2017 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

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project Overview

Timeline

- Project Start Date: June 1, 2015
- Project End Date: May 31, 2017

Budget

- Total $1,200,496
  - DOE share $959,334
  - Contractors share $241,162
- Spent ~ $965,000 (by Mar. 2017)

Giner Researchers

Shuai Zhao and Tom McCallum

Collaborators

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

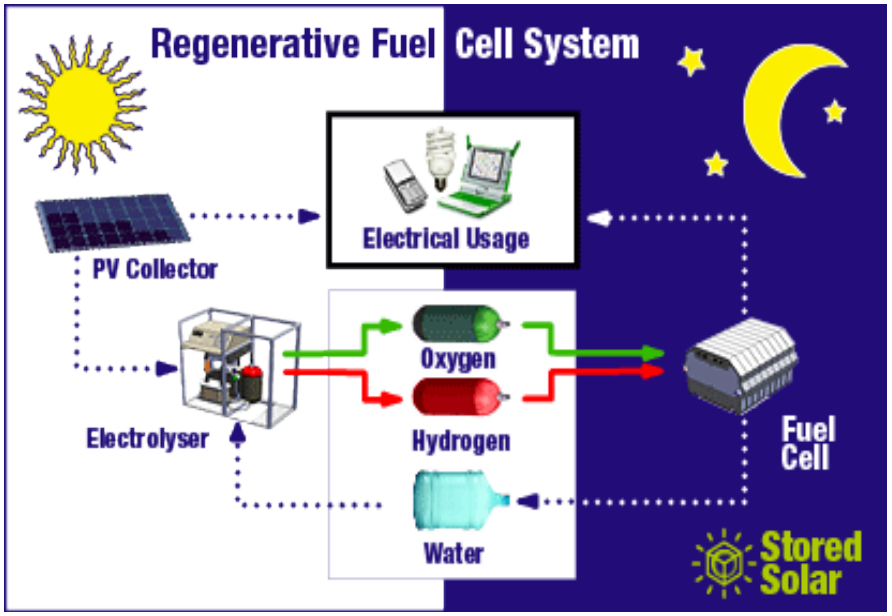
Barriers Addressed

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

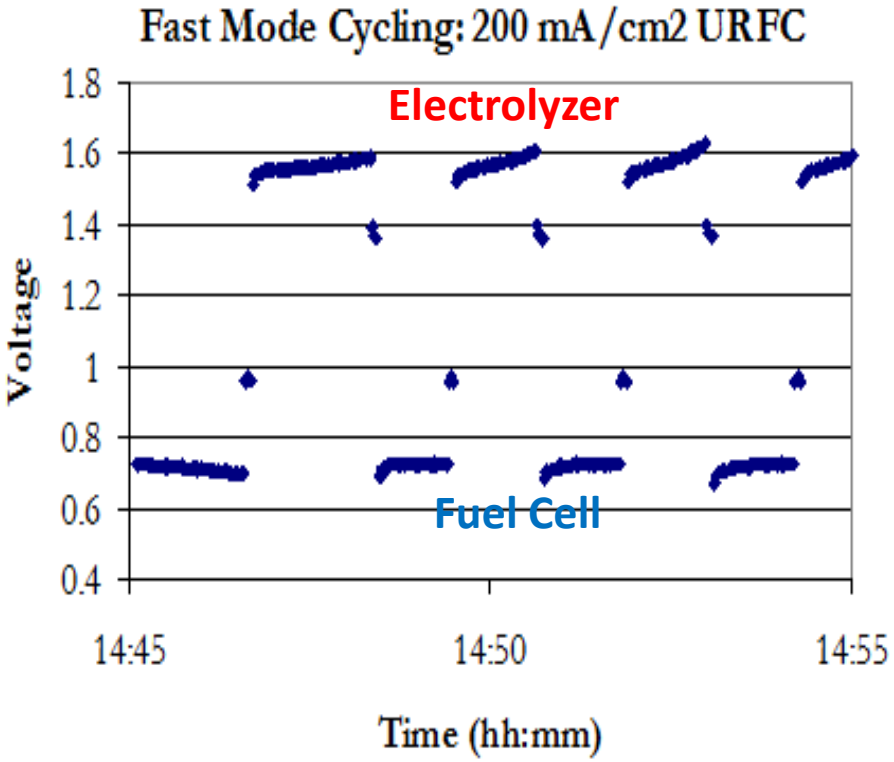
Technical Targets

- 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

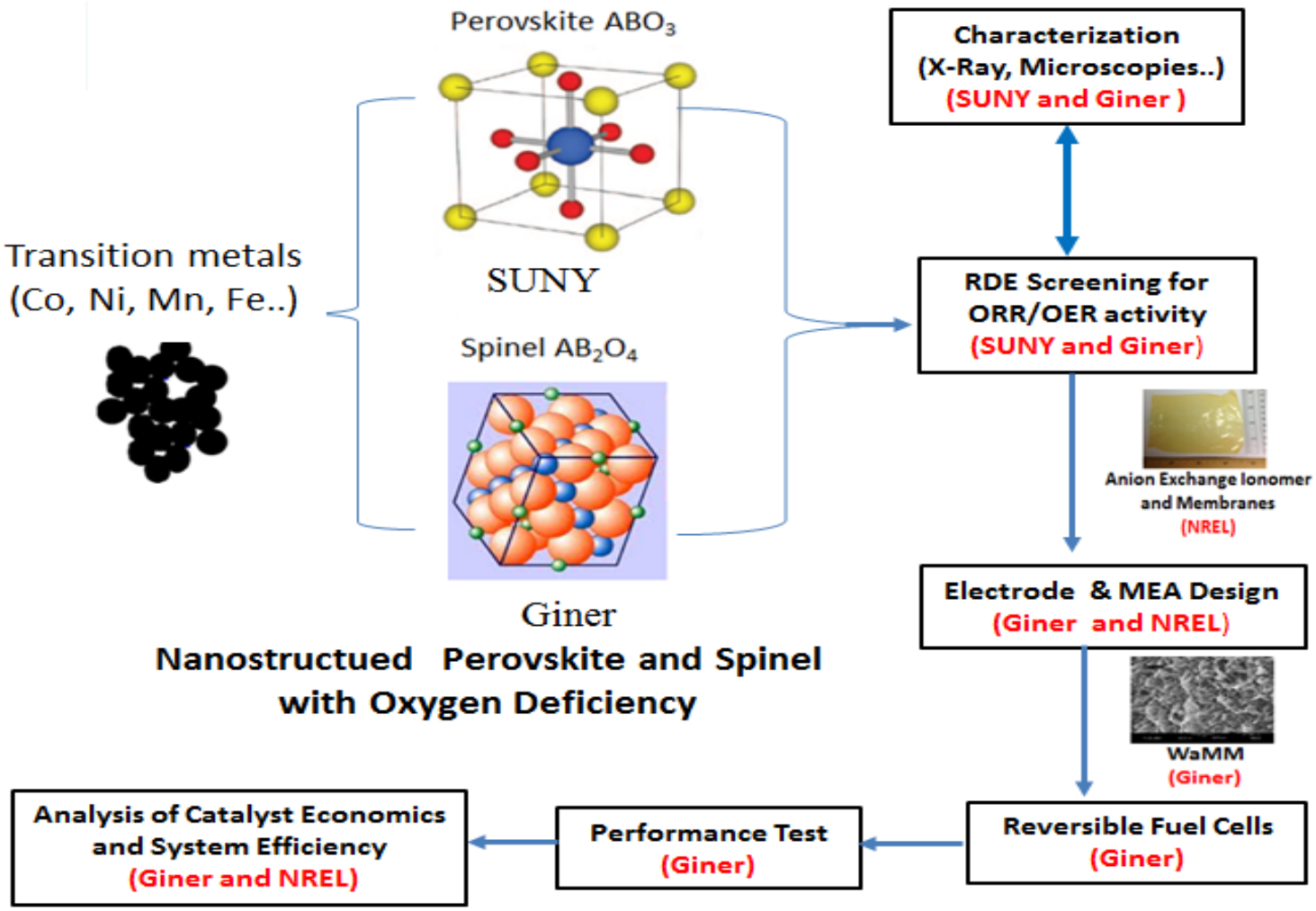


Giner unitized reversible PEM fuel cell



- 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



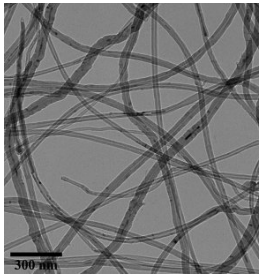
- **Catalyst Long-term Stability;**
- **MEA Fabrication Technology**

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 /R-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	30%
Q8	Generate a full report of catalyst and reversible fuel cell economics	50%

Note: Q6 milestone was partially modified after project review meeting in February 2017

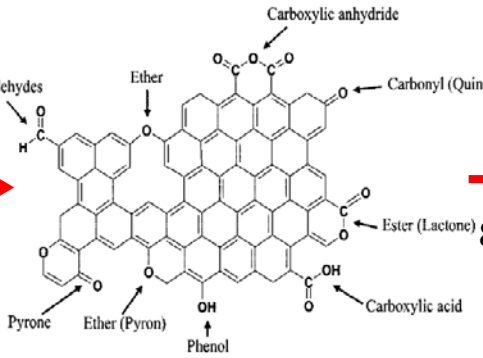
Accomplishment 1: Synthesis of Co_3O_4-oCNT Catalysts (Giner)



MWCNT

Chemically oxidized

H_2SO_4 and $KMnO_4$



Oxidized CNT (oCNT)

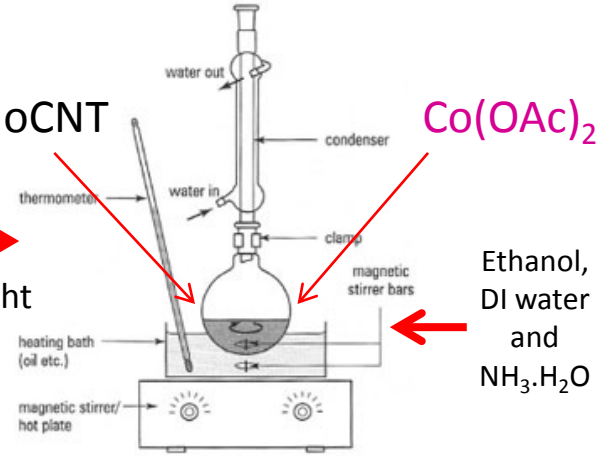
Hydrolysis

80 °C overnight

oCNT

$Co(OAc)_2$

Ethanol, DI water and $NH_3.H_2O$



Hydrothermal, pressurized heating

150 °C for 5h in Parr Bomb

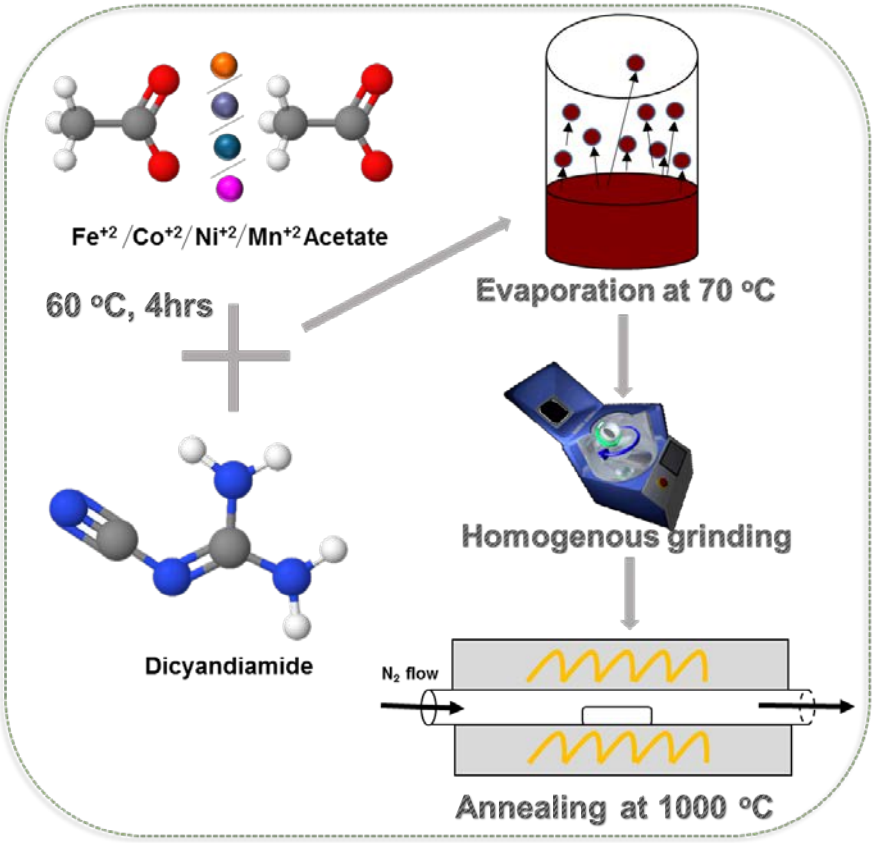
Post-treatment, ammonia reduction

250 °C for 6h in 5% NH_3/Ar

Zhao et al, Applied Catalysis B: Environmental, **2017** *203*, 138-145.

Accomplishment 2: Development Stable Mn based Graphitized Carbon Nanostructure (UB)

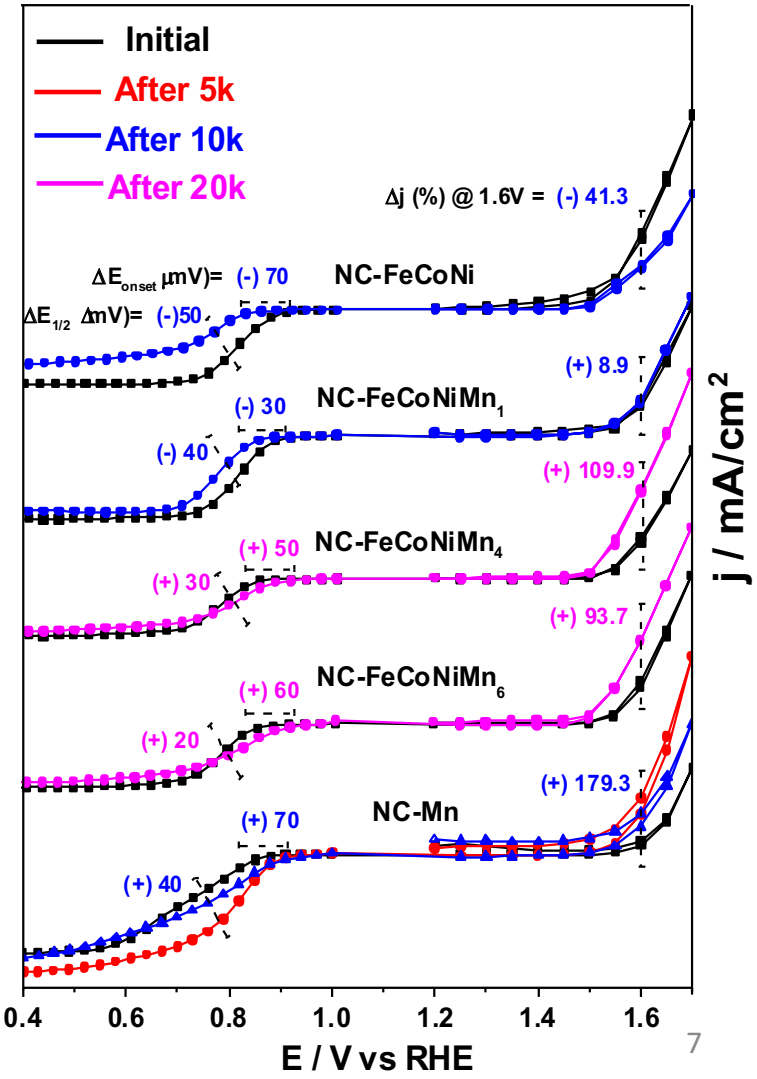
Low-cost and scalable synthesis



- Inexpensive precursors and scalable one-step thermal treatment synthesis
- Mn doping was discovered to stabilize the ORR/OER bifunctional nanocarbon catalysts

Promotional role of Mn doping

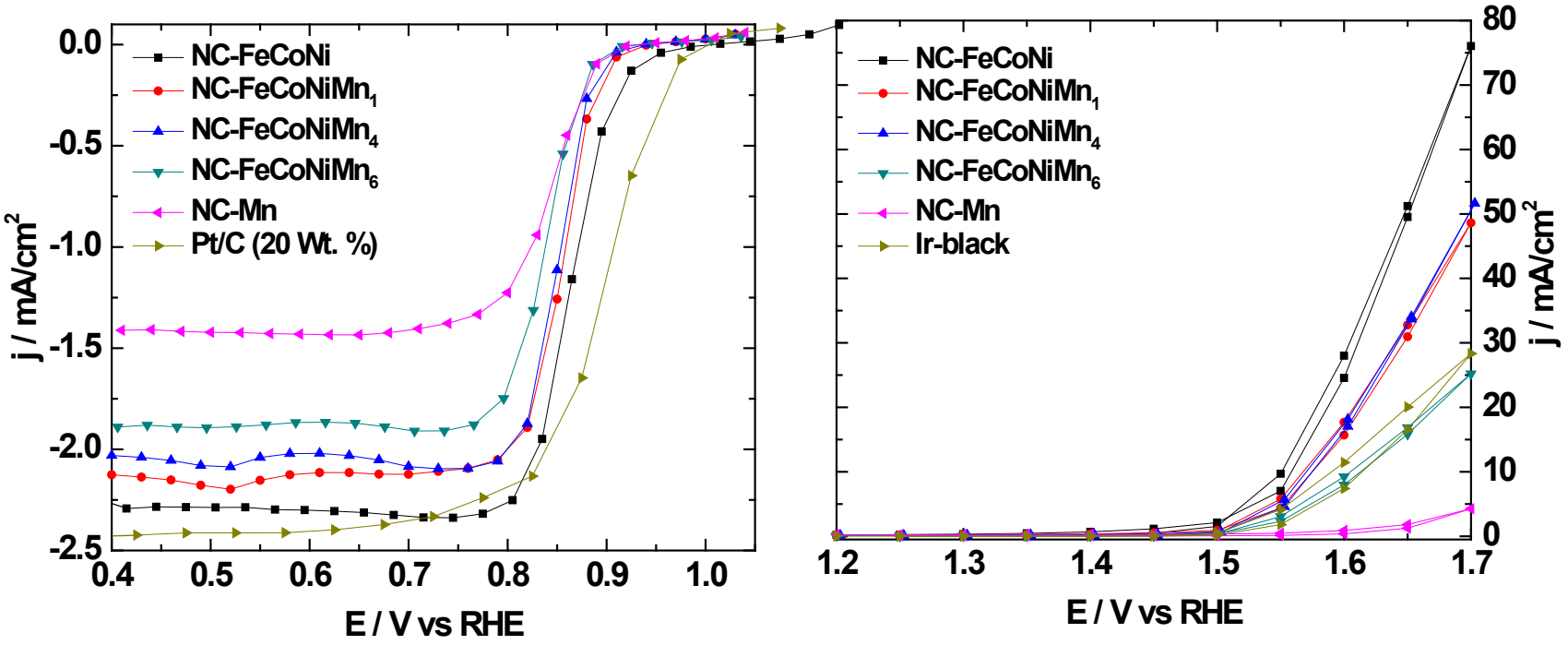
0.0 to 1.9 V in O_2 saturated 0.1 M NaOH, 500 mV/s



Remarkable Stability of Mn-based Nanocarbon Catalysts

Mn doping compromises the initial ORR and OER activity

All Activity measurements were recorded in O_2 saturated 1.0 M NaOH with 900 rpm and 1600 rpm for ORR and OER, respectively.

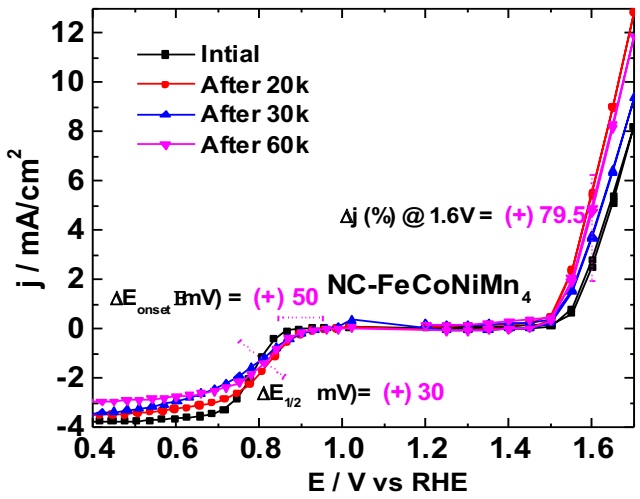


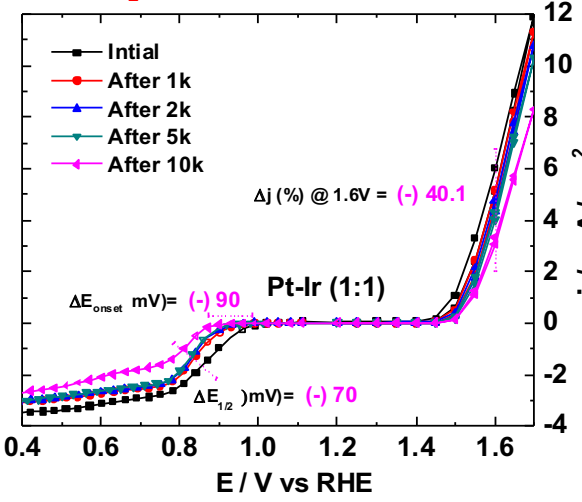
- ORR and OER initial activities decreases as Mn is introduced
- A Mn content of *x* = 4 is the recommended for a tradeoff of activity and durability
- RRDE test shows oxidation current is a sole outcome of oxygen evolution and not carbon oxidation.

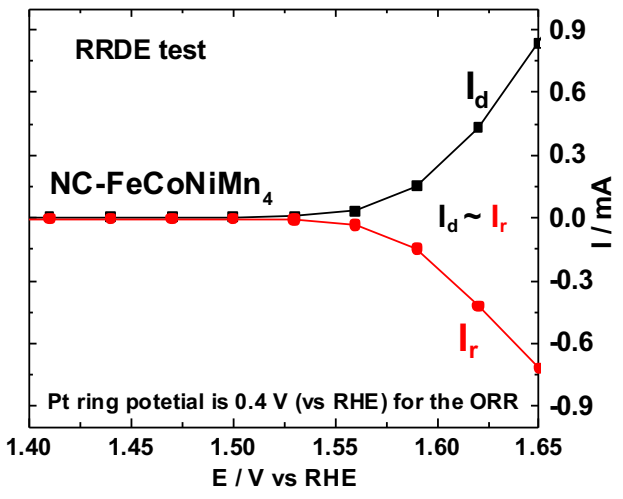
Remarkable Stability of Mn-based Nanocarbon Catalysts

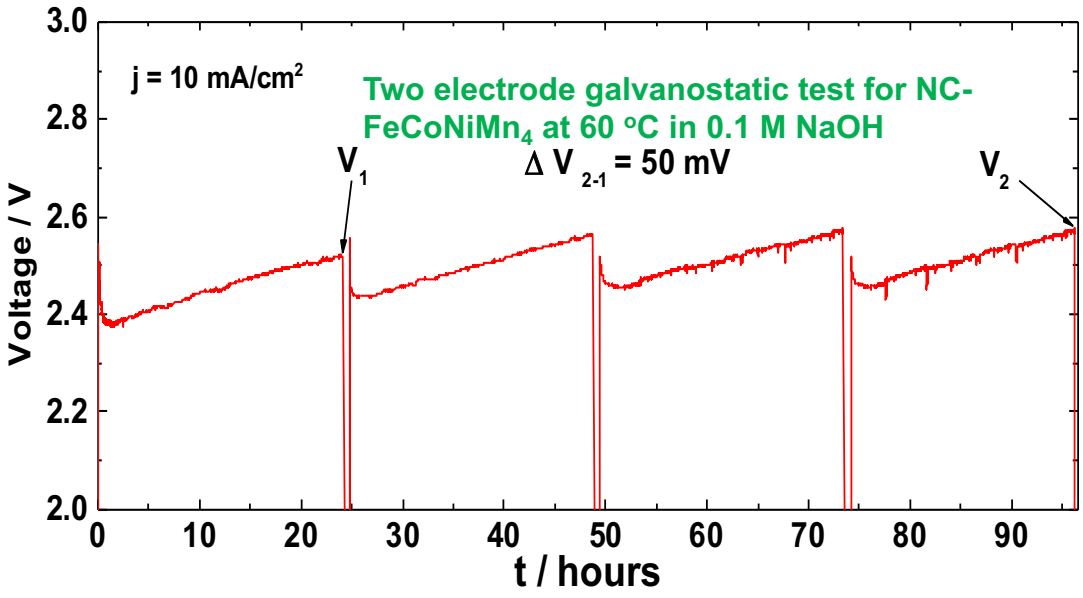
Comparison between Mn and Pt-Ir black catalyst

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





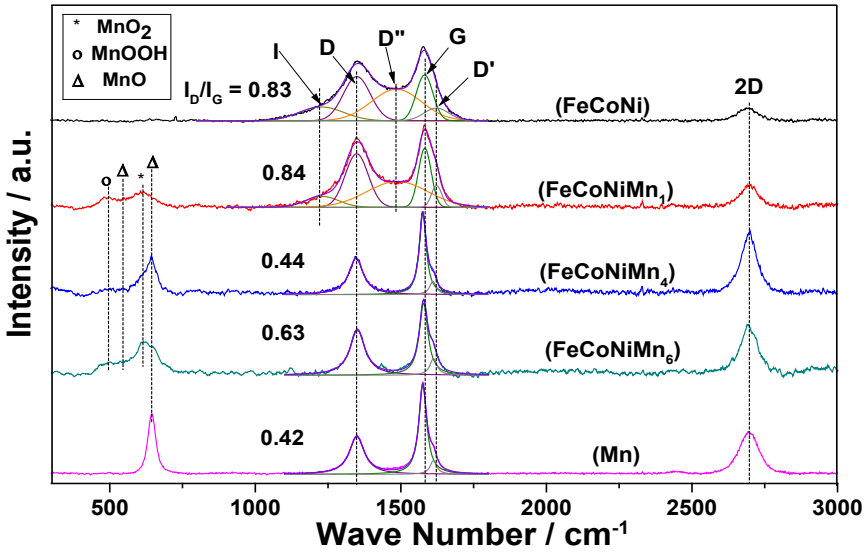




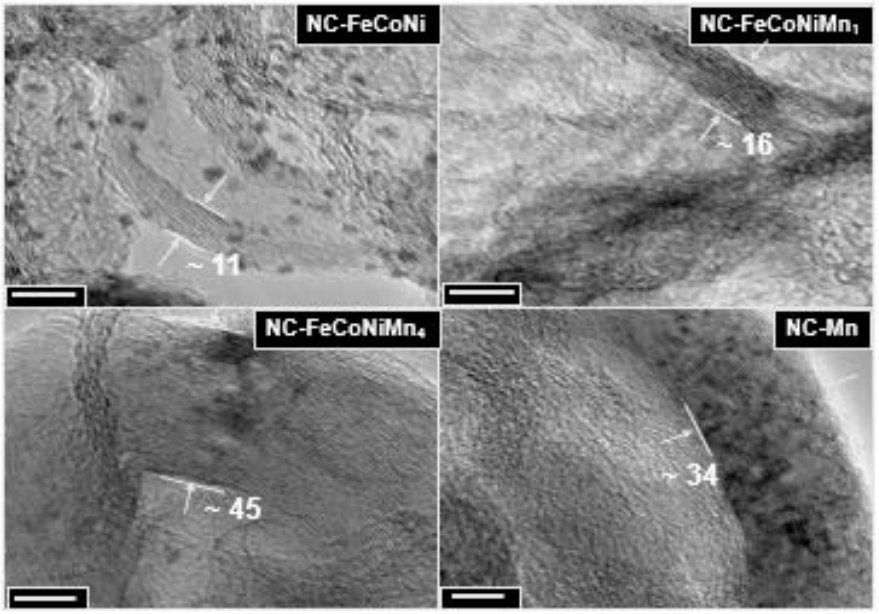
- Instead of degradation, enhancement was observed in ORR and OER activity during potential cycling tests for 60,000 cycles (~100 hours)
- Superior stability compared to Pt-Ir
- RRDE indicates the OER current is solely due to O_2 evolution rather than carbon oxidation.
- High-temperature (60°C) electrolyzer tests further verify the remarkable stability of Mn-based nanocarbon

Mechanistic Evaluation of the Stability Enhancement

Raman Spectroscopy

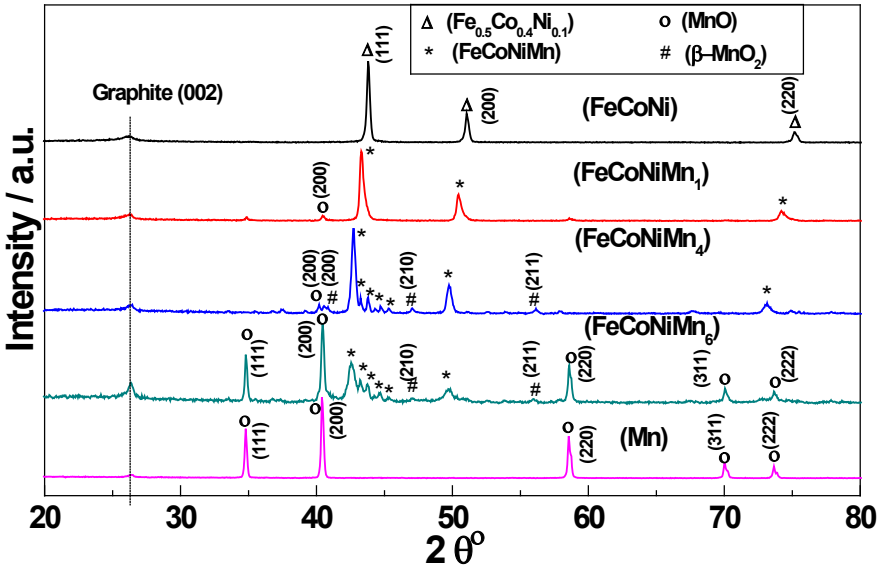


HR-TEM images



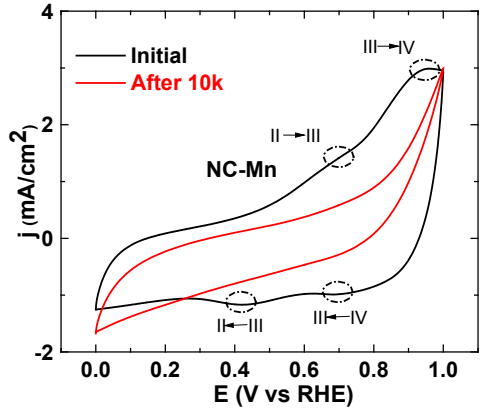
Scale bar equals 5 nm

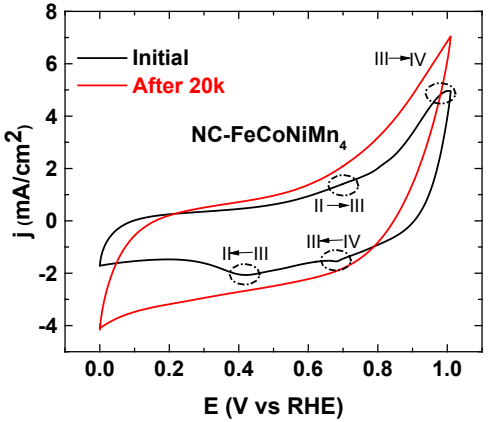
XRD Patterns

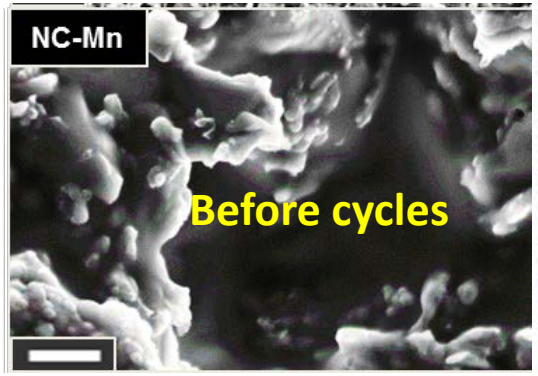


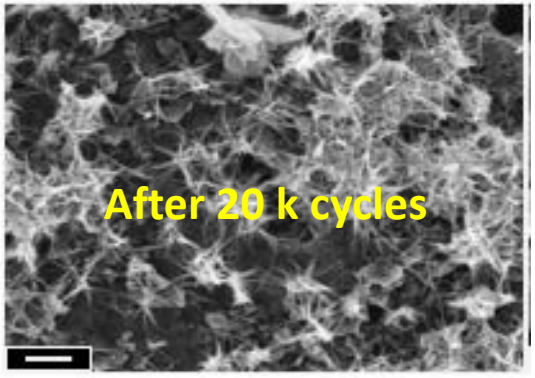
- Higher degree of carbon graphitization was achieved because of sufficient Mn doping .
- Larger number of carbon layers in Mn-rich catalysts leads to better corrosion resistance of carbon
- Existence of MnO and FeCoNiMn alloys provide protection to carbon

Mechanistic Evaluation of the Stability Enhancement

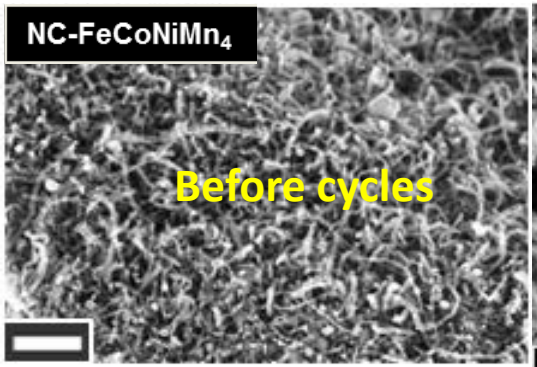


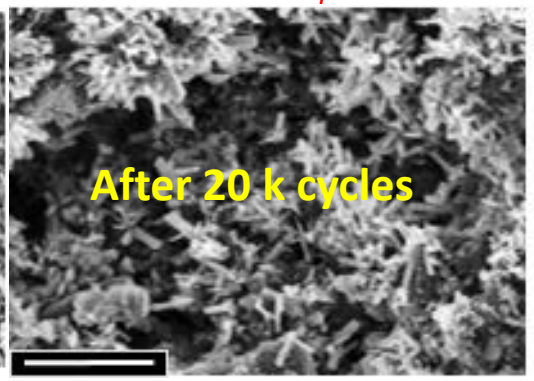




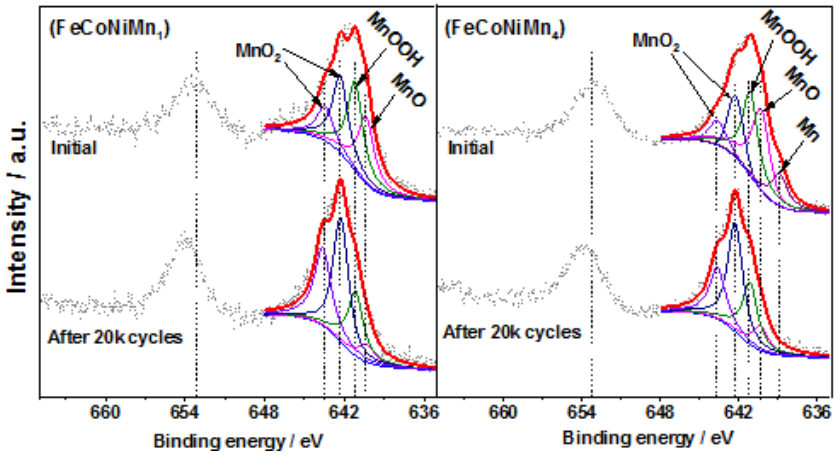


Scale bar equals 500 nm





XPS

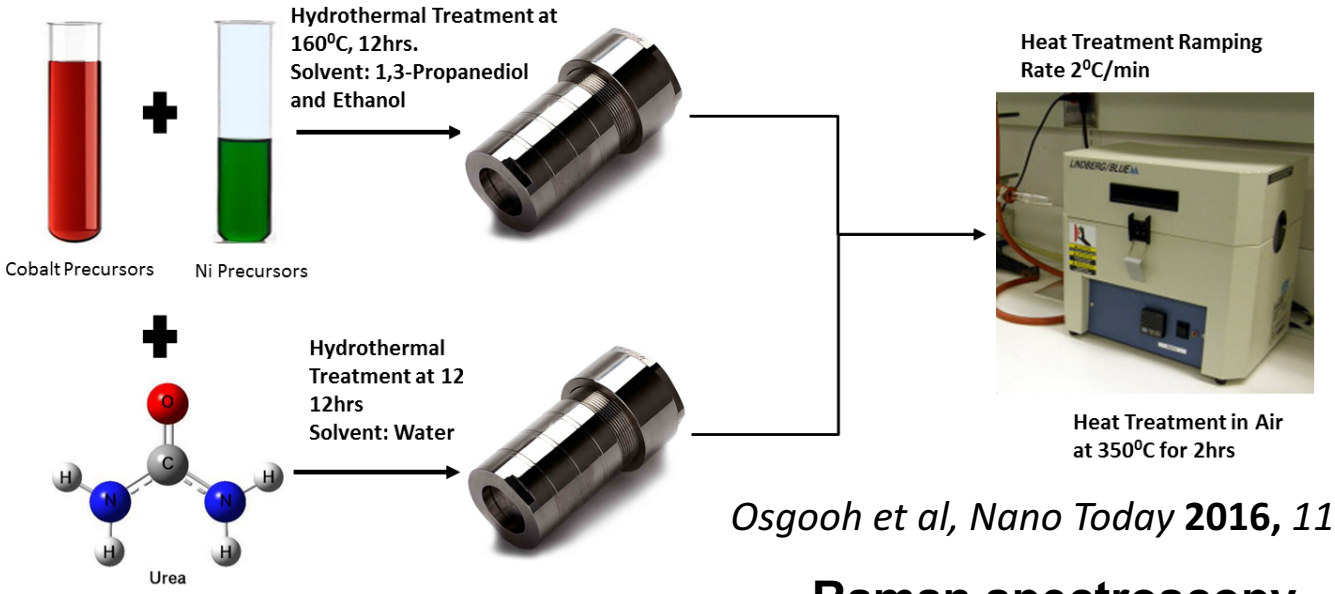


- Formation of MnO_2 promotes ORR/OER activity verified by CV and XPS.
- Dense graphite structure is maintained with appearance of nanorods and flakes, which may be attributed to MnO_2

Irreversible formation of MnO_2

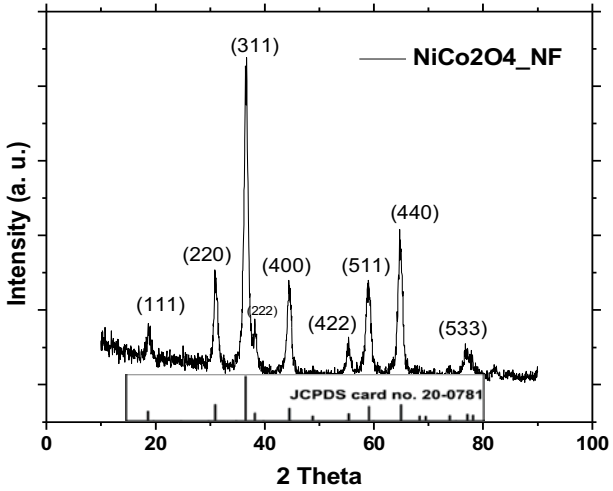
Accomplishment 3: Carbon-free Metal Oxide Catalysts (UB)

Low-cost and scalable hydrothermal synthesis

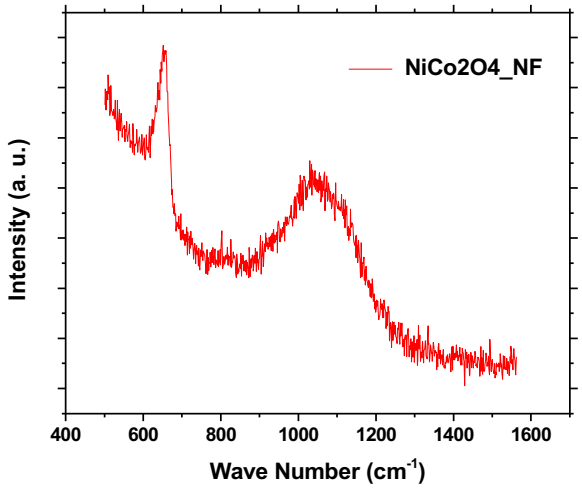


Osgooh et al, Nano Today **2016,** *11*, 601–625

XRD Patterns



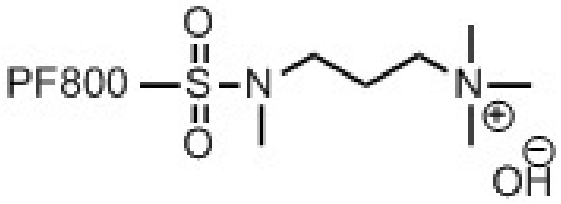
Raman spectroscopy



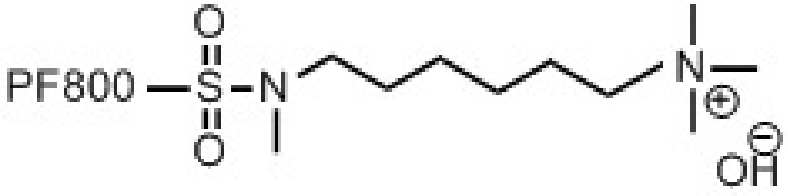
The XRD and Raman confirmed $NiCo_2O_4$ phase and peaks for Nickel-Cobalt Oxide are well in agreement confirmation the formation of $NiCo_2O_4$ phase.

Accomplishment 4: New AEMs (NREL)

Gen 1 PF AEM Polymer



Shown to have poor durability. Not surprising due to proximity of cation and electron withdrawing side chain.

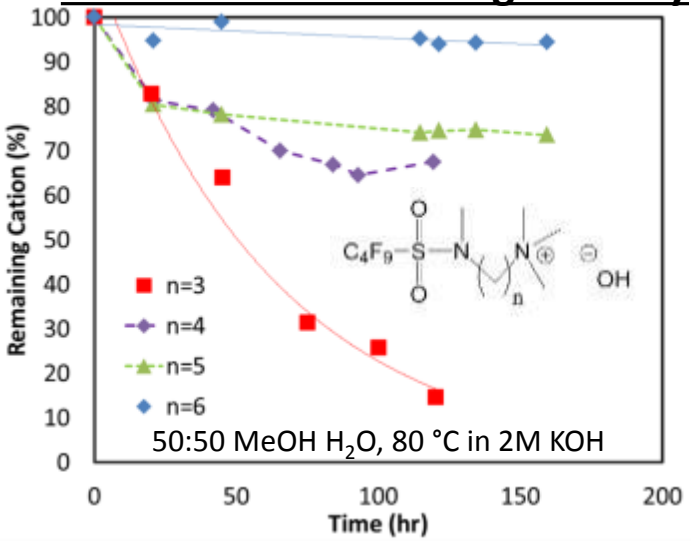


Gen 2 PF AEM Polymer

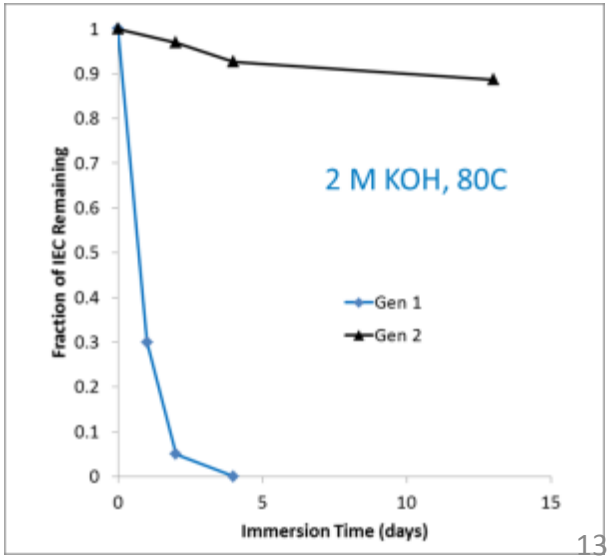
90% of IEC retained after 2 weeks in 2 M KOH at 80°C

Significantly increased stability (30x) achieved through lengthening of the alkyl chain. Stability concerns remain due to the sulfonamide linkage (alternative tethering strategies are being investigated).

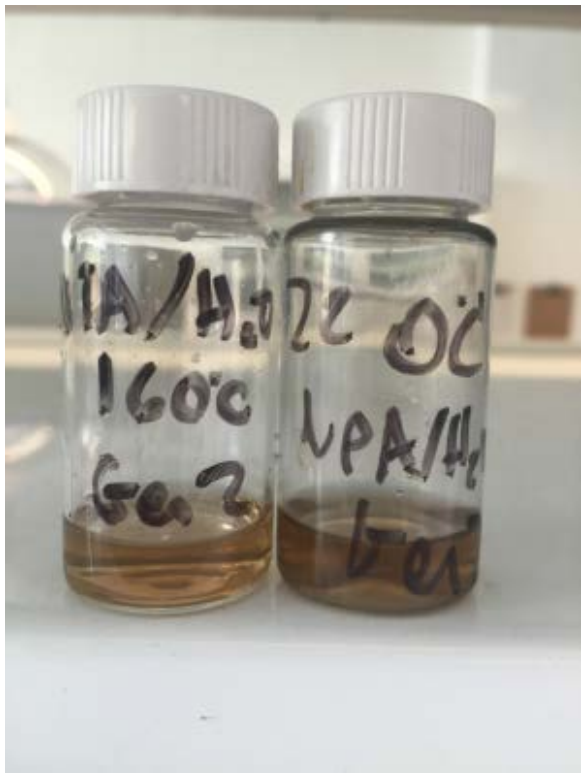
Small Molecule Analog Stability

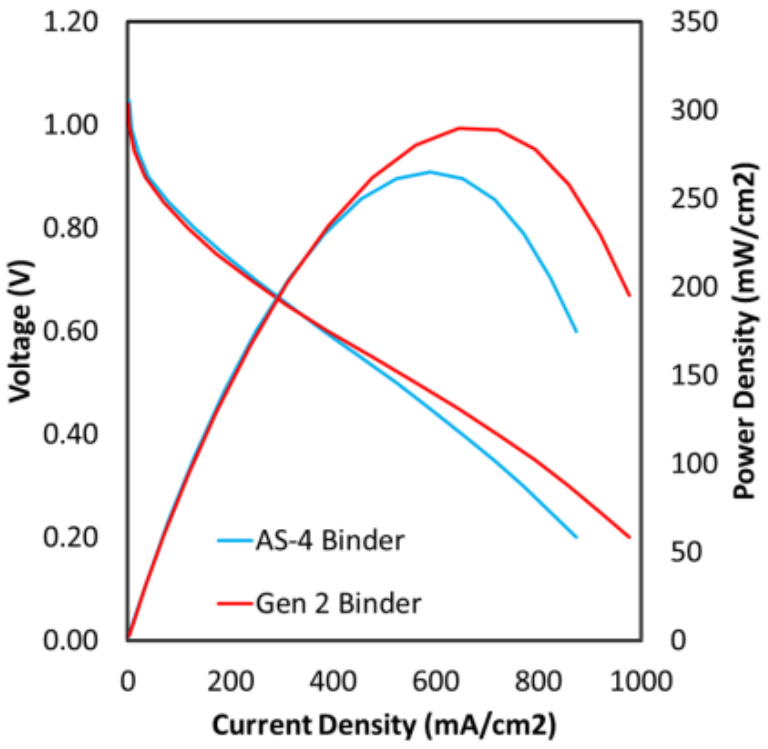


Ex-situ PFAEM Polymer Stability



PF AEM Ionomer Dispersions





Tested MEAs

1. Red

NREL Gen 2 PFAEM (34 µm)
NREL Gen 2 ionomer

2. Blue

NREL Gen 1 PFAEM (45 µm)
Tokuyama AS-4 ionomer

MEA specifications

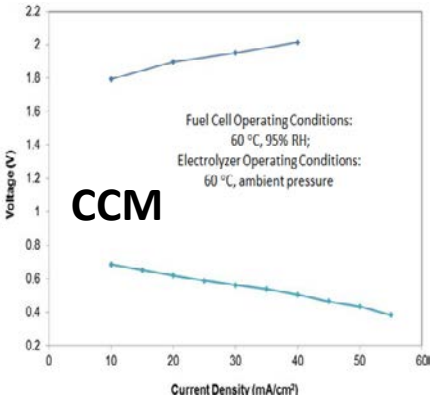
Pt/HSC: 0.4 mg_{Pt}/cm^2 A/C
Temp: 60°C
RH: 100% A/C
Pressure: 121 kPa A/C
Flow: 0.2 L/min
Gases: H_2/O_2
HFR: 145 mΩ-cm^2

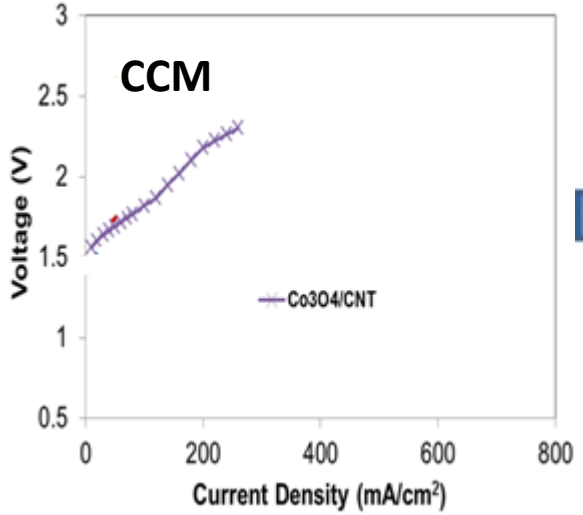
PFAEM Gen 2 polymer has been dispersed in n-propanol/water mixtures and successfully utilized as AMFC electrode binder

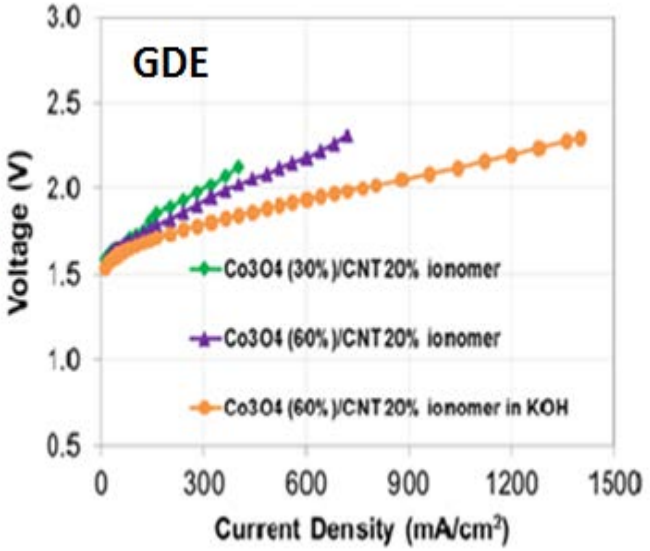
PF AEM electrode performance has surpassed commercial AS-4 ionomer with equivalent and symmetrical electrode loadings. Optimization underway.

Accomplishment 5: MEA Performance Evolution (Giner)

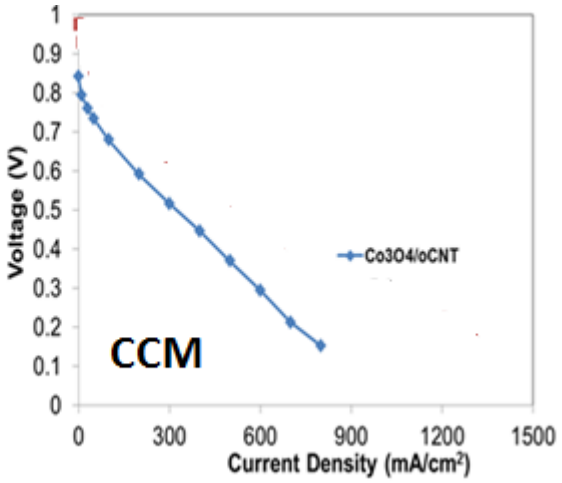
Electrolyzer

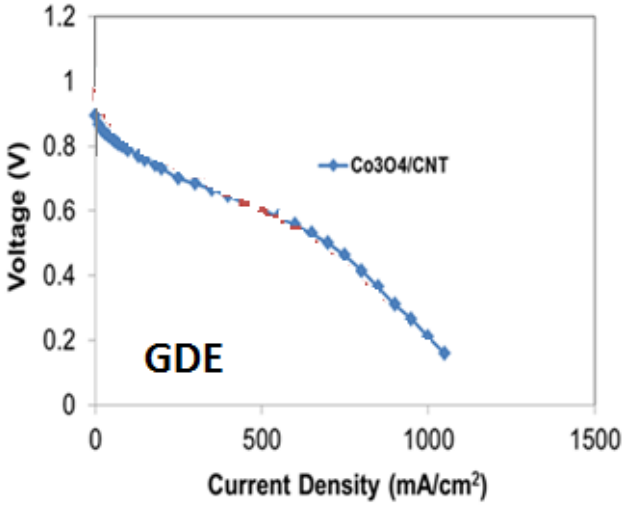






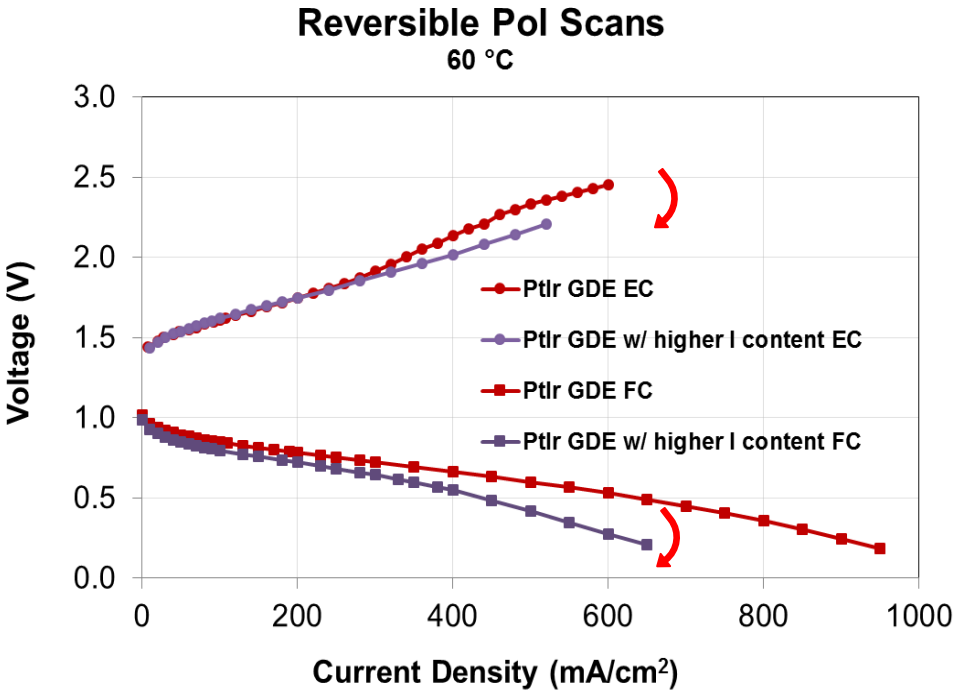
Fuel Cell





- **Steady Progress has been made for MEA performance improvement**

Baseline MEA Performance and MEA Design



MEA Design

1. Varying Catalyst
2. MEA fabrication method
3. Ionomer Content
4. Cell Temperature
5. Liquid electrolyte

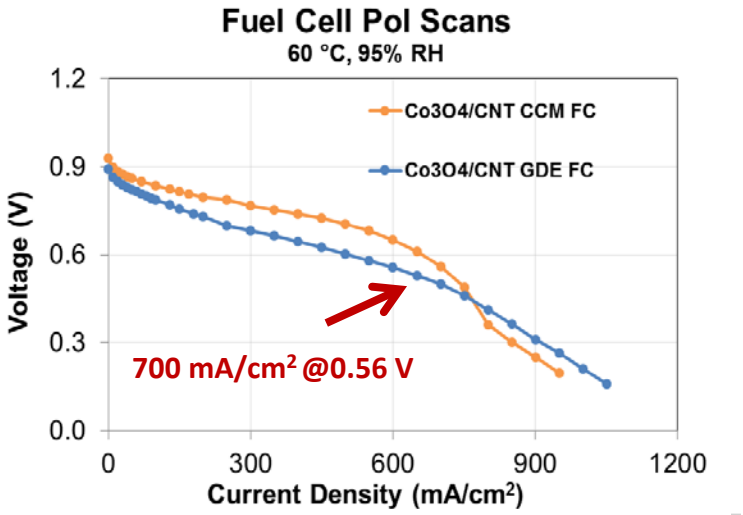
Membrane: Tokuyama A201
Ionomer: NREL Gen 2 or U. Delaware PAP-based

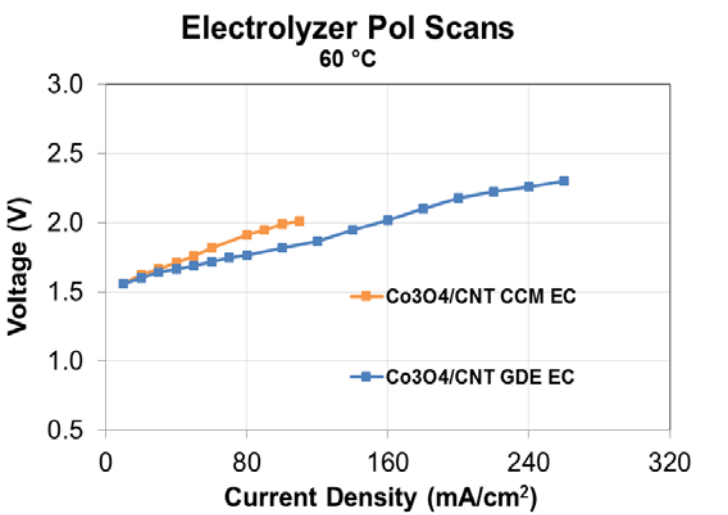
Cathode: PtIr (0.75_{Pt}+0.75_{Ir} mg/cm^2, Ionomer=20%) Anode: PtRu/C (0.7 mg_{PtRu}/cm^2, I/C=0.8)
Fuel Cell test conditions are identical : H_2/O_2 flowing at 1000 ccm/min, at the temperature of 60 °C (relative humidity of 95%), and H_2/O_2 backpressure of 30 psia

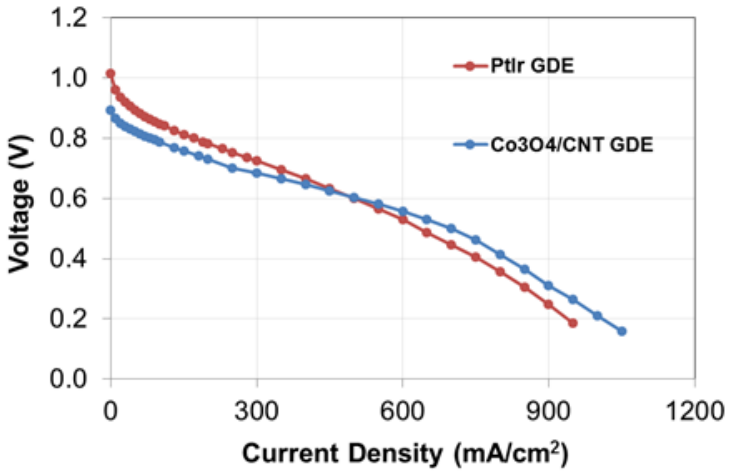
- Baseline fuel cell and electrolyzer performance attained with PGM catalysts
- Higher ionomer content (25% vs. 20%) can further improve water electrolyzer performance

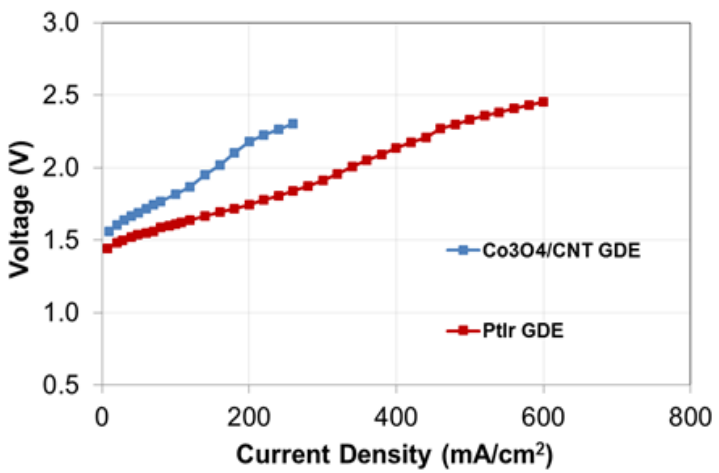
Leverage with other DOE project FC154

Giner Co_3O_4/CNT Operation Performance







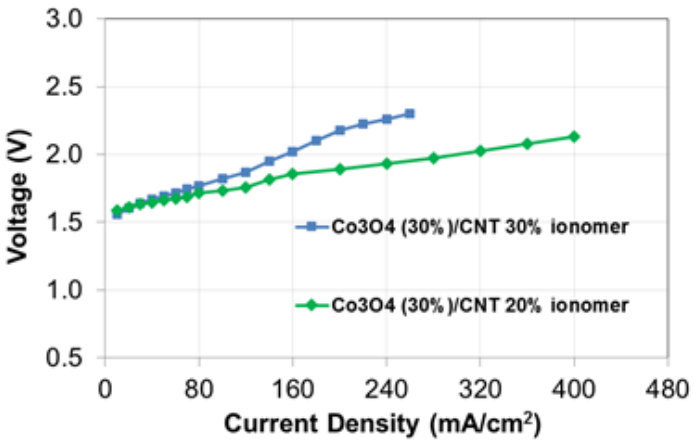


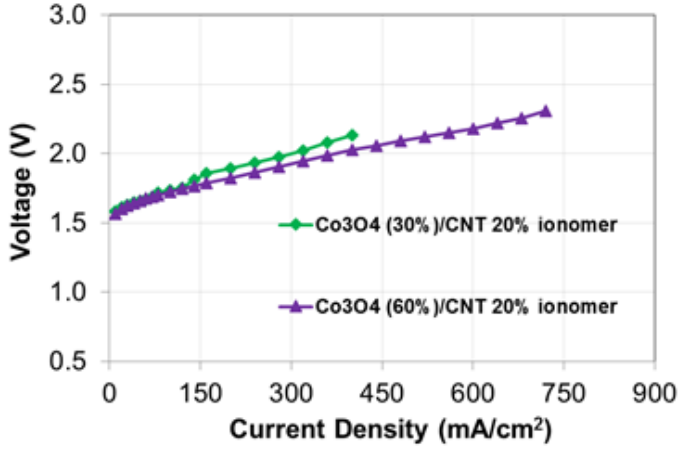
Anode are identical for all tests: PtRu/C (0.7 mg_{PtRu}/cm^2, I/C=0.8); Cathode: PtIr (0.75_{Pt}+0.75_{Ir} mg/cm^2, Ionomer=20%); Co_3O_4/oCNT, 3 mg/cm^2, 30% ionomer, Tokuyama A201 membrane, NREL Gen 2 ionomer, otherwise noted

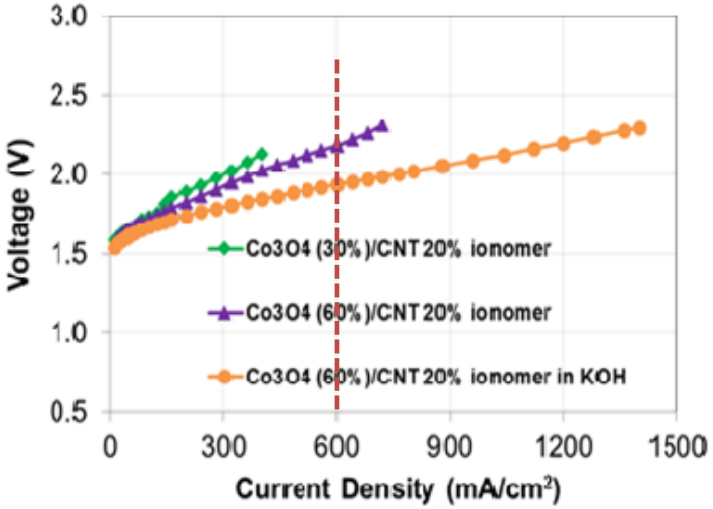
- In fuel cell, both CCM and GDE configuration surpassing milestone 0.55 @ 600 mA/cm^2
- In electrolyzer cell, GDE configuration demonstrated much better performance than CCM one

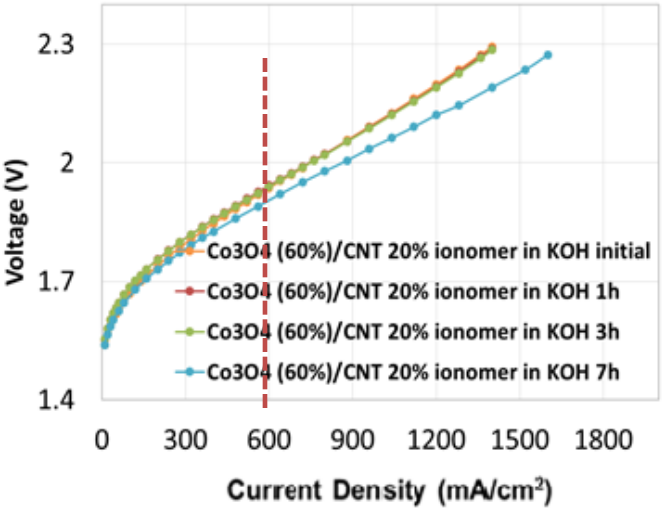
Co_3O_4/CNT Electrolyzer Performance Improvement

T= 60 ℃





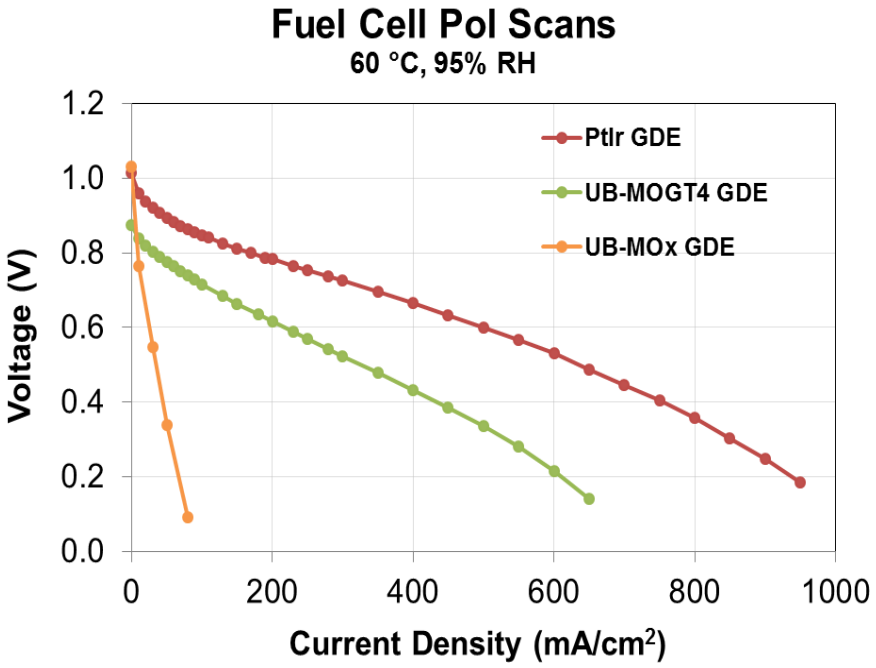


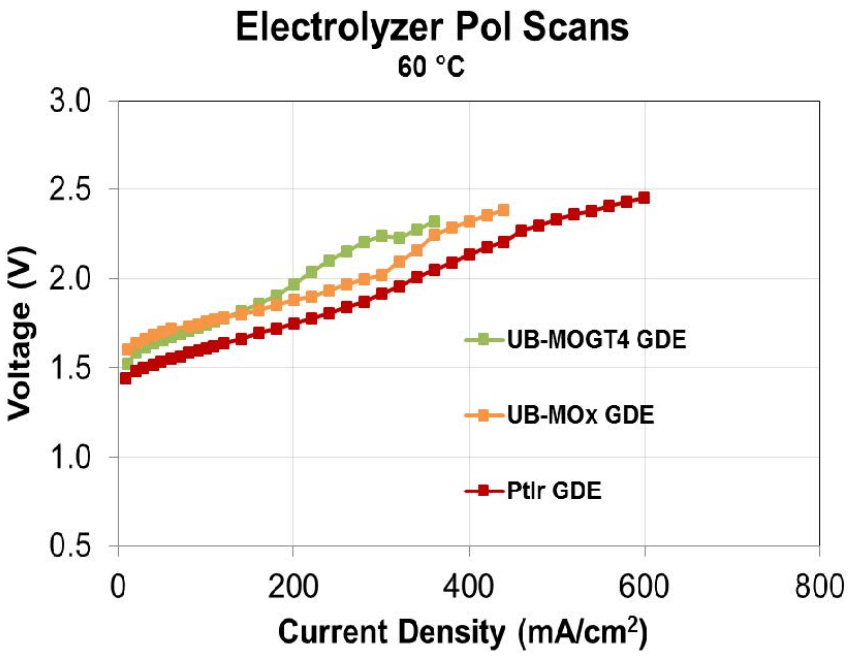


- Feeding diluted KOH solution (instead of pure water) significantly improved the electrolyzer performance
  - Performance beat modified target : 2.0 V @ 600 mA/cm^2
- Performance had no decay after 7 hours, demonstrating catalyst stability

SUNY Nickle Cobalt Oxide (UB-MO_x) and Graphene Tube (UBGT-4) Performance (GDE)

UB-MOGT4: Nickel Cobalt Oxide mixed with UBGT-4 in the ratio of 1:2

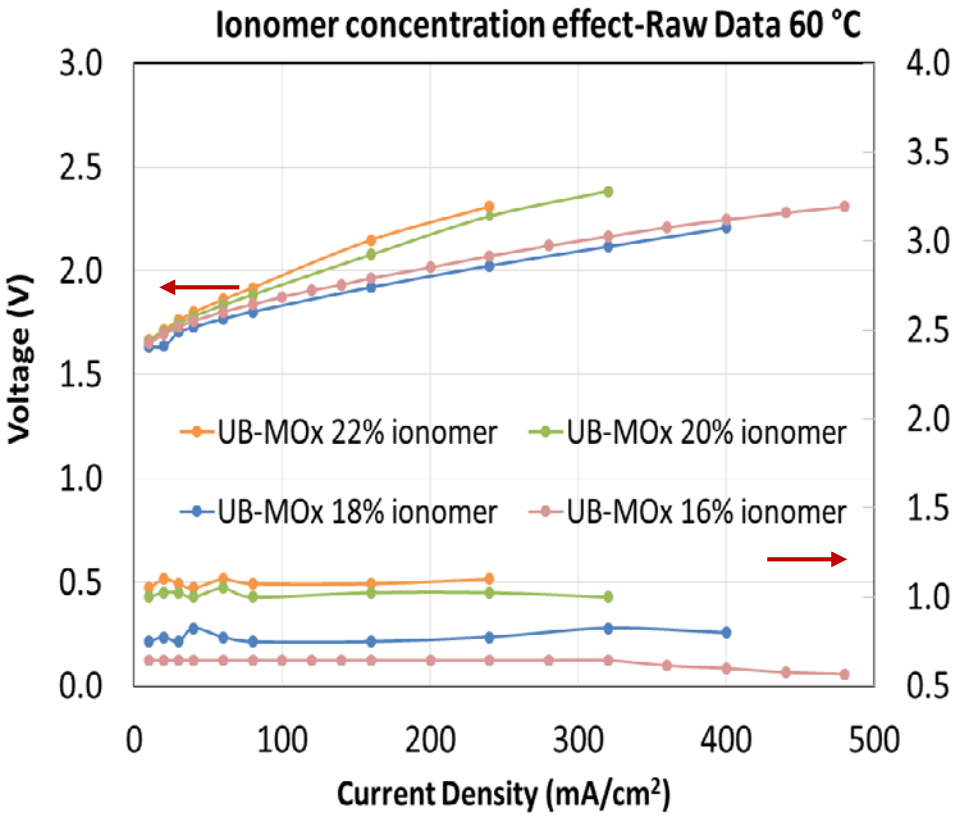


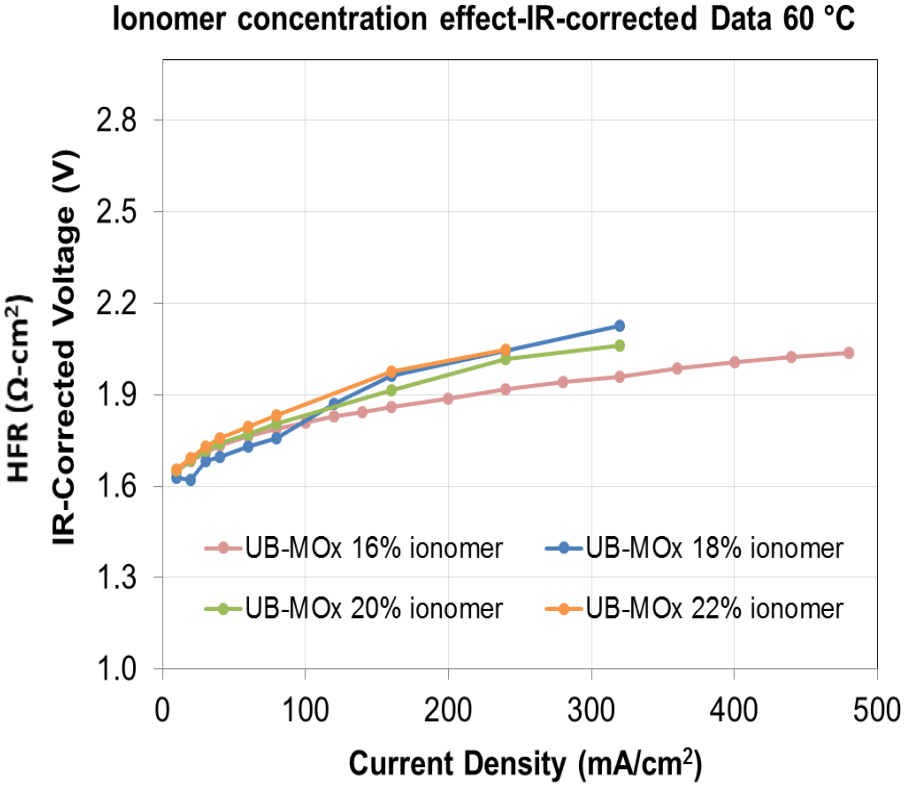


Fuel Cell test conditions: H_2/O_2 flowing at 1000 ccm/min, at the temperature of 60 °C (relative humidity of 95%), and H_2/O_2 backpressure of 30 psia

- MOx demonstrated great electrolyzer performance but poor fuel cell performance
- MOGT4: A performance trade off between fuel cell and electrolyzer cell

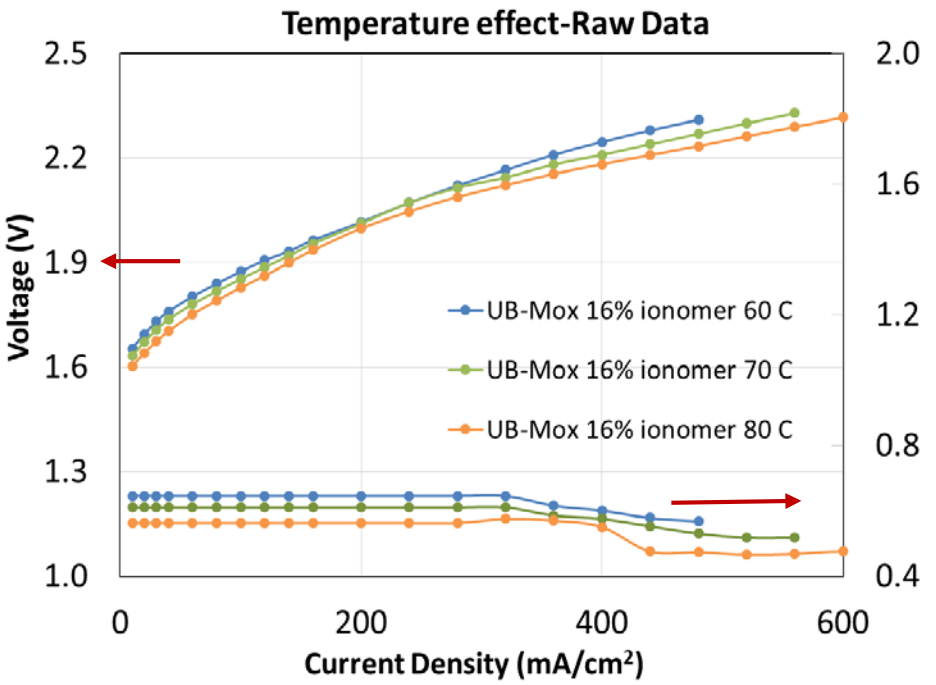
Electrode Ionomer Content Influence

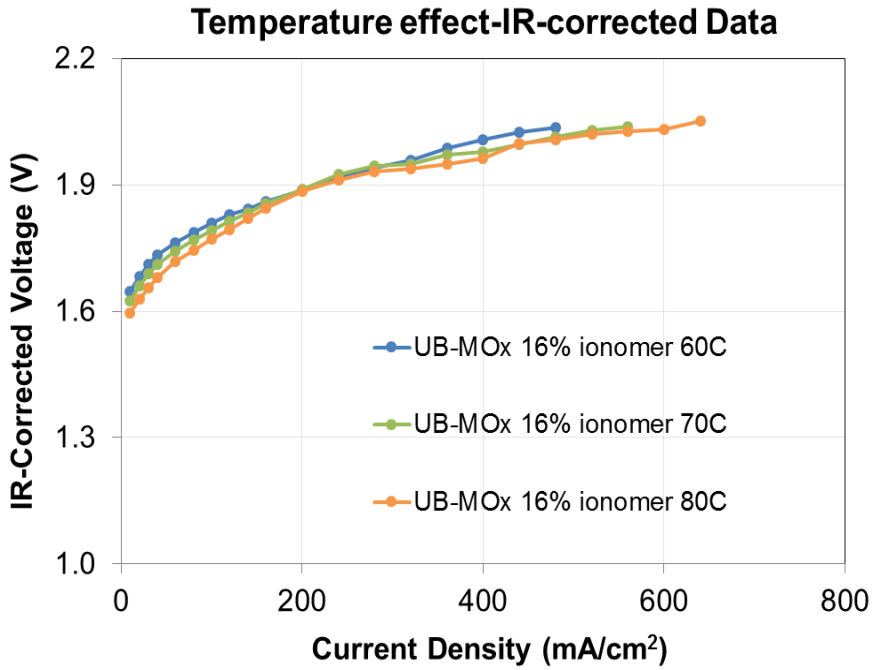




- Electrolyzer cell performance varied with various ionomer concentrations
  - Optimal ionomer concentration for MO_X between 16%~18%

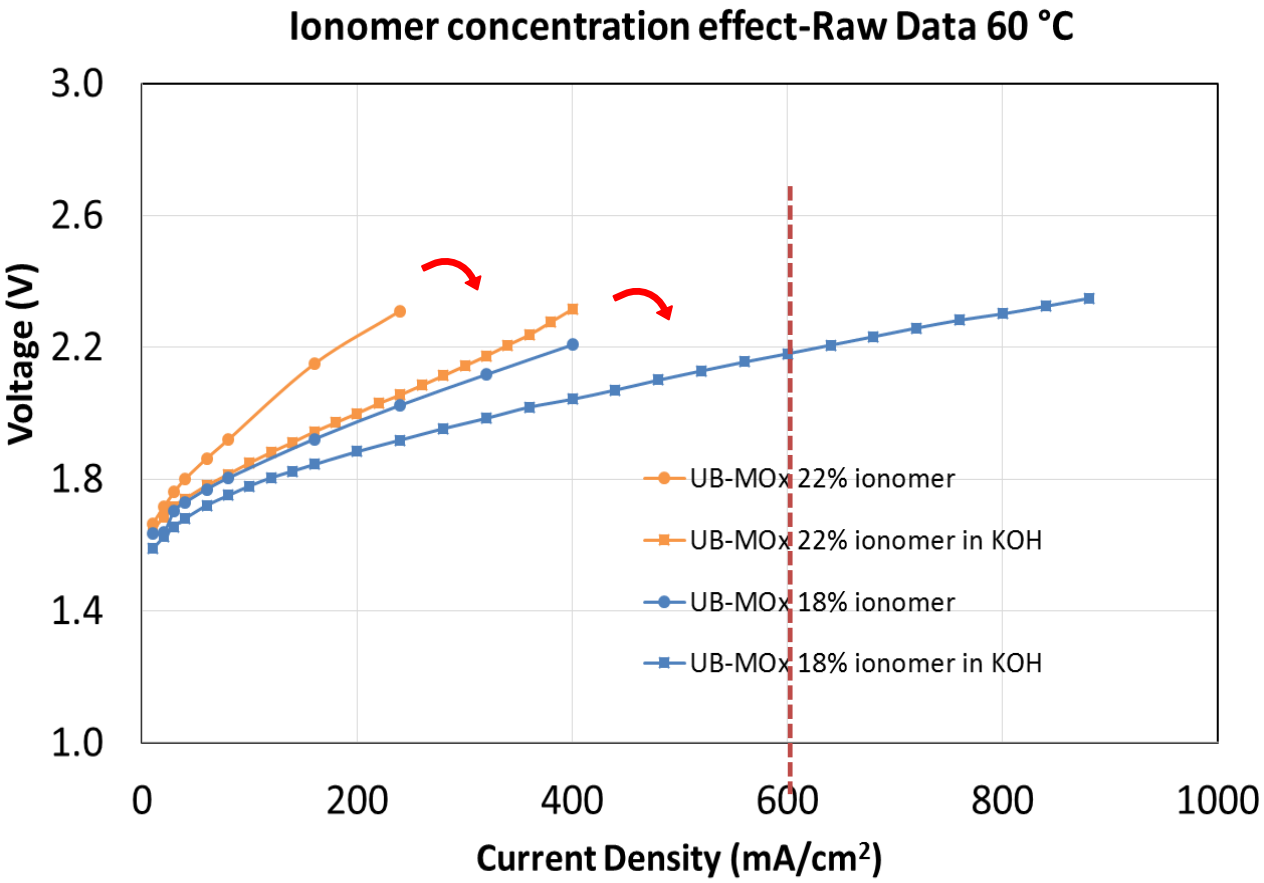
Cell Temperature Influence





- Increased temperature improved electrolyzer performance most likely due to cell resistance decrease and improved kinetics
  - Electrolysis performance achieved in pure water: 2.3 V at 600 mA/cm^2

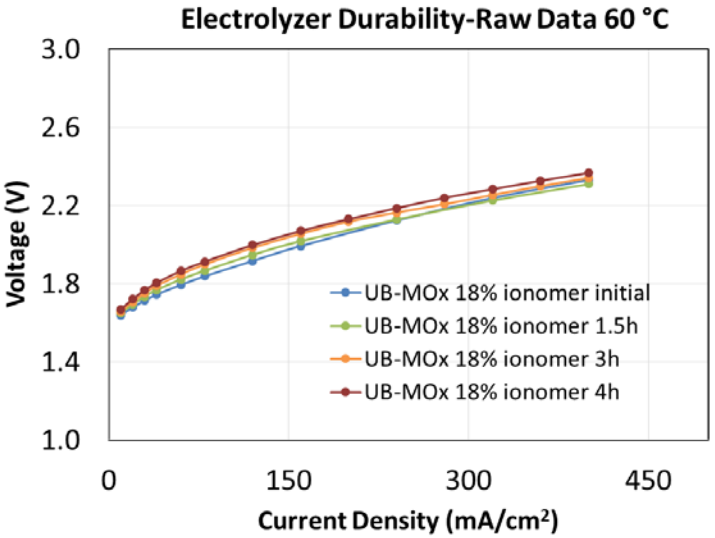
Liquid Alkaline Solution Impact

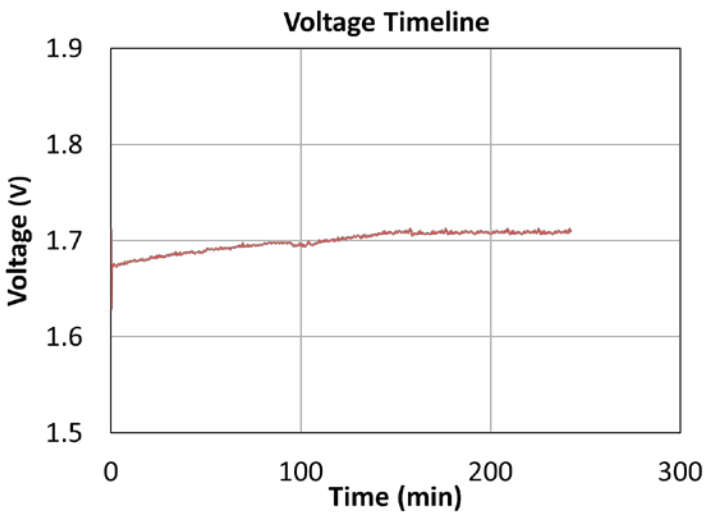


- Feeding diluted KOH solution (instead of pure water) further increased the electrolyzer performance:
  - Over-potential dropped by 300 mV.
  - Close to modified milestone 2.0 V @ 600 mA/cm^2

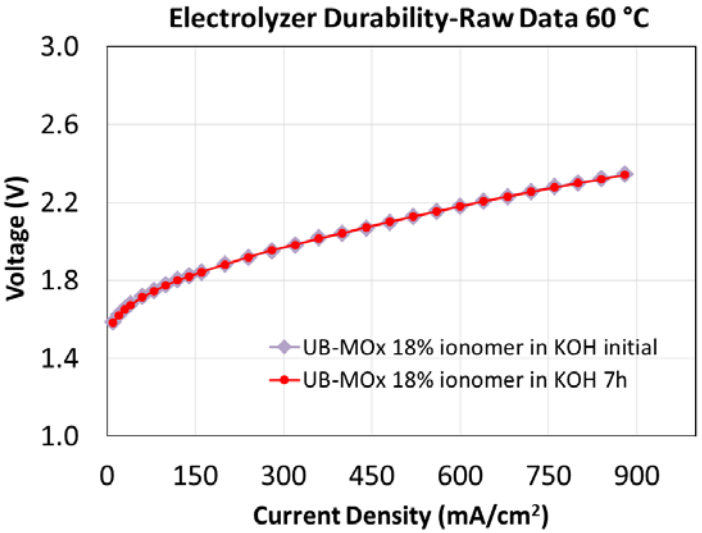
Electrolyzer Cell Durability Tests

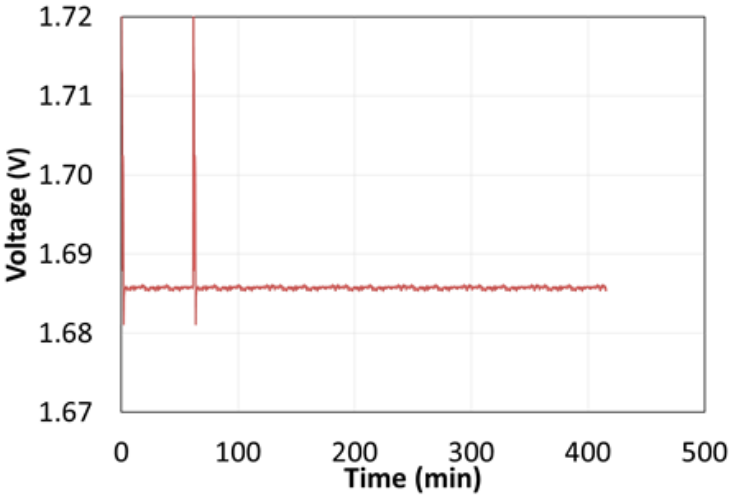
Water





0.1 M KOH





- Electrolysis performance in pure water decreased after 4 hours
- Electrolysis performance in diluated KOH solution remained stable

Summary

- A variety of of OER/ORR catalysts (Giner: Co_3O_4/CNTs and SUNY: NC-FeCoNiMn /$NiCo_2O_4$) have been optimized with improved activity and durability:
  - Graphitization degree is a key to nanocarbon stability, which can be enhanced by Mn doping;
  - Interconnected carbon nanotubes growing from a dense graphitic carbon framework is the most preferred C structure.

- Bifunctional electrodes and MEAs have been fabricated and tested and crucial factors impacting the cell performance investigated:
  - Electrode fabrication (CCM vs GDE)
  - Ionomer content optimization was dependent on catalyst composition
  - Elevated cell temperature enhanced cell performance
  - Introduction of diluted liquid electrolyte significantly improved electrolyzer performance

- Fuel cell MEA using Giner Co_3O_4/CNT surpassed the milestone 0.55 V @ 600 mA/cm^2 and electrolyzer performance was tremendously improved towards the target 2.0 V @ 600 mA/cm^2)

Collaborations

Institutions	Roles
Giner Inc. (Giner) Hui Xu (PI), Shuai Zhao, Tom McCallum	Prime, oversees the project; metal oxide supported on CNTs; bi-functional MEA fabrication and optimization; reversible fuel cell design; cost analysis
SUNY -Buffalo(SUNY) Gang Wu and Shiva Gupta	Graphene tube and metal oxide based OER/ORR bi-functional catalyst development; MEA fabrication
National Renewable Energy Laboratory (NREL) Bryan Pivovar, Shaun Alia, and Andrew Park	AEM development; HOR/HER catalyst development; MEA fabrication and test

Future Plans

- Further improve the electrolyzer cell performance
  - Membrane/ionomer from Univ. of Delaware enables operation > 90 ℃
- Complete dual operation durability test up to 500 hours
- Perform techno-economical analysis

Acknowledgments

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- **DOE Program Managers**
  - Dr. David Peterson
  - Donna Ho
- **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

Publications

- Zhao, S., Rasimick, B., Mustain, W., & Xu, H. Highly durable and active Co_3O_4 nanocrystals supported on carbon nanotubes as bifunctional electrocatalysts in alkaline media. *Applied Catalysis B: Environmental*, **2017** *203*, 138-145.
- Gupta, S.; Zhao, S.; Ogoke, O.; Lin, Y.; Xu, H.; Wu, G., Engineering Favorable Morphology and Structure of Fe-N-C Oxygen-reduction Catalysts via Tuning Nitrogen/Carbon Precursors. *ChemSusChem* **2017,** *10* (4), 774–785.
- Zhang, H.; Osgood, H.; Xie, X.; Shao, Y.; Wu, G., Engineering nanostructures of PGM-free oxygen-reduction catalysts using metal-organic frameworks. *Nano Energy* **2017,** *31*, 331-350.
- Osgood, H.; Devaguptapu, S. V.; Xu, H.; Cho, J. P.; Wu, G., Transition Metal (Fe, Co, Ni, and Mn) Oxides for Oxygen Reduction and Evolution Bifunctional Catalysts in Alkaline Media. *Nano Today* **2016,** *11*, 601–625.
- Gupta, S.; Qiao, L.; Zhao, S.; Lin, Y.; Vamsi, D. S.; Xu, H.; Wang, X.; Swihart, M.; Wu, G., Highly active and stable graphene tubes decorated with FeCoNi alloy nanoparticles via a template-free graphitization for bifunctional oxygen reduction and evolution. *Advanced Energy Materials* **2016,** *6* (22), 1601198.
- Wu, G.; Santandreu, A.; Kellogg, W.; Gupta, S.; Ogoke, O.; Zhang, H.; Wang, H.-L.; Dai, L., Carbon Nanocomposite Catalysts for Oxygen Reduction and Evolution Reactions: from Nitrogen Doping to Transition-Metal Addition. *Nano Energy* **2016,** *29*, 83–110.
- Chen, C. F., King, G., Dickerson, R. M., Papin, P. A., Gupta, S., Kellogg, W. R., & Wu, G. (2015). Oxygen-deficient BaTiO 3− x perovskite as an efficient bifunctional oxygen electrocatalyst. *Nano Energy*, *13*, 423-432.
- Gupta, S.; Kellogg, W.; Xu, H.; Liu, X.; Cho, J.; Wu, G., Bifunctional Perovskite Oxide Catalysts for Oxygen Reduction and Evolution in Alkaline Media. *Chemistry - An Asian Journal* **2016,** *11* (1), 10–21.
- Wang, X.; Li, Q.; Pan, H.; Lin, Y.; Ke, Y.; Sheng, H.; Swihart, M. T.; Wu, G., Size-controlled large-diameter and few-walled carbon nanotube catalysts for oxygen reduction. *Nanoscale* **2015,** *7*, 20290-20298.

Response to Major Review Comments

Comment: *CNTs have been selected as a stable nanocarbon support for the OER in spite of exhibiting what appears to be persistent corrosion at potentials higher than 1.7 V.*

Response: The carbon nanotube was identified as a kinetically stable nanocarbon evidenced by long-term potential cycling tests from 0 to 1.9 in O_2 saturated alkaline electrolytes. Thus, this new finding guides us to explore the metal oxides/CNT composite bifunctional ORR/OER catalysts

Comment: *need for careful investigation of stability for carbon-based supports; lack of detailed insight into catalyst structure before, during, and after electrochemical cycling; and lack of in situ methods for structural characterizations of catalysts.* quantitative analysis of the metal oxide catalysts before and after electrochemical cycling is needed... *No details were provided about the nature of graphene oxide tubes, including surface areas and corrosion analysis.*

Response: Extensive stability tests of newly developed Mn-doped nanocarbon composite catalysts were carried out by using 0-1.9 V cycling in RDE (25^{o}C and 60^{o}C) and two-electrode electrolyzers (60^{o}C) . Promising durability was demonstrated. Addition of Mn can significantly improve stability of nanocarbon composite catalysts. The designed RRDE tests further indicated that the current measured during the OER is solely due to O_2 evolution, rather than carbon oxidation to CO_2. The structure and nitrogen doping of nanocarbon catalysts were analyzed before and after durability tests. We have provided detailed surface area and porosity information for these new nanocarbons as well.

Comment*: A project weakness is the completely wrong selection of materials (carbon-based supports or catalysts) for ORR and OER.*

Response: Although metal oxides are well known for their stability for the OER, their activity for the ORR along with poor electrical conductivity are far away sufficient for applications. On the other hand, nitrogen-doped nanocarbons have demonstrated superior ORR activity to Pt in alkaline media. Although carbon is thermodynamically unstable at the high potentials, highly graphitized nanocarbons compositing with highly OER active metal/metal oxides hold greatly promise to be kinetically stable during the OER. Therefore, our new approach is to developing novel metal oxide/nanocarbon composite catalysts with sufficient activity and stability for the bifunctional ORR/OER applications, which have been demonstrated by using both RDE and MEA studies.