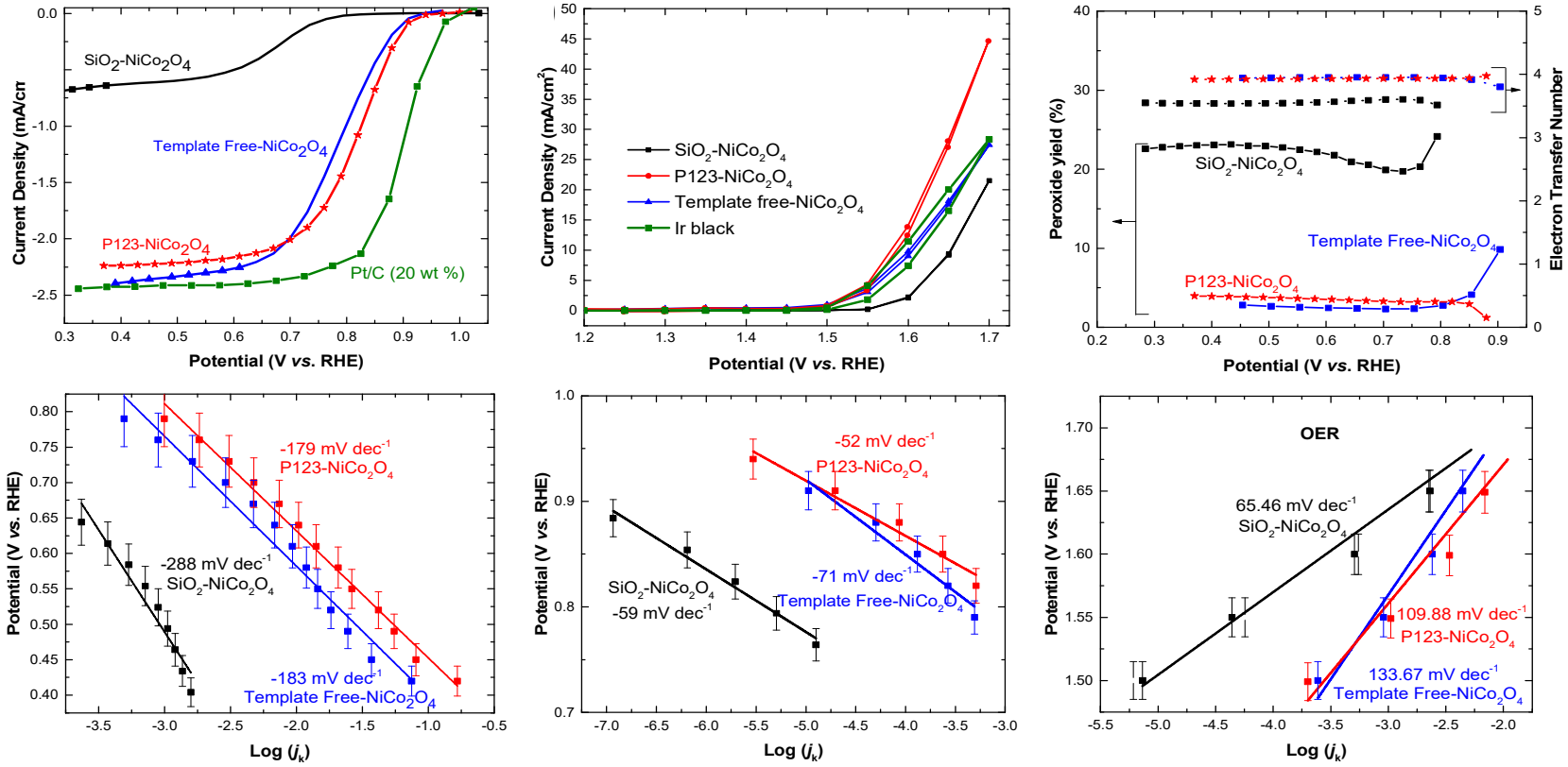


- Different morphologies of $NiCo_2O_4$ catalysts were achieved with different synthesis templates: (a) template-free, (b) P-123 soft template, and (c) SiO_2 hard template.
- The XRD pattern for template free and soft template assisted $NiCo_2O_4$ were well in agreement with the spinel-like $NiCo_2O_4$.

RDE Activity and Mechanistic Evaluation of $NiCo_2O_4$ Catalysts

Comparison between different morphologies

Steady state polarization plots for the ORR and the OER of various $NiCo_2O_4$ catalysts recorded in O_2 saturated 1.0 M NaOH at 900 and 1600rpm

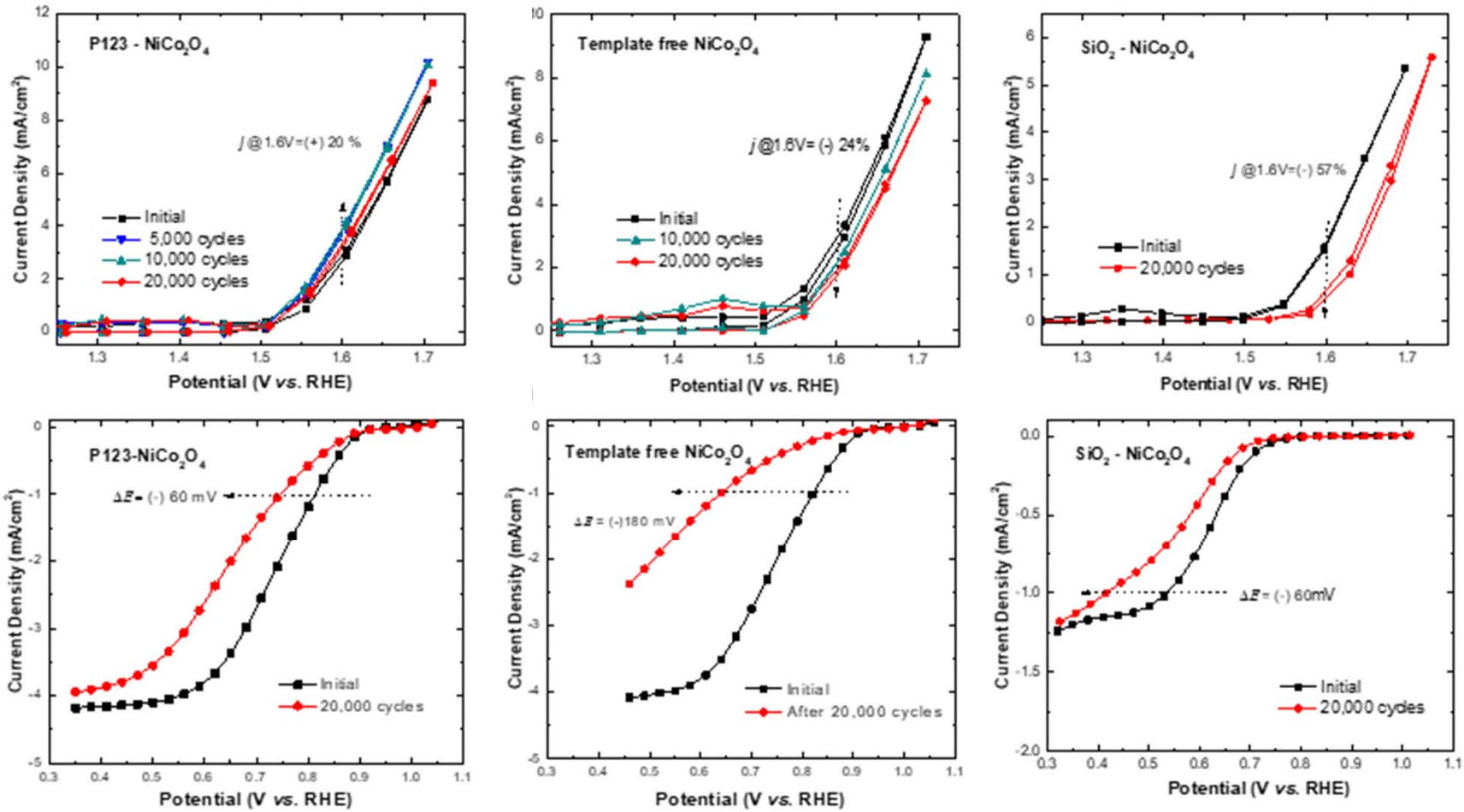


- The best activity was observed with the soft-templated $NiCo_2O_4$ catalyst, achieving onset (E_{onset}) and half-wave potentials ($E_{1/2}$) of 0.94 V and 0.82 V, representing one of best oxide ORR catalysts
- The formation of peroxide HO_2^- was monitored using ring currents measured from RRDE tests for selectivity study
- Tafel slopes for the ORR and OER were further determined to elucidate the overall reaction mechanisms.

RDE Stability Evaluation of $NiCo_2O_4$ Catalysts

Comparison between different morphologies

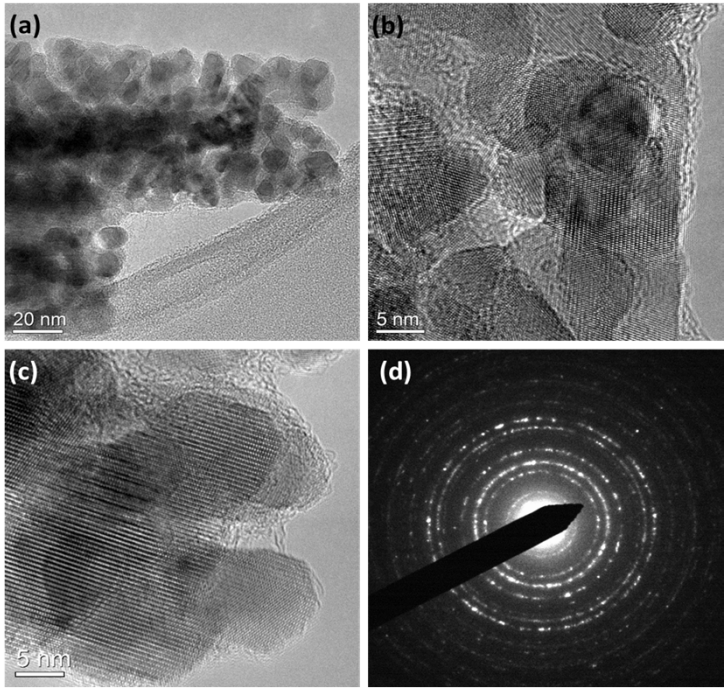
0.0 to 1.9 V in O_2 saturated 0.1 M NaOH, 25°C, 500 mV/s



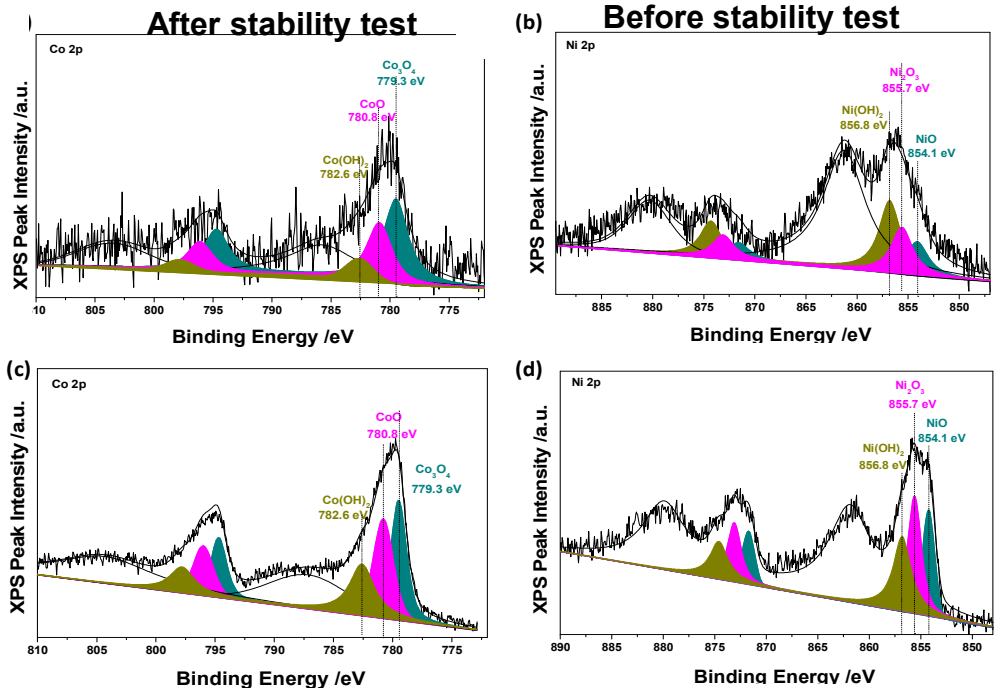
- Best performing soft-templated $NiCo_2O_4$ was also highly stable up to 20,000 cycles even with a 20% increase in current density generated at 1.6 V
- Much larger ORR degradation was observed with template-free $NiCo_2O_4$ catalyst with a loss of 220 mV in $E_{1/2}$

Mechanistic Evaluation of the Stability Enhancment

HR-TEM images

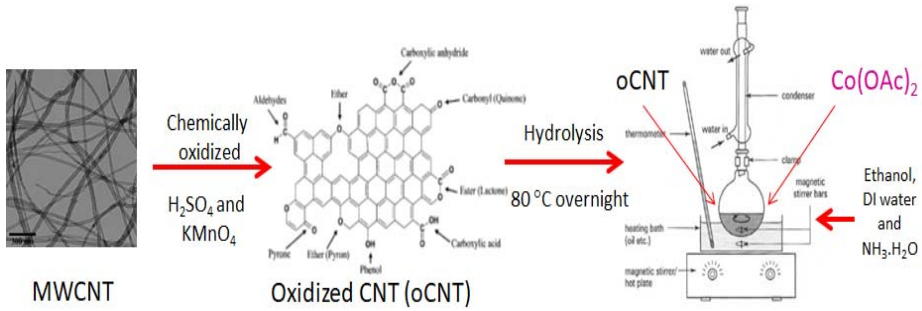


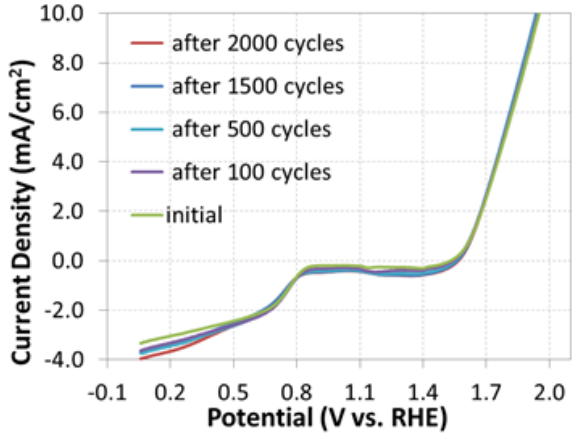
XPS Spectra

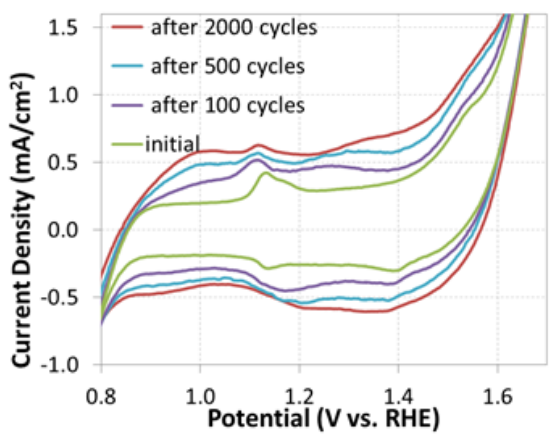


- The crystallinity of $NiCo_2O_4$ particles was well retained after 20,000 potential cycles from 0-1.9 V.
- After 20,000 potential cycles, Co species and their ratio at the catalyst surface remained nearly the same, the content of CoO was slightly increased after cycling, which could promote the OER.
- Ni species was not stable during the AST. $Ni(OH)_2$ became dominant over Ni_2O_3 and NiO.
- The formation of additional CoO and $Ni(OH)_2$ was likely responsible for the ORR activity loss .

Accomplishment 2: Scale–up of Co_3O_4/CNT Catalyst Synthesis (Giner)



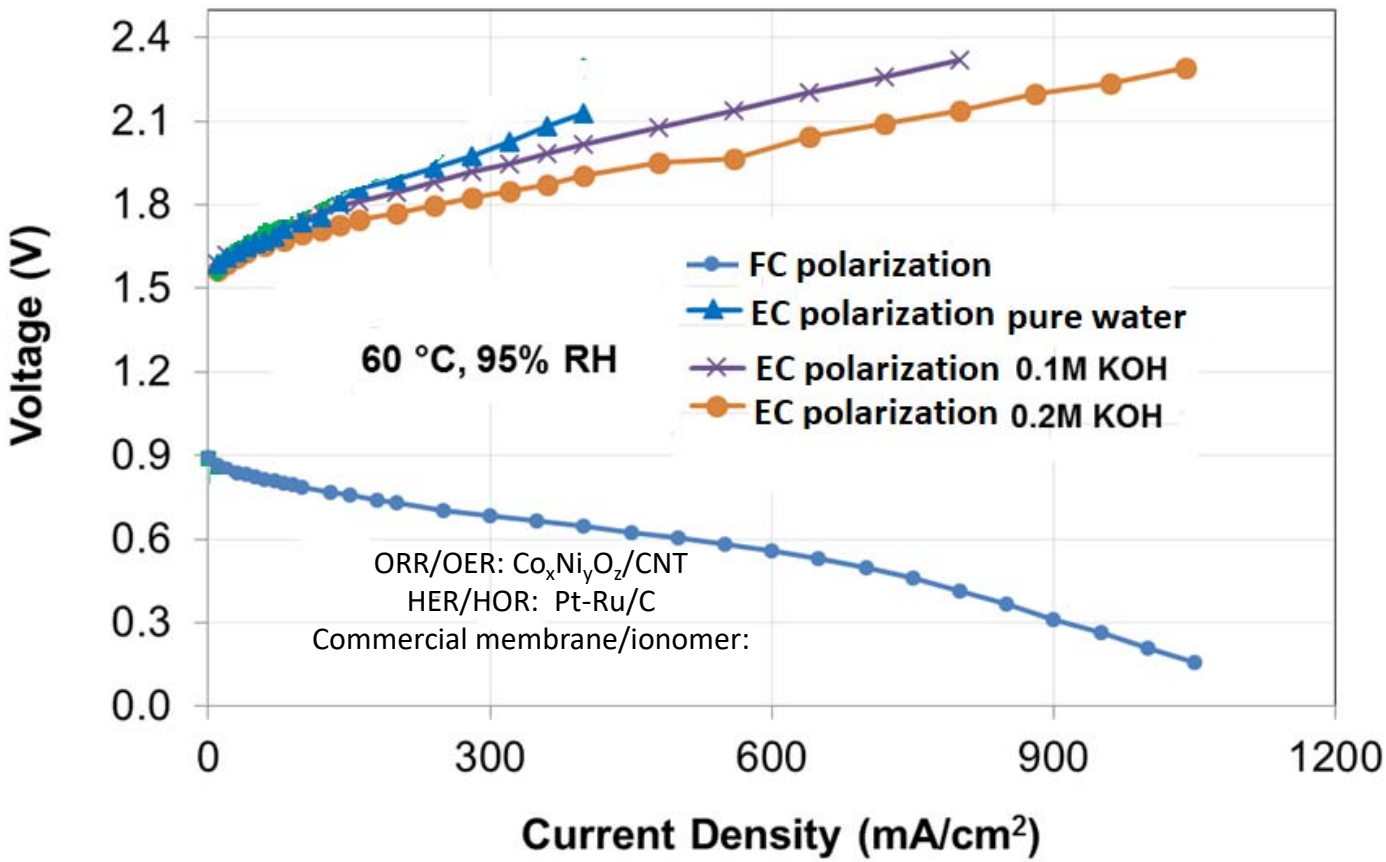




5 grams of catalyst has been synthesized, with reproducible RDE esults

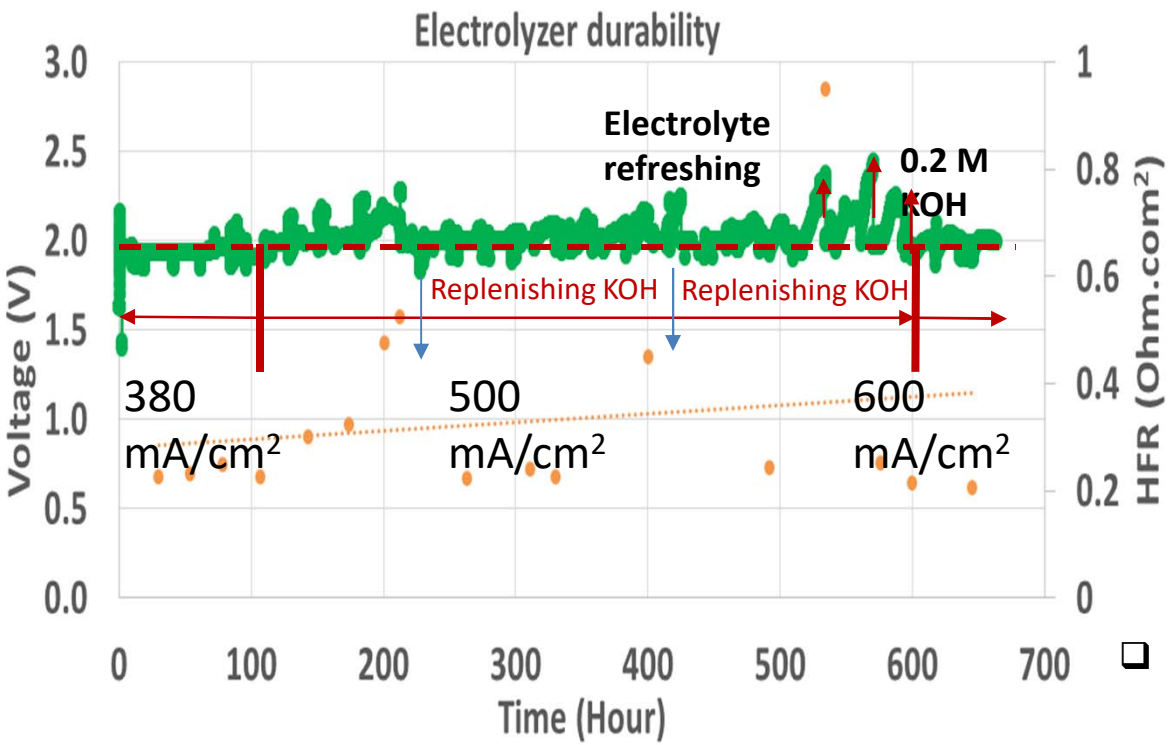
- ❑ SUNY $NiCo_2O_4$ will be mixed with Giner Co_3O_4/CNT → $Co_xNi_yO_z$/CNT

Accomplishment 5: MEA Performance Evolution (Giner)

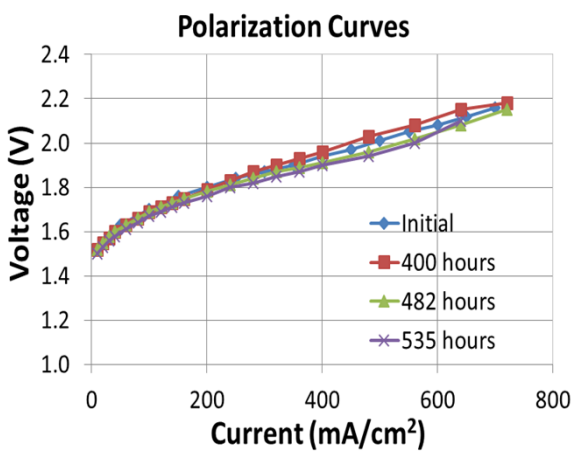


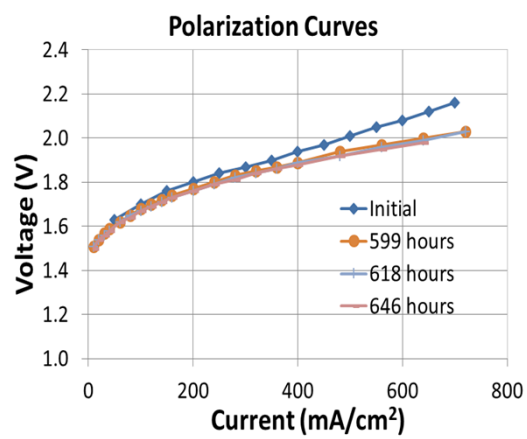
- The Co3O4/CNT demonstrates good reversibility between FC and EC
- Poor EC performance w/o water can be improved by adding diluted KOH

Electrolyzer Cell Durability Tests



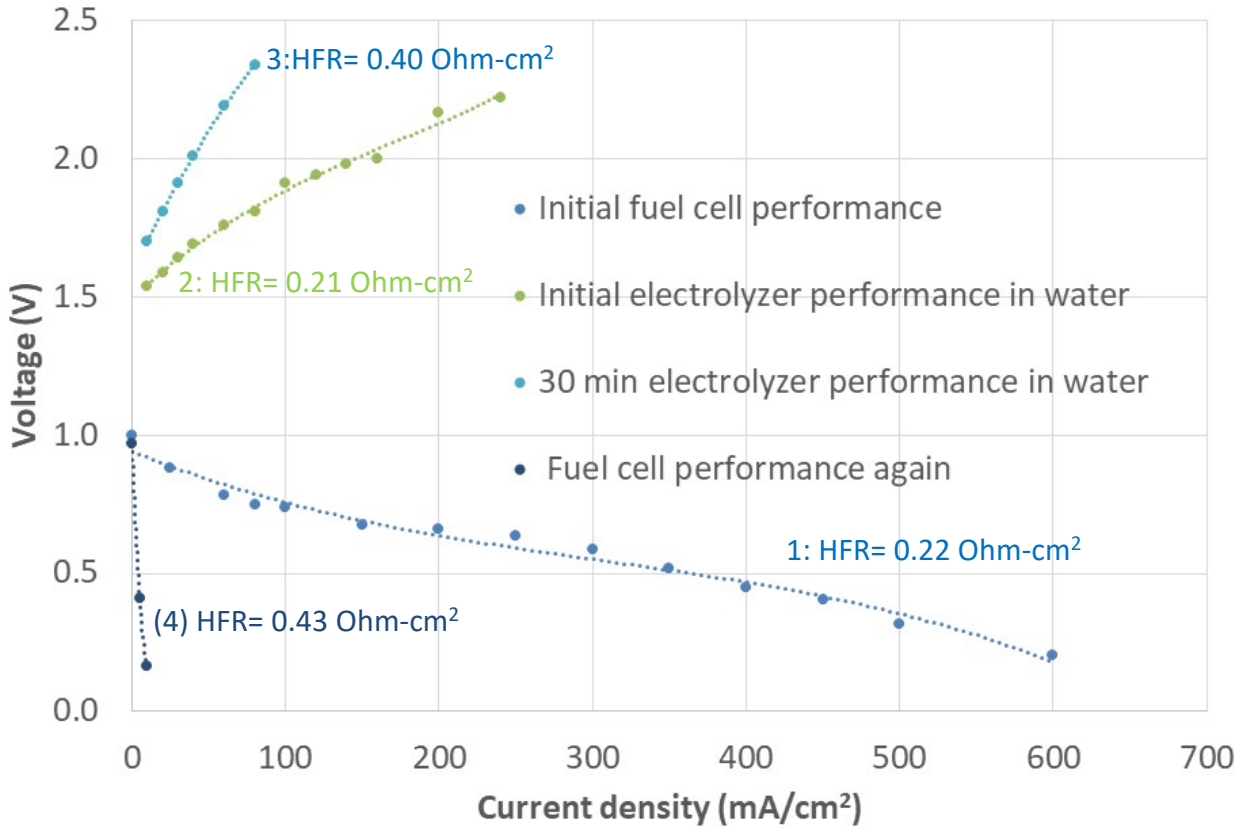
EC test conditions
Cell T=60 °C,
(0.1 M KOH, 0.2 M KOH after 500 h)
Cathode: $Co_xNi_yO_z$/CNT
(2 mg/cm², ionomer=20 w.t %)
Anode: PtRu/C
(0.7 mg/cm², Ionomer=26 w.t. %).





- EC Durability test for 600 hours showed no performance decay, surpassing millstone:
  - **2.0V @ 600 mA/cm²**
  - **>10% decay after 500 hours**
- Feeding diluted KOH solution improved EC performance
- HFR increased as the KOH wad depleted and replenishing KOH lower the HFR and improve the EC performance

Reversible Operation with Water in EC



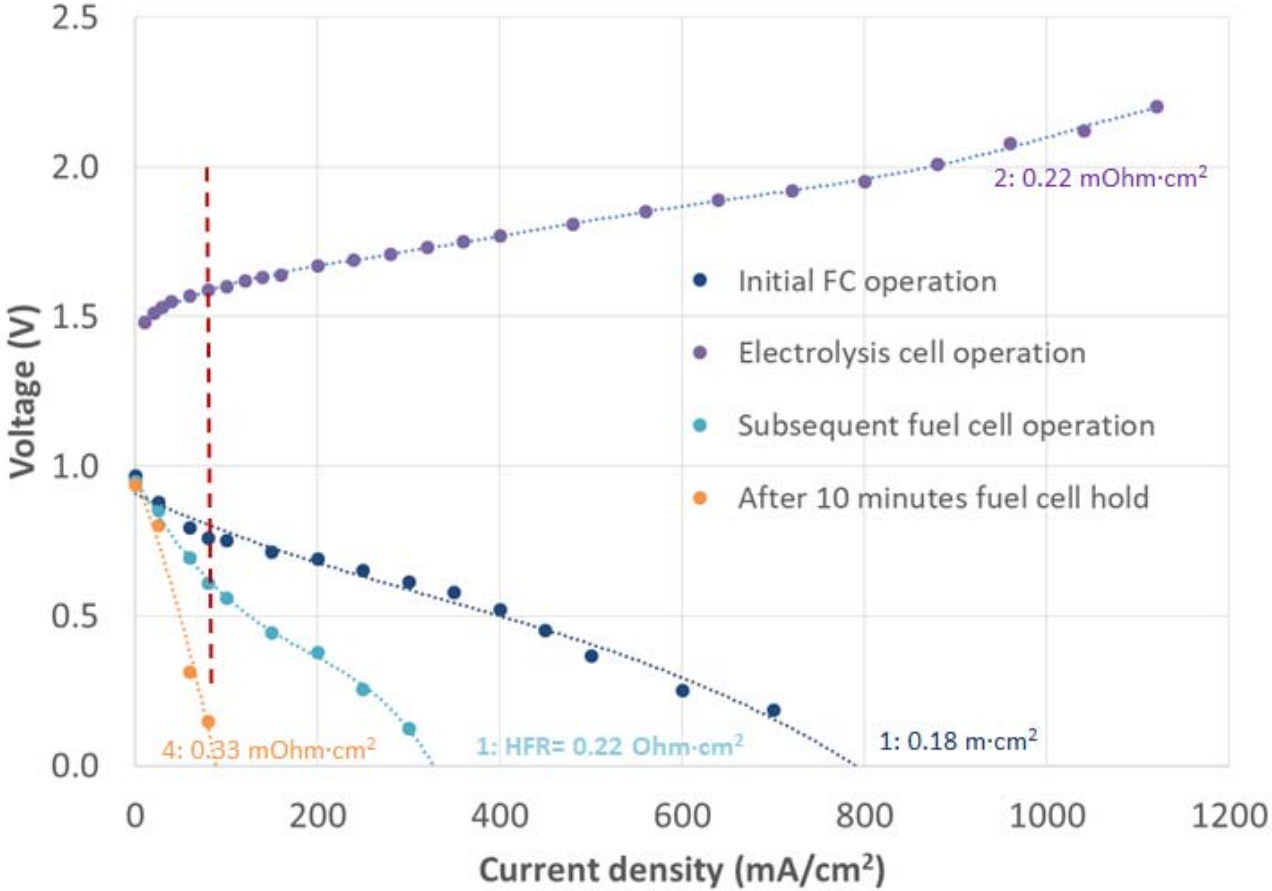
MEA
Cathode: $Co_xNi_yO_z$/CNT
(2 mg/cm^2, ionomer=20 w.t.%)
Anode: PtRu/C
(0.7 mg/cm^2, ionomer=26%).

FC Conditions
Cell T= 60 °C,
Anode/cathode T: 57/60 °C
H_2/O_2 backpressure: 35 psia.

EC test conditions
Cell T= 60 °C,
DI water feeding

- ❑ EC performed poorly with pure water feeding
  - Performance degraded even after 30 minutes
- ❑ FC performance cannot be recovered after EC test
- ❑ HFR increased after 30-minute EC test, indicating alkaline membrane

Reversible Operation with KOH Solution in EC



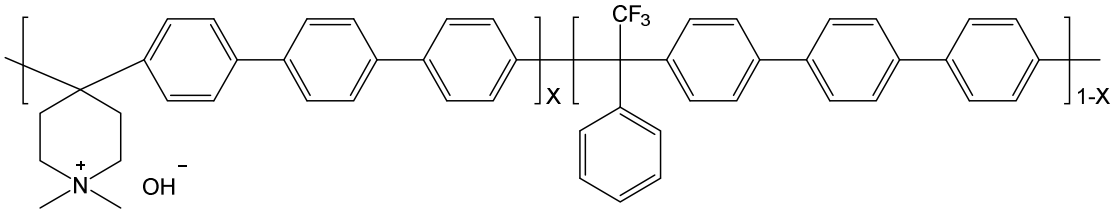
MEA
Cathode: $Co_xNi_yO_z$/CNT
(2 mg/cm^2, ionomer=20 w.t.%)
Anode: PtRu/C
(0.7 mg/cm^2, ionomer=26%).

FC Conditions
Cell T= 60 °C,
Anode/cathode T: 57/60 °C
H_2/O_2 backpressure: 35 psia.

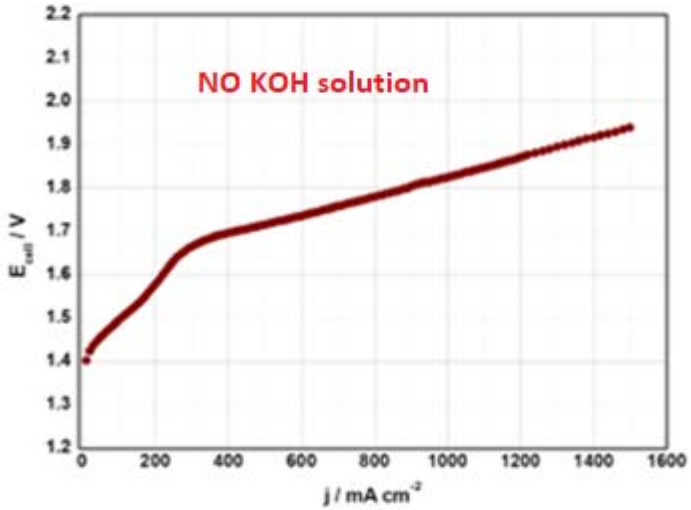
EC test conditions
Cell T= 60 °C,
DI water feeding

- Introduction of KOH introduction in the water tremendously improve the EC performance
  -Due to improved OH^- transport in the electrode
- FC performance cannot be recovered due to likely degraded membrane and ionomer under EC operation, evidenced by increased HFR

New Membrane and Ionomer: Enabled Electrolysis Operation without KOH



#1 HEMEL Performance of TP-100 ionomer with water-fed @ 80 °C



- Polarization curve obtained by applying current steps (30 sec/step),
- Operation Conditions: T = 80 °C; DI water fed @ 3 mL/min;
- HEMEL Performance: 900 mA/cm² @ 1.8 V.
- AC impedance after the cycles is 135 - 180 mΩ-cm².

Data provided by Prof. Yushan Yan at University of Delaware

- ❑ New membrane and ionomer developed by University of Delaware enabled EC operation without KOH: stable under high potential or oxidation-resistant

Summary

- Bifunctional OER/ORR catalysts $NiCo_2O_4$ and Co_3O_4/CNTs have been optimized with improved activity and durability:
  - Efforts focused more on the non-carbon catalyst development
- Bifunctional electrodes and MEAs have been optimized for durability tests and reversible operations:
  - Commercial alkaline membrane and ionomer are unstable under electrolyzer cell (EC) operation, likely due to high-potential (oxidation) caused materials degradation
  - Introduction of diluted KOH tremendously improved the EC operation but did not improved fuel cell (FC) operation without KOH solution
  - MEA under EC operation demonstrated 600-hour durability barely showing any performance decay, demonstrating remarkable catalyst stability
- Oxidation-resistant alkaline membrane and ionomer are needed to enable EC operation and reversible fuel cell operation without introducing KOH solution

Collaborations

Institutions	Roles
Giner Inc. (Giner) Lead: Hui Xu (PI), Shuai Zhao, Tom McCallum	Oversees the project; metal oxide supported on CNTs; bi-functional MEA fabrication and optimization; reversible fuel cell design; cost analysis
SUNY -Buffalo(SUNY) Sub: Gang Wu and Shiva Gupta	Graphene tube and metal oxide based OER/ORR bi-functional catalyst development; MEA fabrication
National Renewable Energy Laboratory (NREL) Sub: Bryan Pivovar, Shaun Alia, and Andrew Park	AEM development; HOR/HER catalyst development
University of Delaware Collaborator**:** Yushan Yan	Novel alkaline membrane and ionomer development

Future Plans

- Improve fuel cell/electrolysis operational reversibility using oxidation-resistant alkaline membrane and ionomer
- Complete dual operation durability test
- Perform techno-economical analysis

Any proposed future work is subject to change based on funding levels

Acknowledgments

- **Financial support from DOE EERE Fuel Cell Technologies Office**, Incubator Program Award # DE-EE0006960
- **DOE Program Managers**
  - Dr. David Peterson
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- **Giner**: Shuai Zhao, Tom McCallum, Corky Mittelsteadt
- **SUNY**: Prof. Gang Wu, Shiva Gupta, Mengjie Chen, Surya Devaguptapu
- **NREL**: Drs. Bryan Pivovar, Shaun Alia and Andrew Park
- **U. Delaware**: Prof. Yushan Yan