



University at Buffalo
The State University of New York



Advanced Catalysts and MEAs for Reversible Alkaline Membrane Fuel Cells

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Giner Inc.
Newton, MA

Project #
FC 129

DOE 2016 AMR Meeting

June 9, 2016

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: \$362,567 (by 3/31/2015)

Collaborators

- SUNY-Buffalo: Prof. Gang Wu
- NREL: Drs. Bryan Pivovar and Shaun Alia

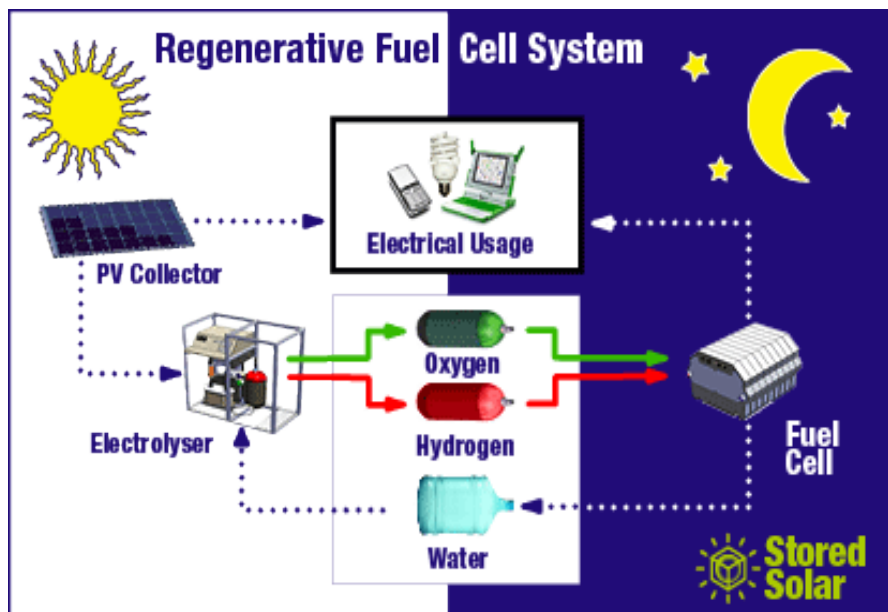
Barriers Addressed

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

Technical Targets

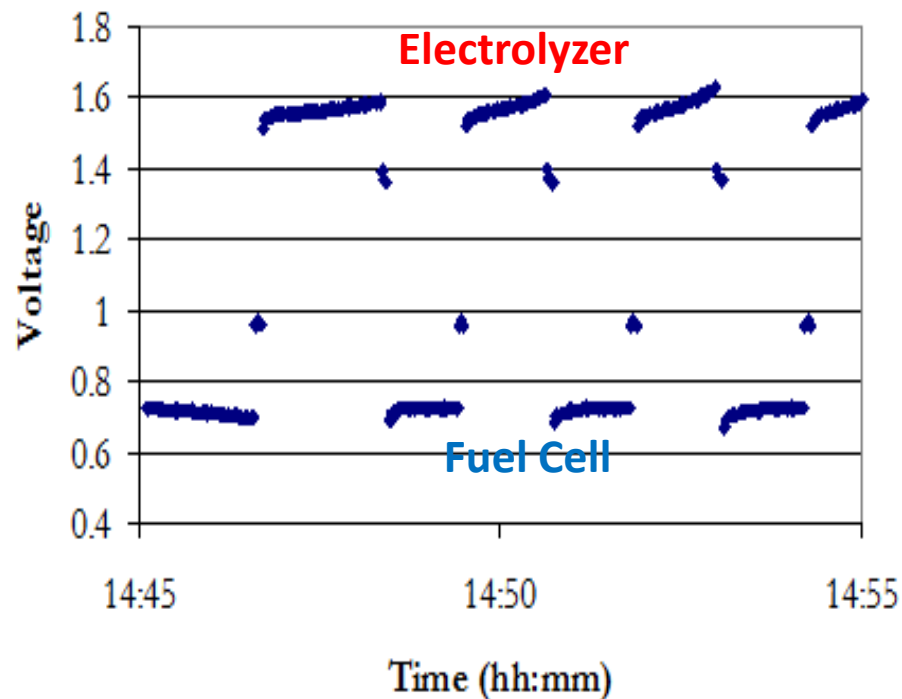
- Design and develop ORR/OER bi-functional oxide catalysts
- Integrate ORR/OER bifunctional oxide catalysts and alkaline membranes to develop highly efficient reversible alkaline membrane fuel cells (AMFCs) for stationary energy storage

Reversible Fuel Cells



Giner unitized reversible PEM fuel cell

Fast Mode Cycling: 200 mA/cm² URFC



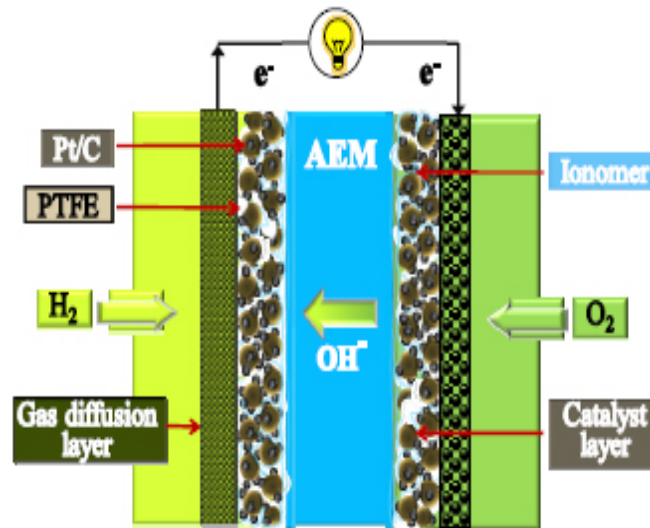
- ◆ Water electrolyzer is an ideal device to store energy from wind mills and solar farms, where surplus (off peak) energy is nearly free
- ◆ Stored H₂ can be used for fuel cells to generate electricity in peak time

Research Objective

Anion Exchange Membrane (AEM) Fuel Cells

Opportunities

- Non PGM based catalysts drives down capital cost;
- New concepts for oxide catalyst design;
- Surplus electricity from renewable energy;
- Gradual maturity of AEM technology

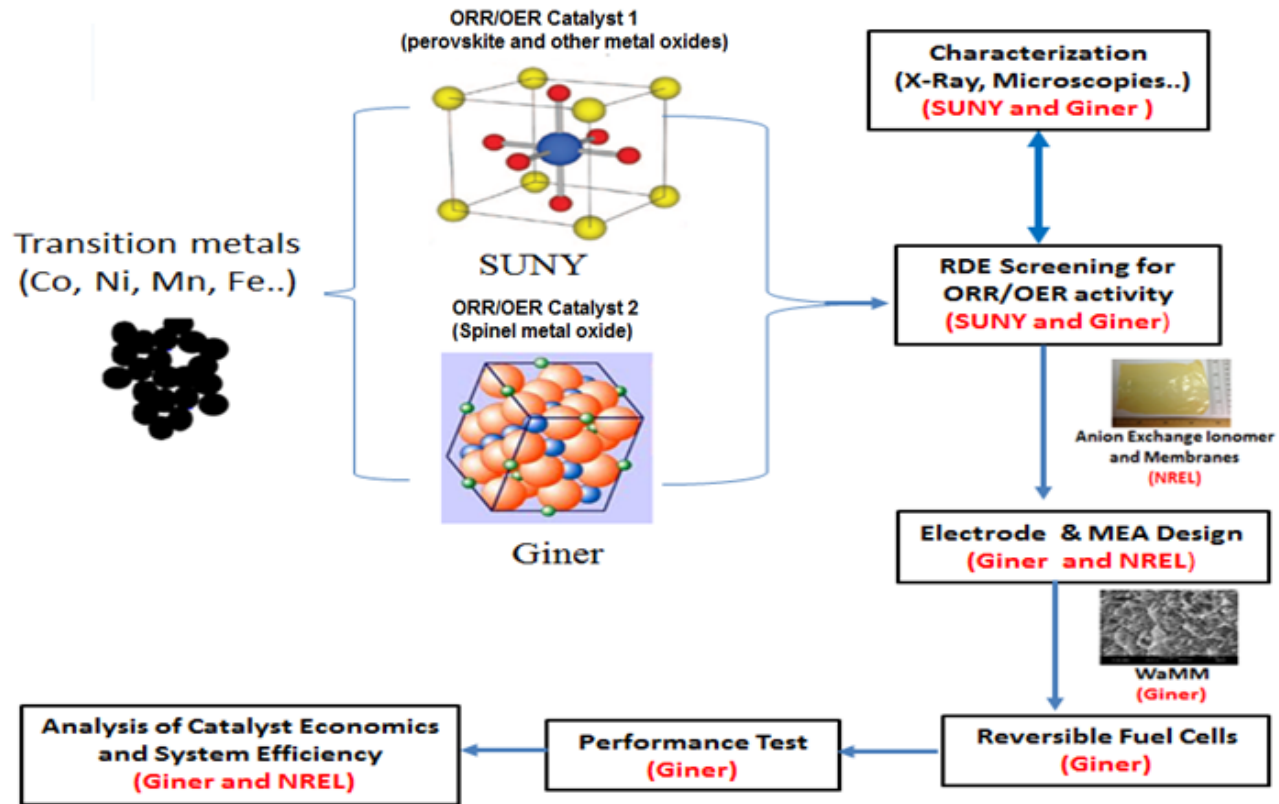


Challenges

- Non-PGM bi-functional oxide catalyst **activity** and **stability**
- Fabrication of non-PGM MEAs for AEM fuel cells NOT extensively studied
- Unitized regenerative fuel cell design and construction

Integrate AEM water electrolyzer and fuel cell together to develop reversible AEM fuel cell for energy storage and conversion

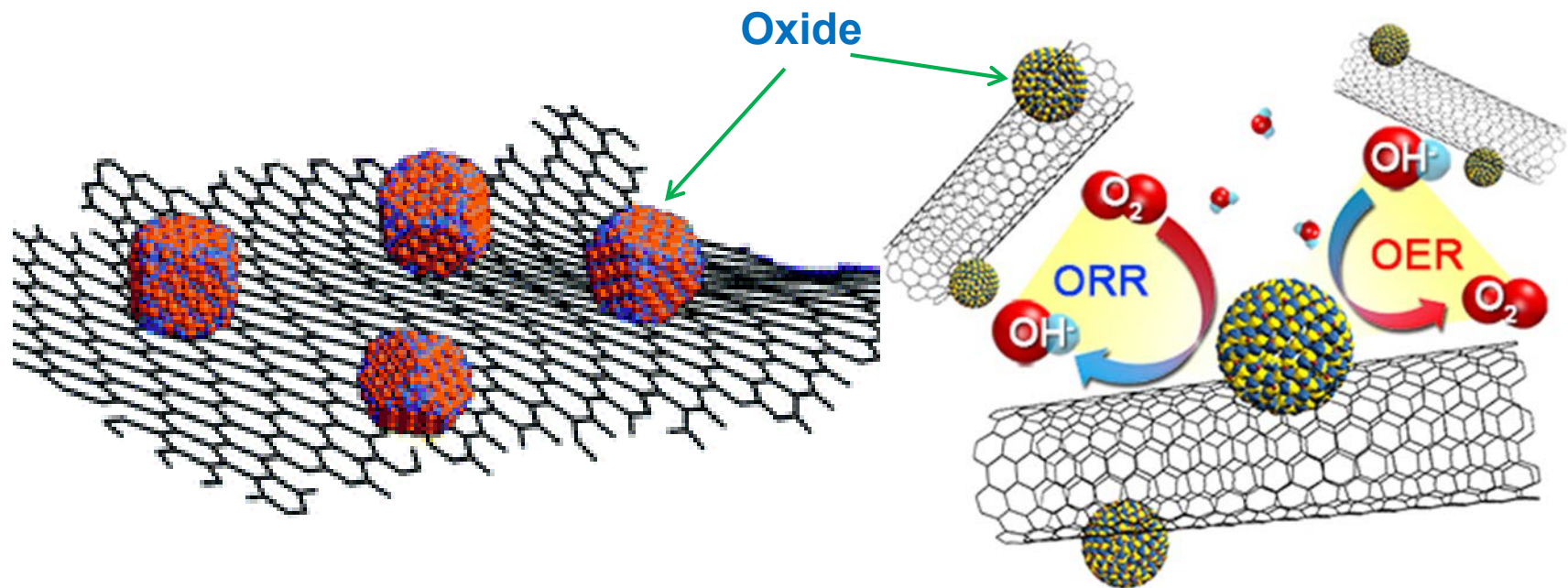
Technical Approaches



- Catalyst Long-term Stability;

- MEA Fabrication Technology

Design of Bifunctional Catalysts: Carbon Supported Metal Oxides

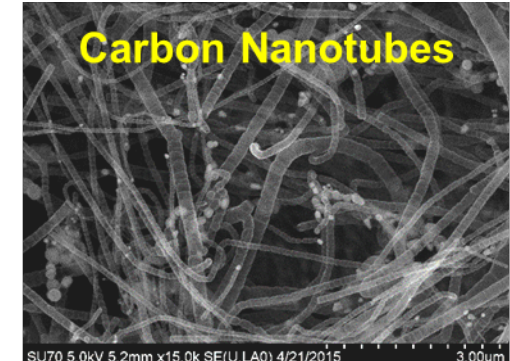
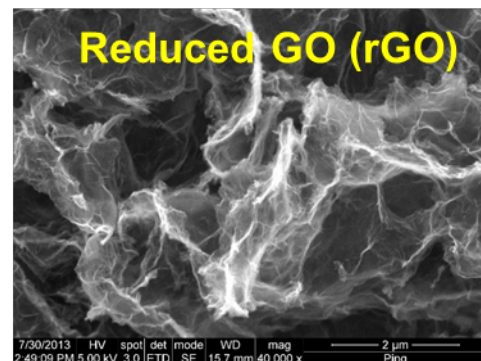
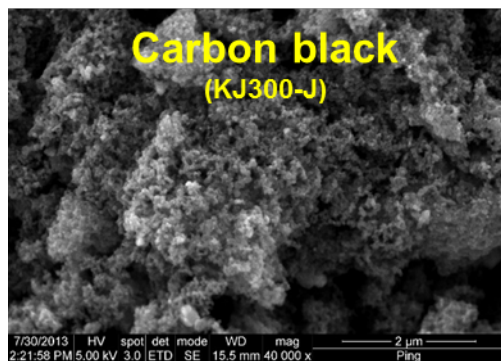
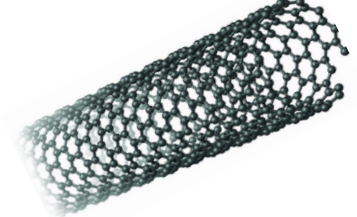
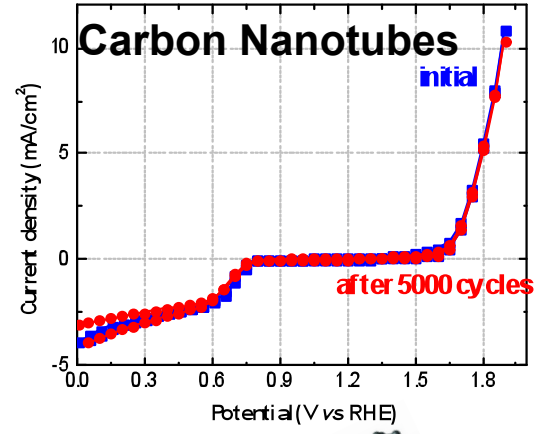
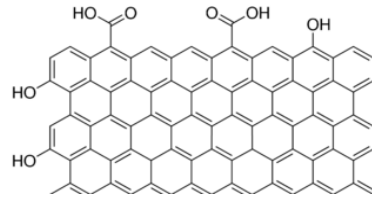
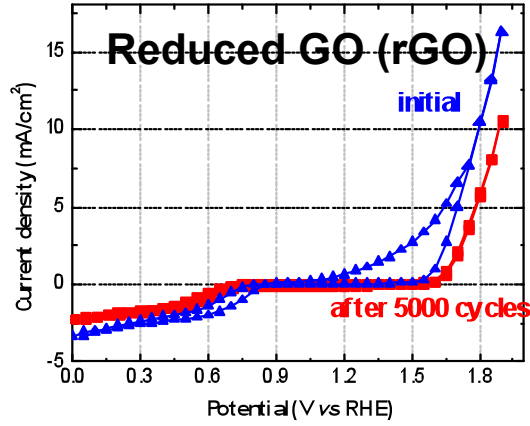
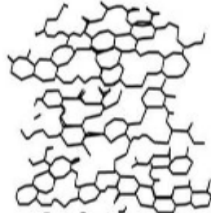
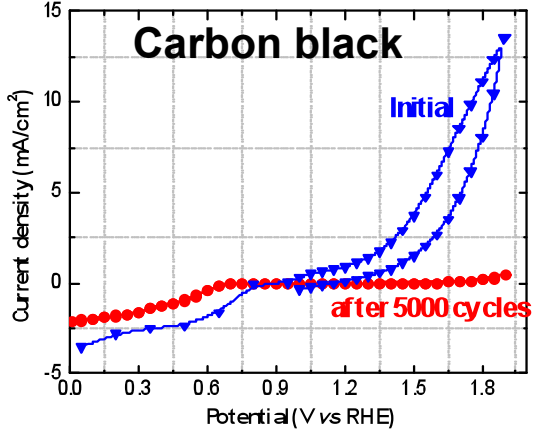


Opportunity: Metal Oxide showing good OER catalytic activity and excellent electrochemical stability

Approach: Hydrothermal methods are used to prepare oxide nanoparticles deposited onto nitrogen-doped carbon matrices (e.g., graphene, nanotubes)

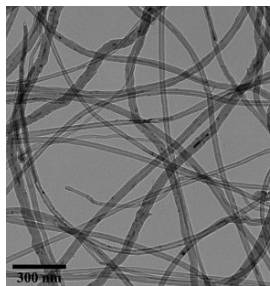
Identifying Stable Nanocarbon for the OER

ORR-OER Cycling Stability Tests in O₂ saturated 0.1 M NaOH, 0-1.9 V, 0.5 V/s

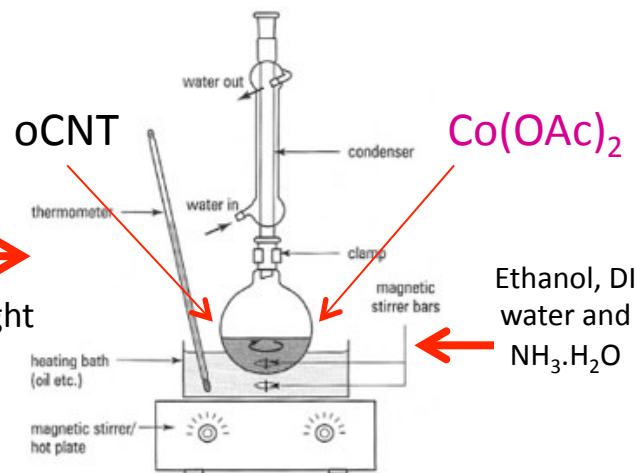
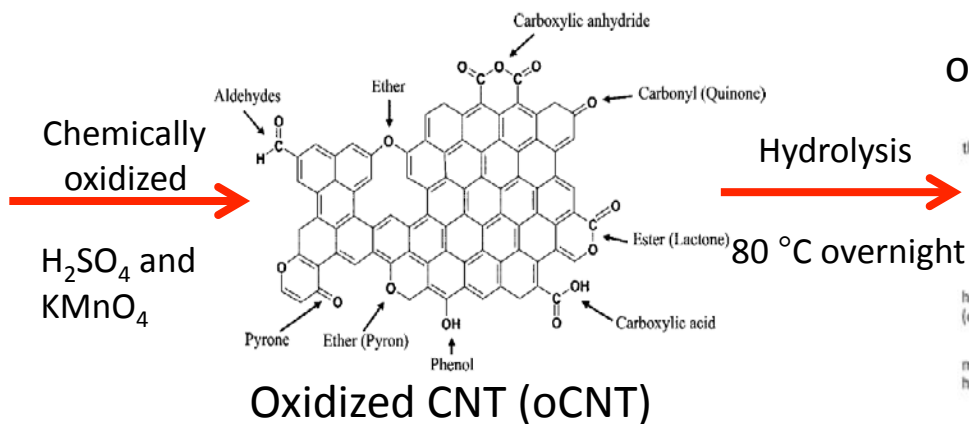


Carbon tubes holding great promise to be stable during the OER

Accomplishment 1: Synthesis Co_3O_4 -oCNT Catalysts



MWCNT



Hydrothermal, pressurized heating



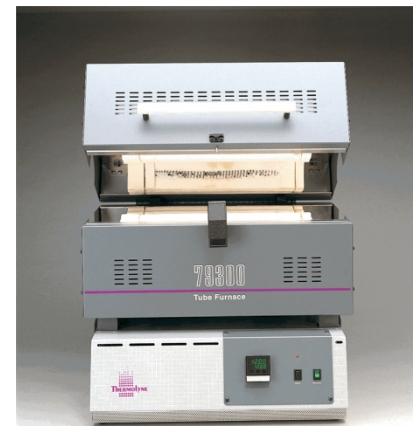
150 °C for 5h in Parr Bomb



Post-treatment, ammonia reduction

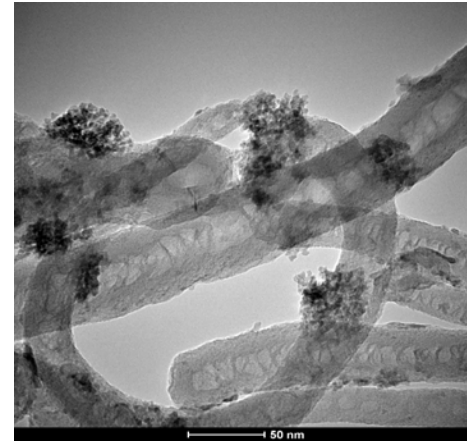
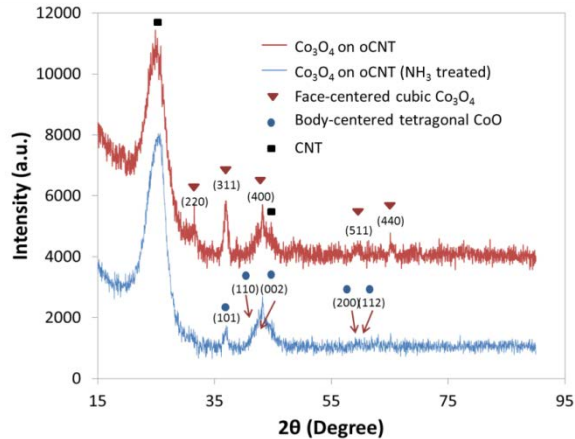


250 °C for 6h in 5% NH_3/Ar

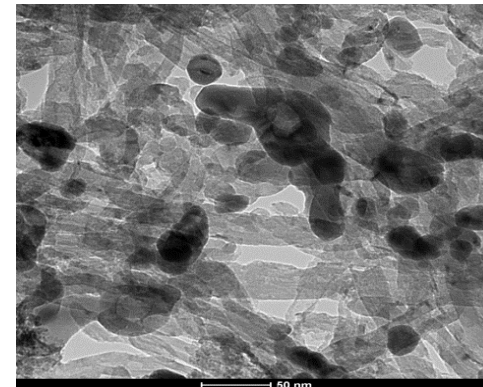
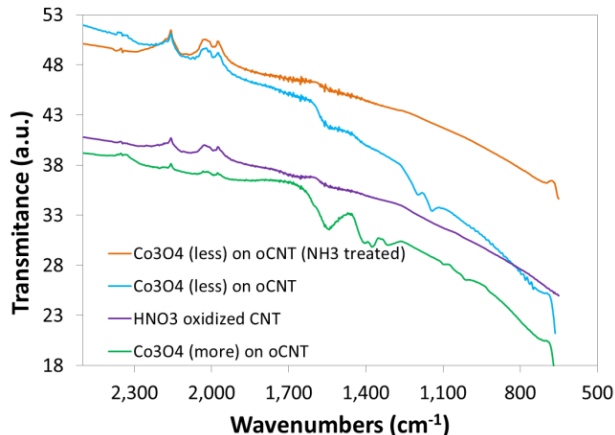


Physical Characterization of Co_3O_4 -oCNT Catalysts

XRD pattern, FTIR and TEM images before and after NH_3 - treatment



before

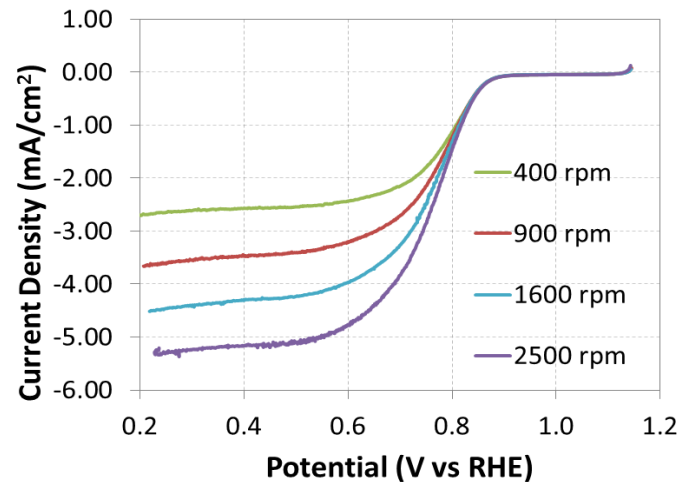
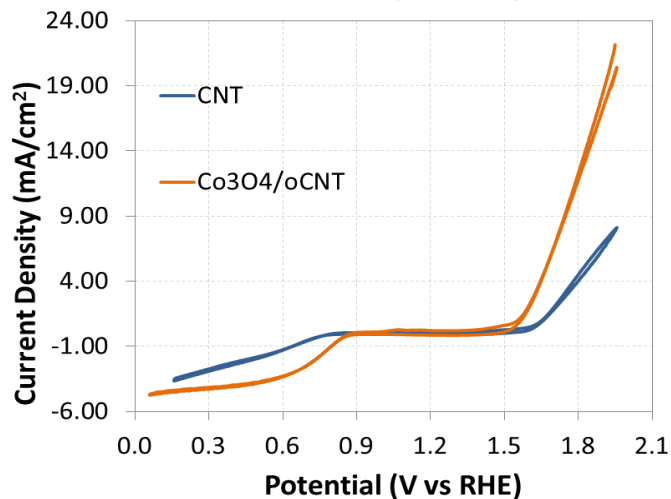
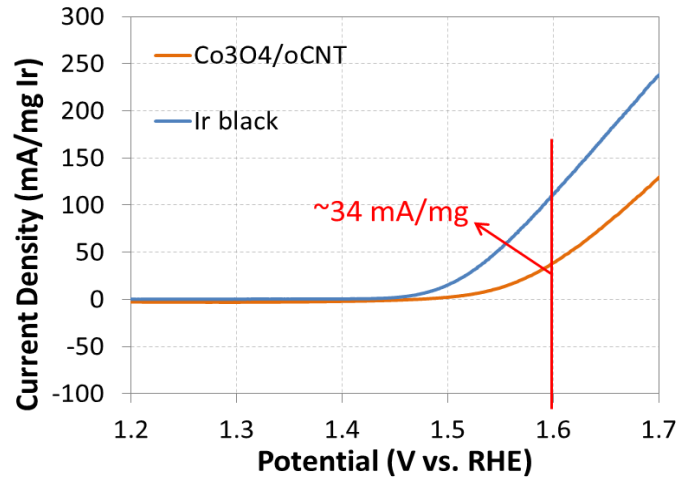
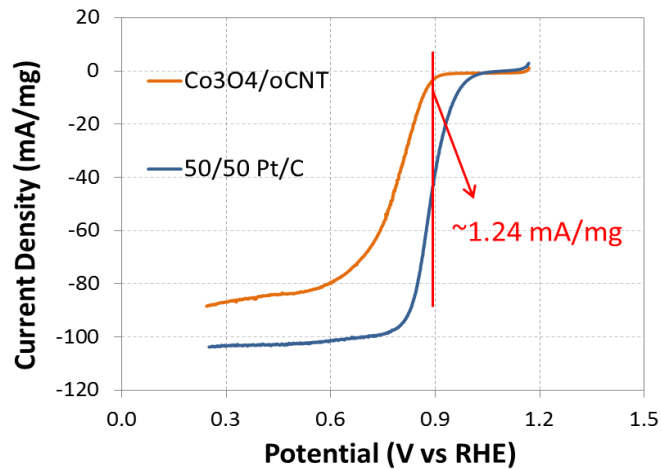


after

- XRD: before-corresponded well with FCC Co_3O_4 ; after: Co_3O_4 feature decreased, but not complete CoO
- TEM: before-smaller particles agglomerate; after- larger particles and round edges to stay in low energy
- FTIR: Both the single and double bonded oxygen functional groups were reduced after NH_3 post-treatment

RDE Activity of Co_3O_4 -oCNT Catalysts

1600 rpm,
0.1 M KOH,
5mV/s

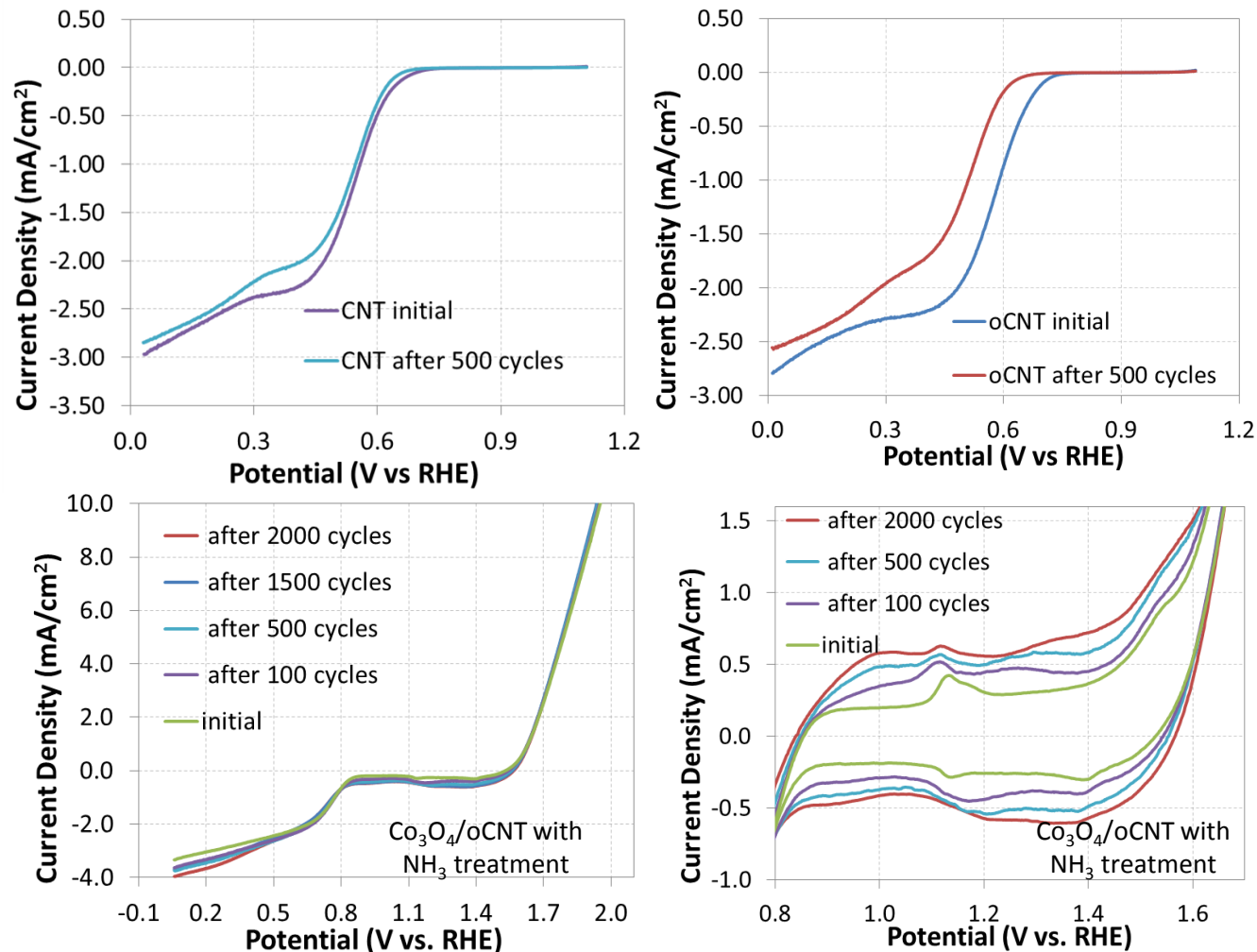


- For ORR: both onset and half-wave potential were ~ 0.1 V lower than that of Pt/C;
- For OER: the onset was ~ 0.07 V higher than Ir black

We have achieved the 1st Year's go/no-go milestone at Q4:

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

RDE Durability of Co_3O_4 -oCNT Catalysts

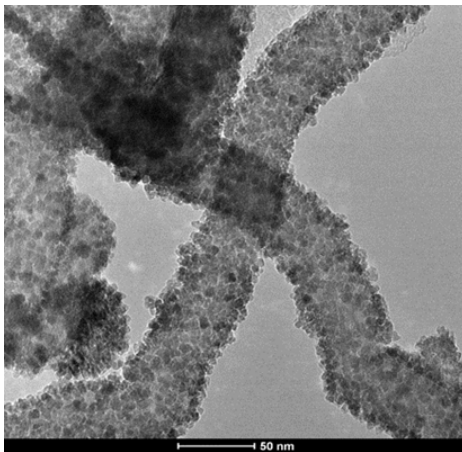


- As-oxidized CNTs lost stability after only 500 cycles, NH_3 reduction treatment stabilized the CNTs
- Co_3O_4 -oCNT exhibited good durability after 2000 cycles subject to voltage cycling

Further Optimization of Co_3O_4 -oCNT Catalysts

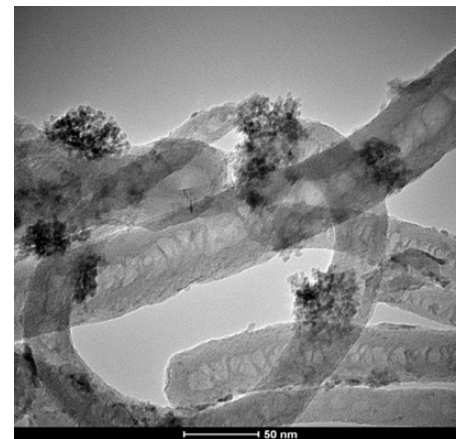
- Oxidation agents (functional groups), length, concentration, T
- Precursor ratio
- CNT type and size (length and O.D.)
- Precursor type
- Post-treatment: NH_3 concentration, T, heating time, heating rate

Metal precursor to oCNT ratio



15:1:

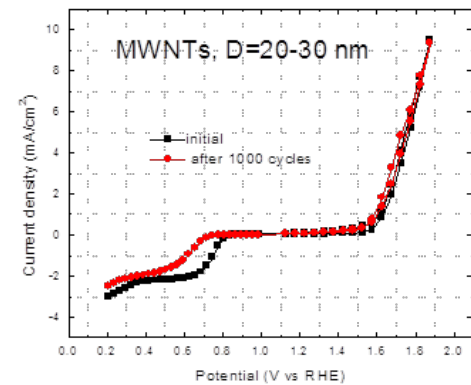
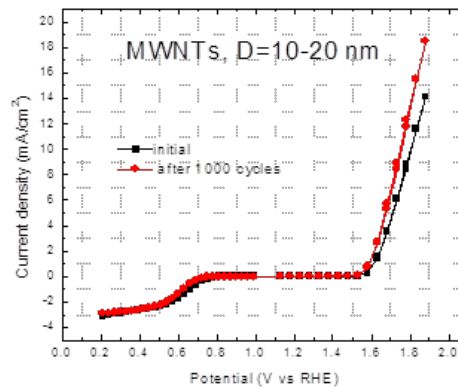
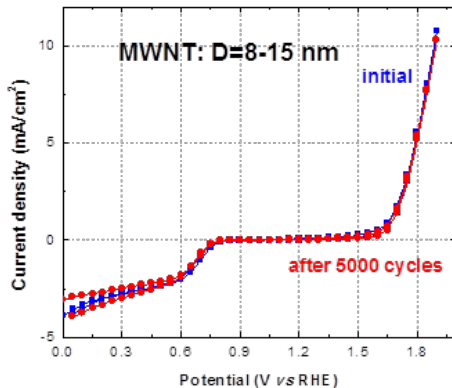
Covered the whole surface of oCNT, large cubic grains around 5-10 nm



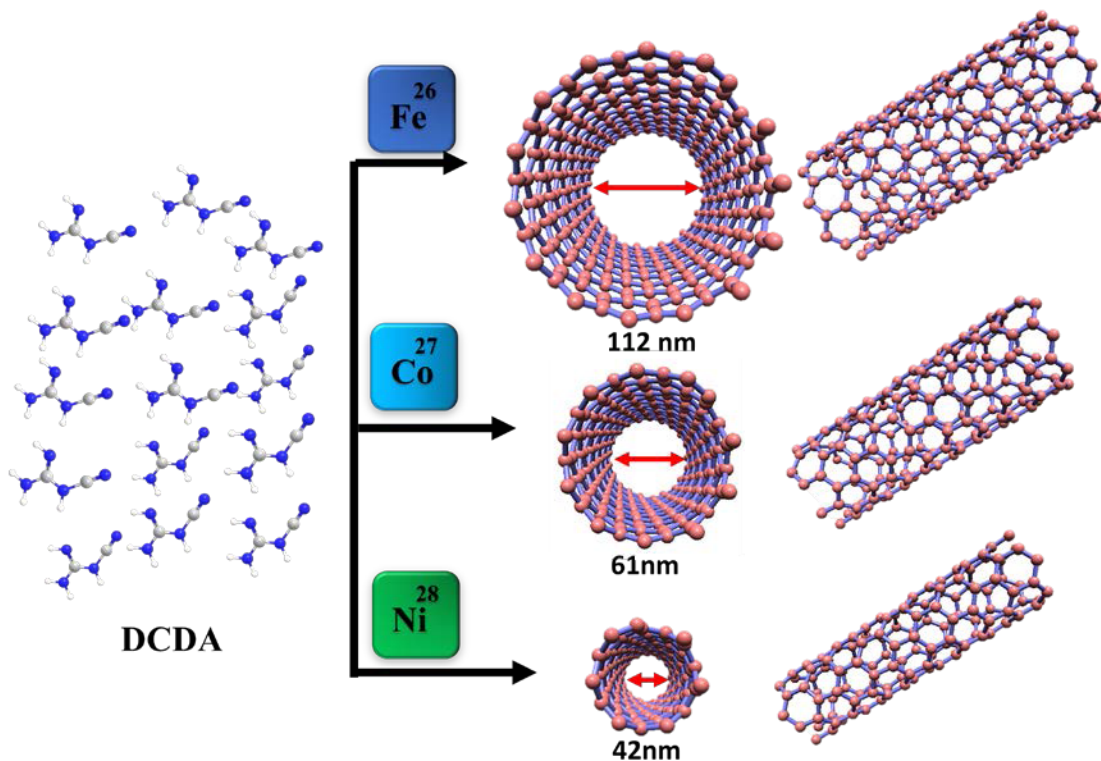
5:3:

Much smaller particles (1-2 nm) gathered specific regions

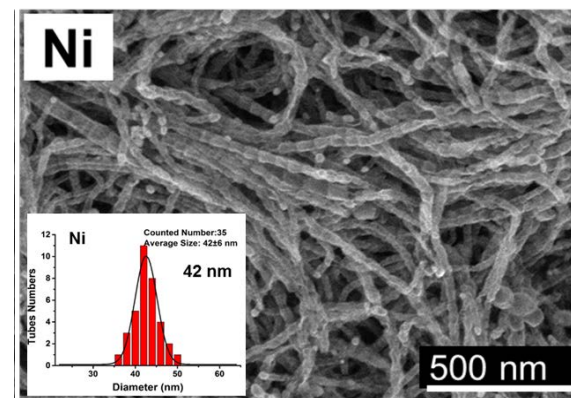
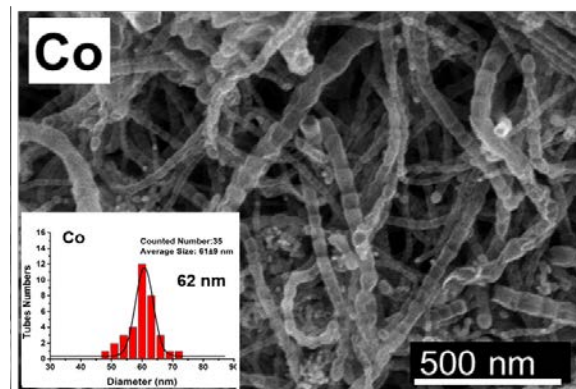
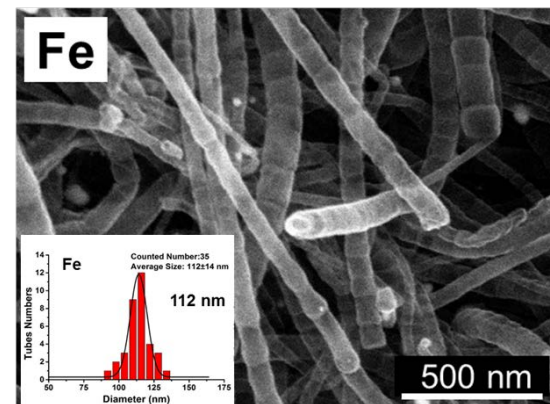
CNT type and size (length and O.D.)



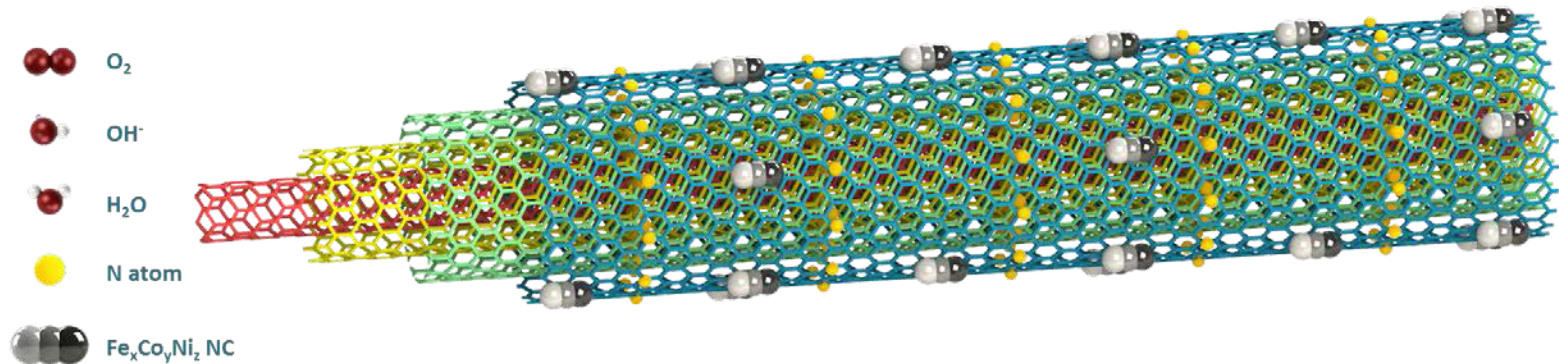
Accomplishment 2: Graphene Tube Based ORR/OER Catalysts (SUNY)



Unique capability to control the tube size by varying the transition metals during the graphitization process



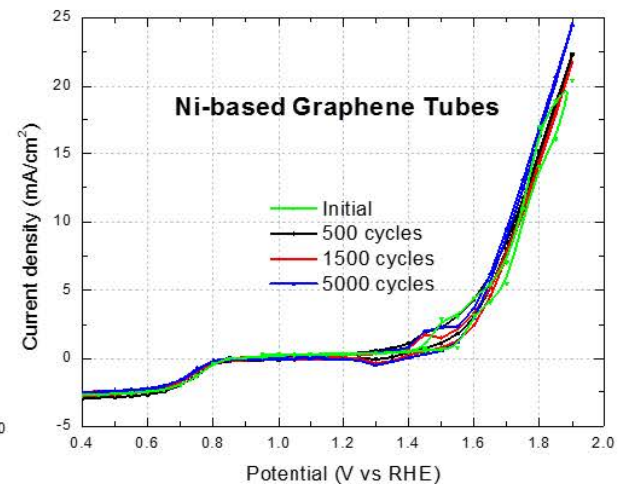
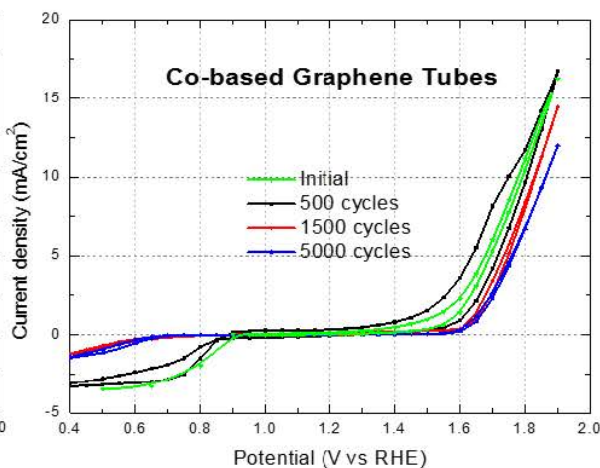
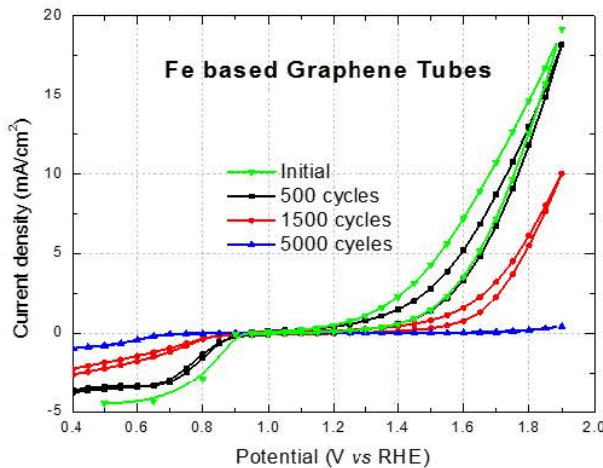
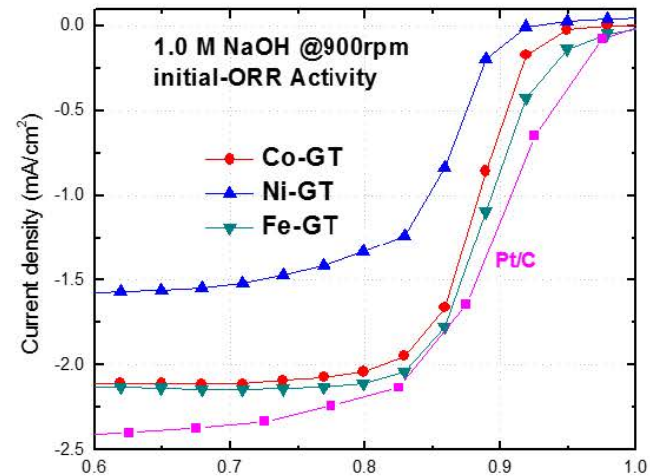
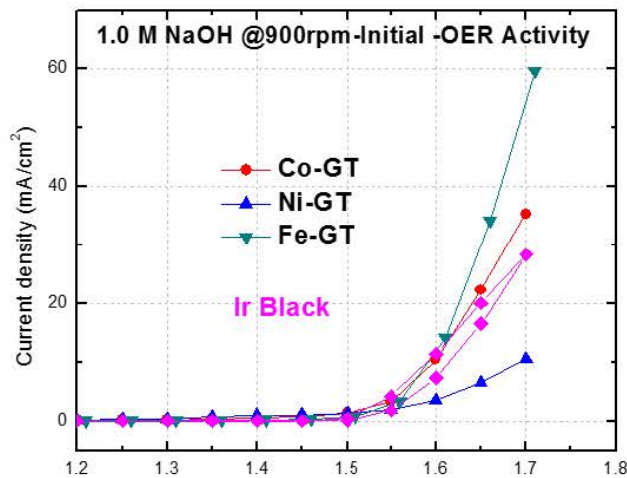
Multi-Walled Graphene Tube Synthesis



Low-cost and scalable synthesis method to produce graphene tubes

Activity and Stability of Graphene Tubes

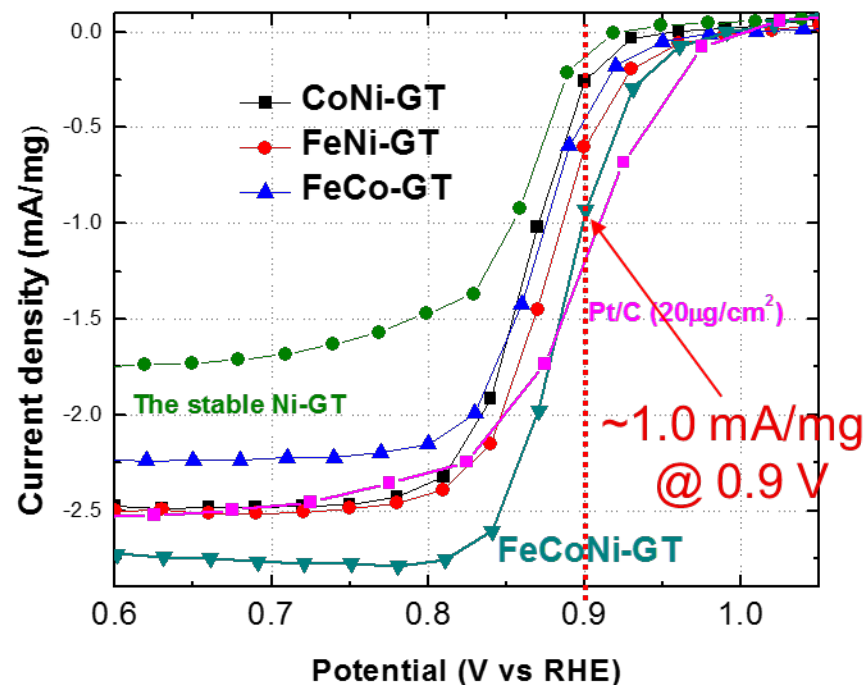
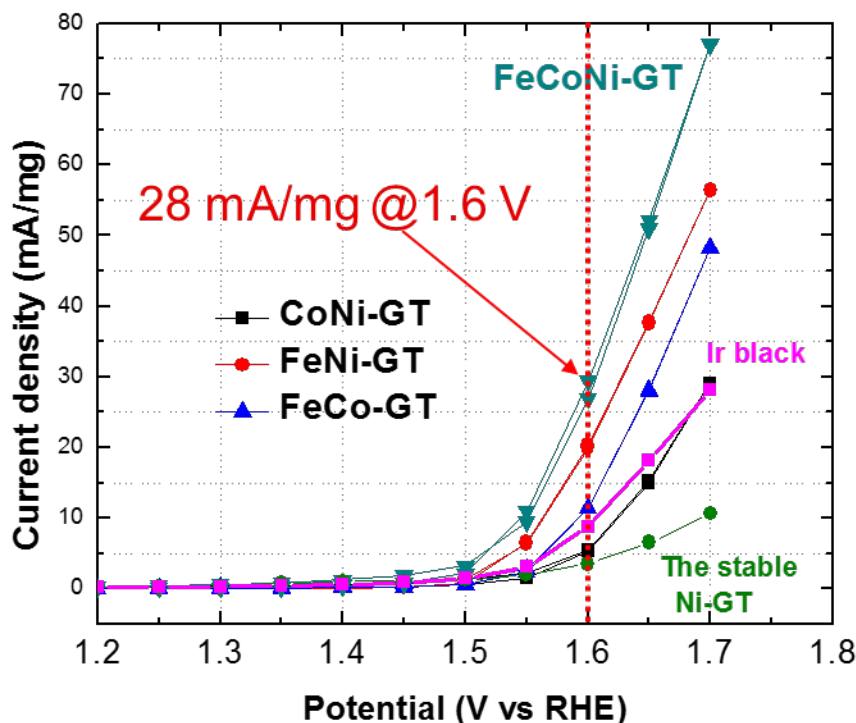
AST: Voltage Cycling from 0.0 V to 1.8V (vs. RHE)



- Fe-derived graphene tubes most active for the ORR and OER, but suffer from poor stability during continuously ORR-OER operation models;
- Ni-derived tubes are stable, but low activity.

Graphene Tube ORR/OER Bifunctional Catalysts

Binary and Ternary metal-derived graphene tubes

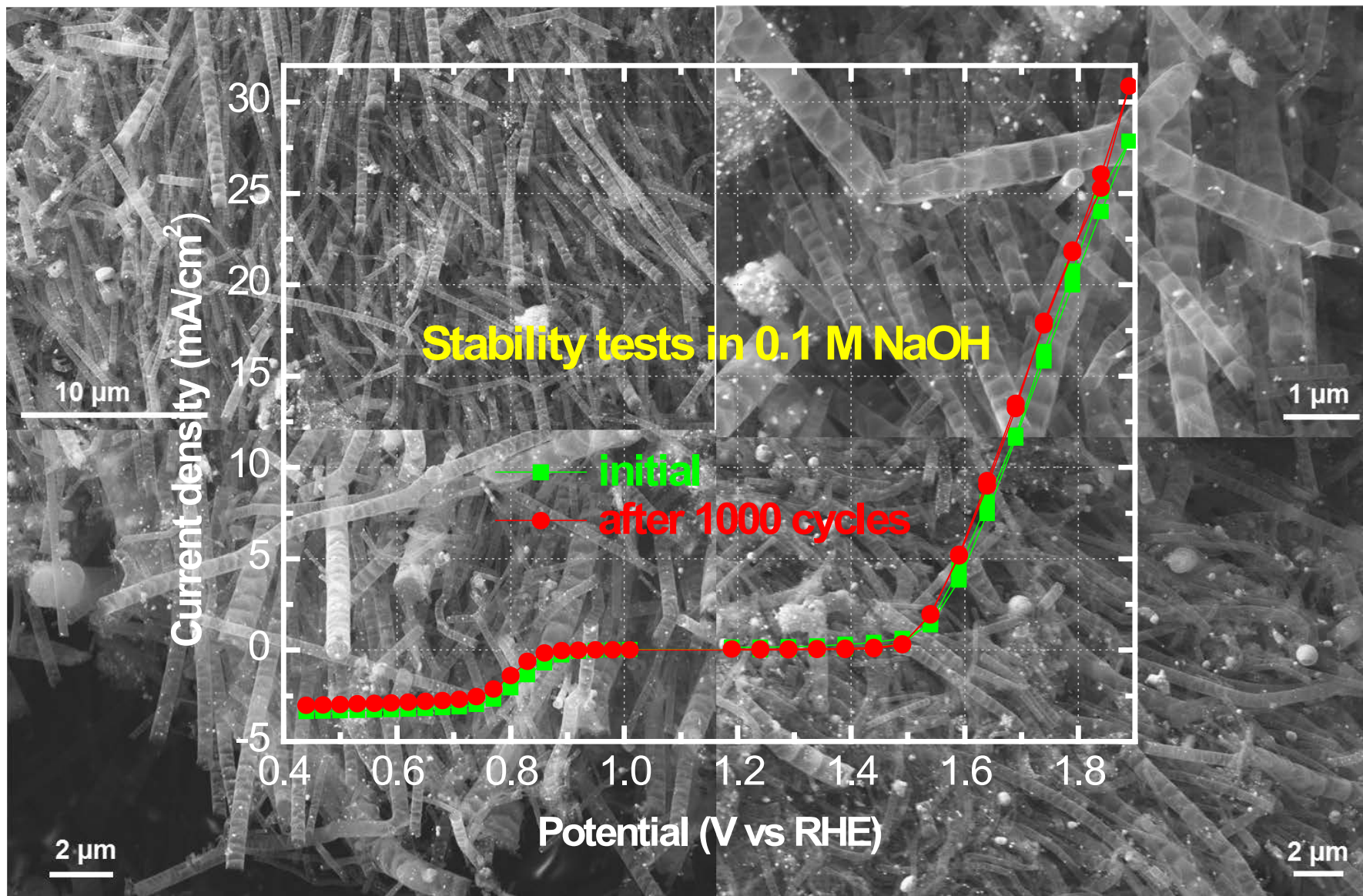


Binary and ternary metal combinations were used to prepare graphene tubes in order to achieve sufficient activity and stability simultaneously .

We have achieved the 1st Year 's go/no-go milestone at Q4.

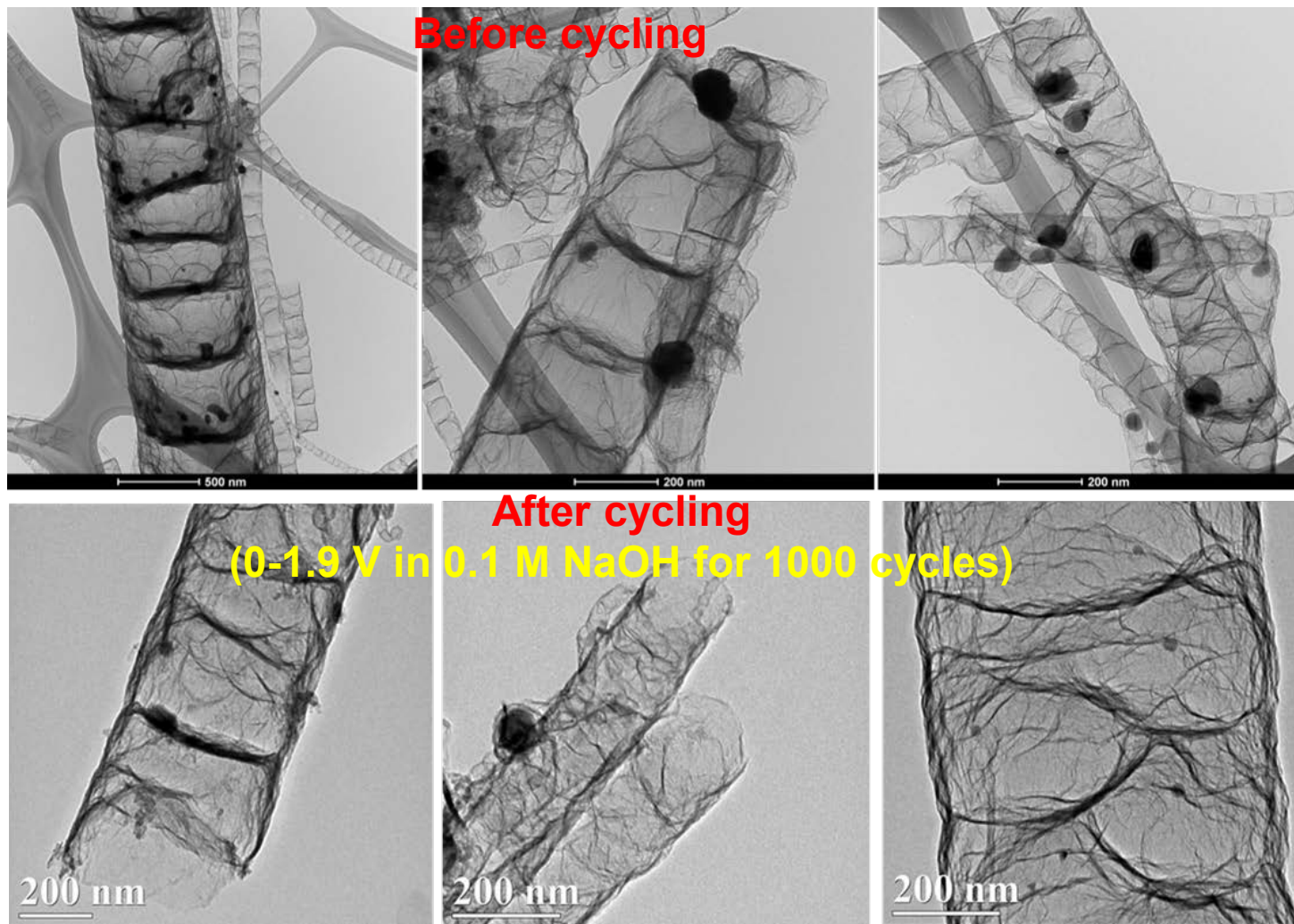
"In RDE, demonstrate ORR activity > 1 mA/mg oxide at IR-free 0.9 V; and OER activity > 15 mA/mg oxide at IR free 1.6 V"

Most Stable Graphene Tube ORR/OER Bifunctional Catalysts



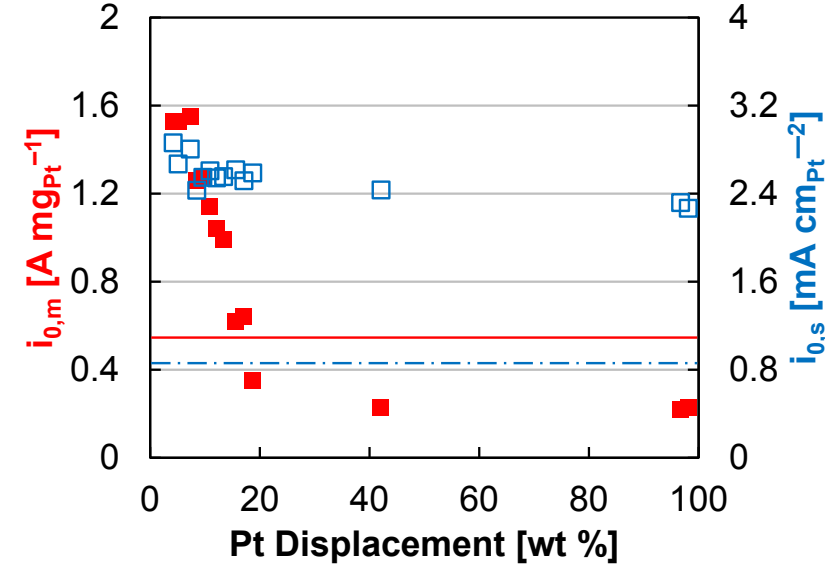
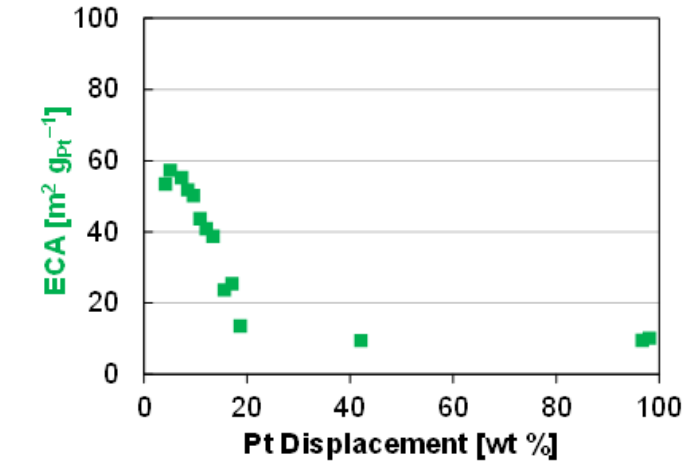
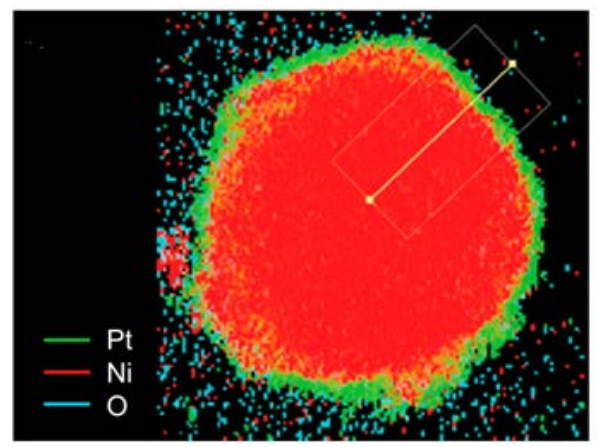
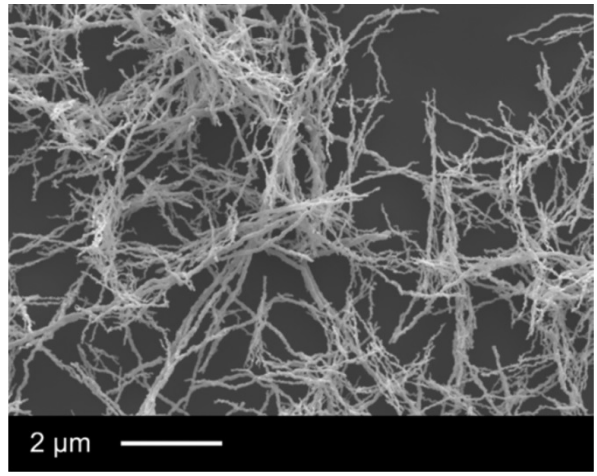
Graphene Tube ORR/OER Bifunctional Catalysts

The Most Stable FeCoNi-derived Graphene Tubes



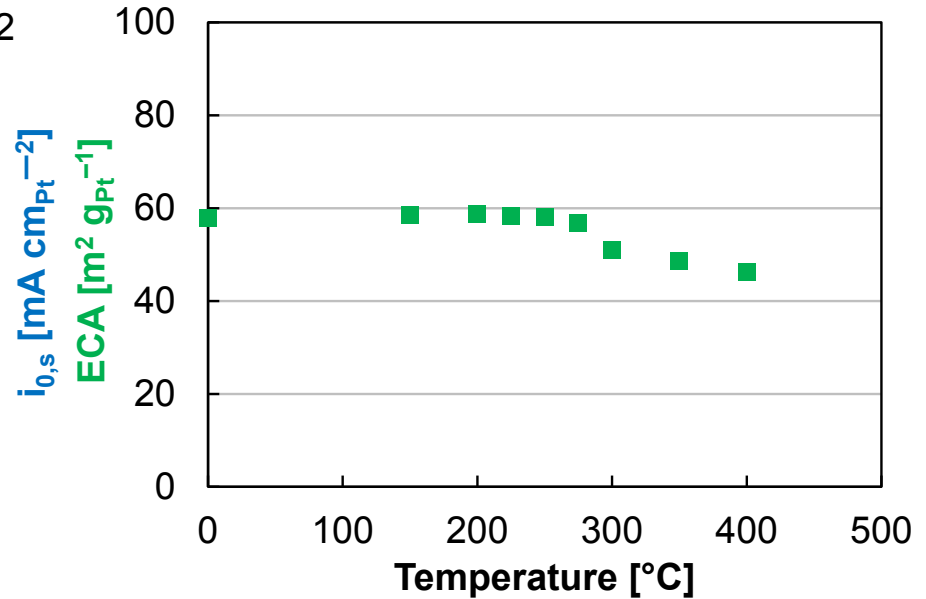
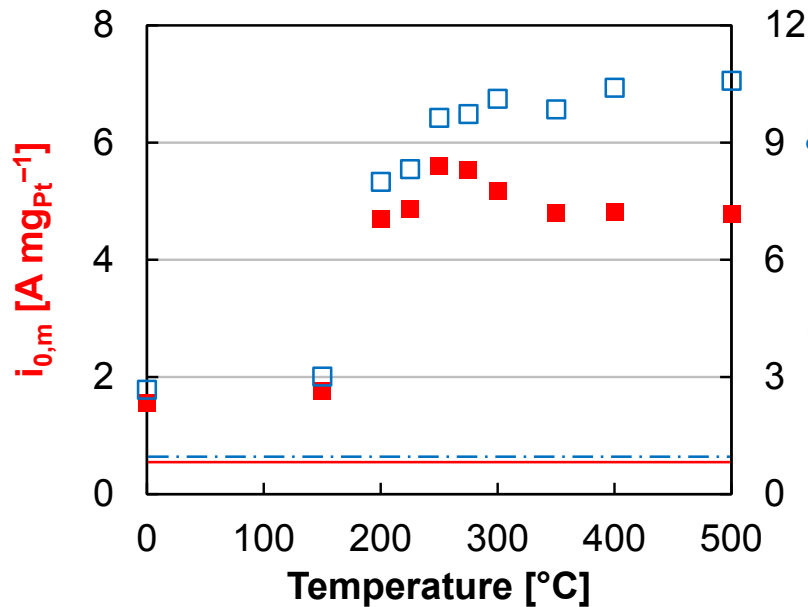
Highly graphitized tube morphology/structure is retained after potential cycling tests

Accomplishment 3: HOR/HER, Pt-Ni Nanowires(NREL)

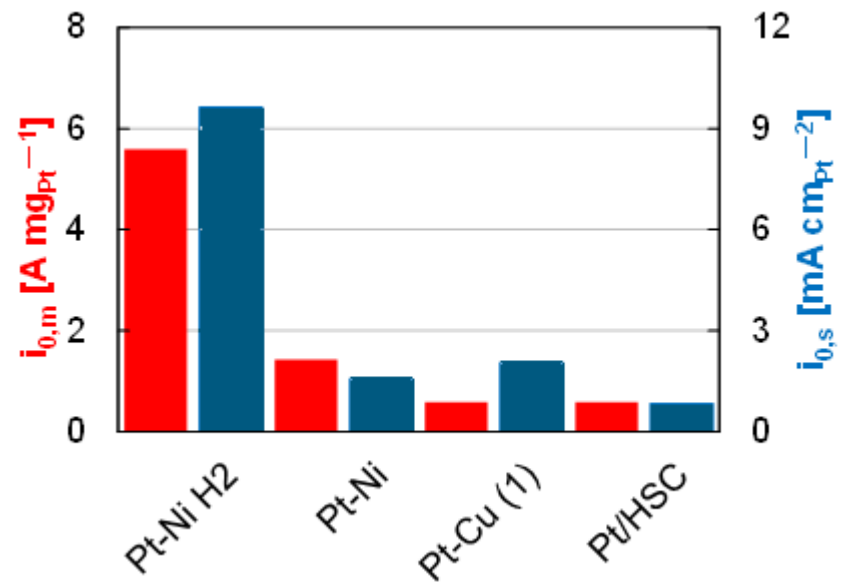


- Increased ECSA at low displacement: $60 \text{ m}^2 \text{g}_{\text{Pt}}^{-1}$ in base
- Activity by exchange current densities
- Site-specific activity constant, higher than Pt/HSC
- Mass activity 2.6 times higher than Pt/HSC

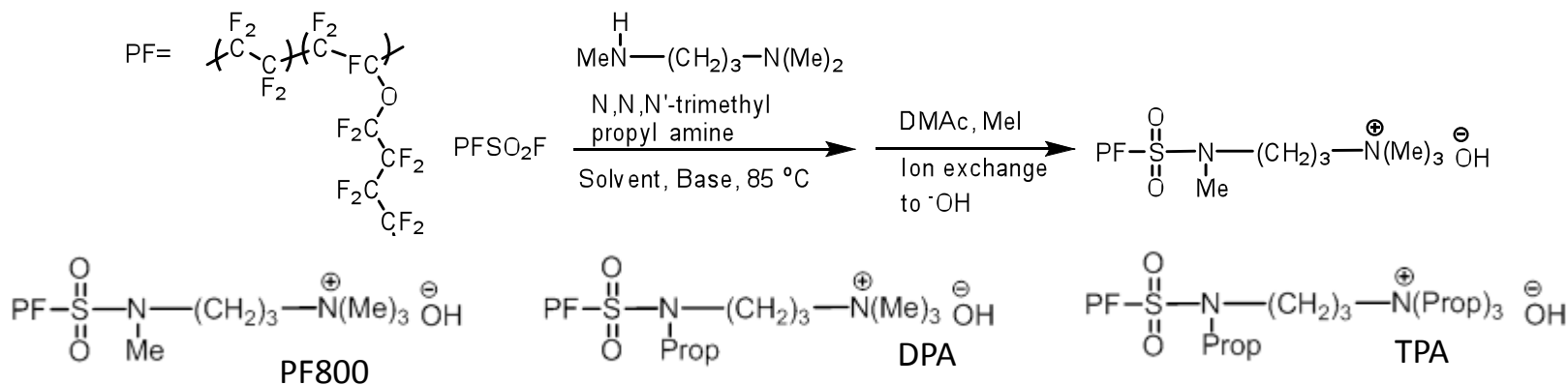
HOR/HER Pt-Ni Hydrogen Annealing



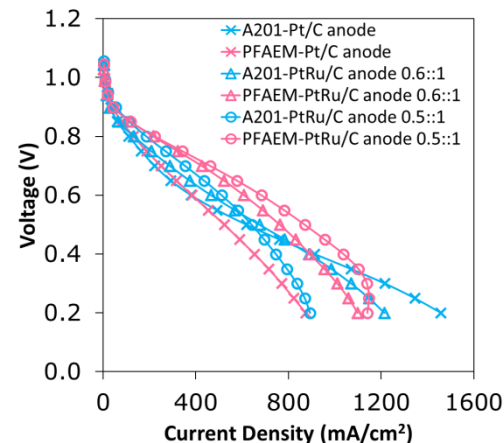
- Surface area constant up to 300°C
 - Microscopy shows loss of surface features, Pt aggregation
 - May increase nanowire dissolution
- Activity
 - Site-specific activity increases with temperature
 - Mass activity peaks (250–300°C)



Accomplishment 4: Providing New AEMs (NREL)



- First polymer was synthesized from perfluorosulfonyl fluoride polymer (800 equivalent weight) and N,N,N'-trimethylpropyldiamine (PF800)
- For stability methyl group on linker amide was changed to propyl (DPA) and a third polymer was synthesizing using all propyl groups on amines (TPA)
- PFAEM demonstrates superior performance to Tokuyama in most current regions



Cathode: 0.32 mg Pt/cm²

Anode: 0.32 mg Pt/cm² or 0.30-0.35 mg PtRu/cm²

- AEM work is leveraged from other DOE project FC147;
- 15 g of membranes and 5 g of ionomer solution will be provided to Giner

Conclusions

- ❑ Tube-like structures prove to be stable subject to extensive voltage cycling (0.0 V to 1.8 V) in RDE under alkaline media; directing a viable application in developing bi-functional ORR/OER catalyst;
- ❑ Both $\text{Co}_3\text{O}_4/\text{o-CNT}$ and FeCoNi-derived graphene tubes catalysts have achieved superior activity for the ORR/OER, exceeding Go/No-Go milestone at Q4; these catalysts are very stable subject to voltage cycling (0.0 V to 1.8 V);
- ❑ PtNi Nanowire catalysts demonstrated higher HOR/HER activity than Pt/C
- ❑ NREL AEMs are comparable or superior to Tokuyama membranes for fuel cell performance in most current regions.

Future Plans

- ❑ Explore MEA fabrication for bifunctional catalysts and optimize test conditions for both fuel cell and electrolyzer mode
 - Ongoing MEA test for dual modes
- ❑ Modify fuel cell configuration and test station to operate fuel cell (discharge)/electrolyzer (charge) intermittently
 - Unitized reversible fuel cell design

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)	90%
Q3	Prepare 3 A _x B _{1-x} C ₂ O 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)	50%
Q5	3 AEI ionomer categories and 5 ionomer loadings will be evaluated to identify the best electrode composition	30%
Q6	Achieve RFC performance 0.55V for fuel cell and 1.6V for electrolyzer, both at 600mA/cm ²	0%
Q7	Achieve fuel cell and electrolyzer life of 500 hours with less than 10% performance decay	0%
Q8	Generate a full report of catalyst and reversible fuel cell economics	0%

Collaborations

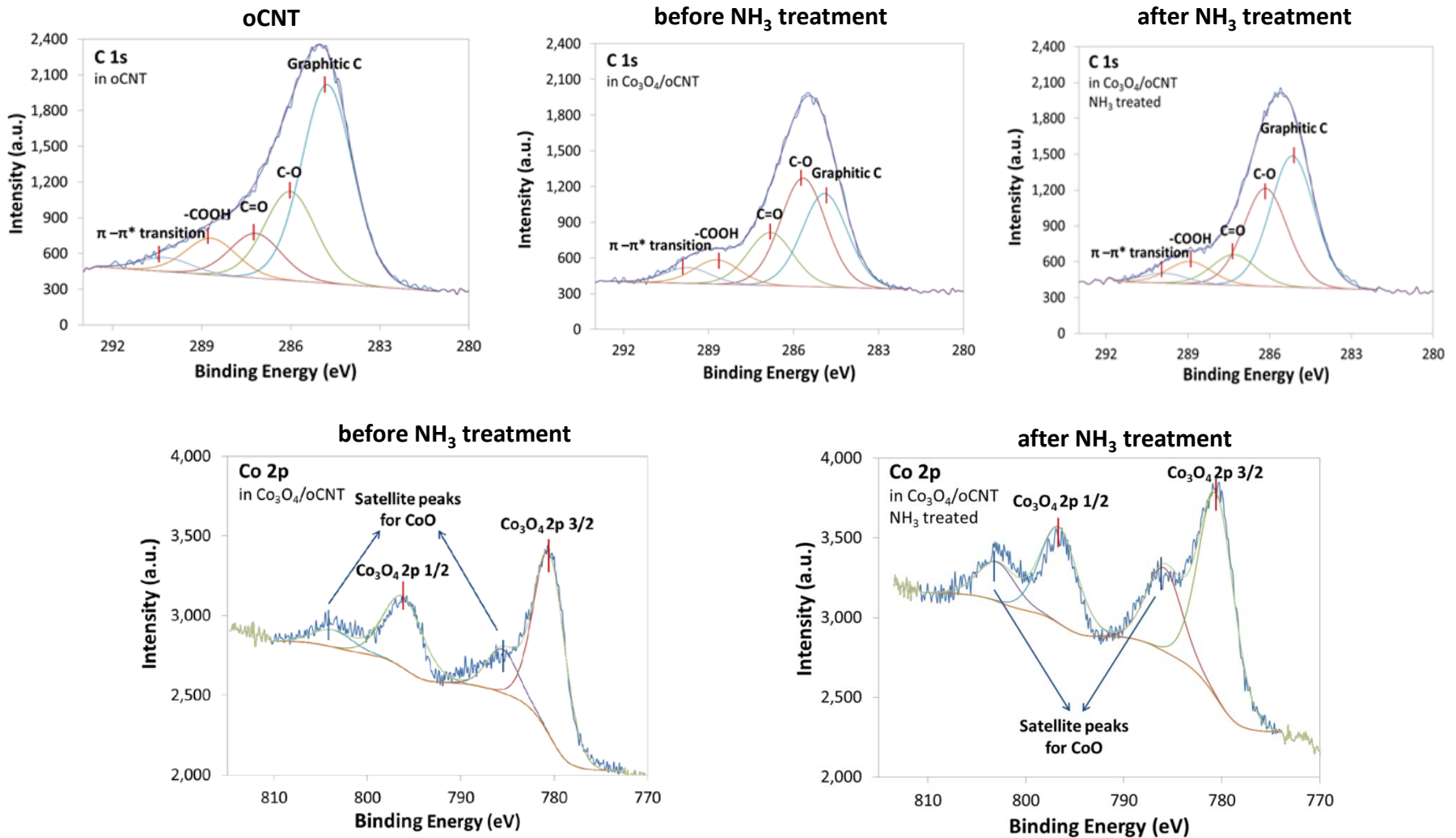
Institutions	Roles
<u>Giner Inc. (Giner)</u> Hui Xu (PI), Shuai Zhao, Brian Rasimick, Meagan Rich	Prime, oversees the project; metal oxide supported on CNTs; bi-functional MEA fabrication and optimization; reversible fuel cell design; cost analysis
<u>SUNY -Buffalo(SUNY)</u> Gang Wu and Shiva Gupta	Graphene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

Acknowledgments

- Financial support from DOE EERE Fuel Cell Technologies Office, Incubator Program Award # DE-EE0006960
- DOE Program Managers
 - Dr. David Peterson
 - Donna Ho
- Giner Personnel
 - Shuai Zhao, Brian Rasimick, Meagan Rich, Corky Mittelsteadt
- SUNY: Prof. Gang Wu
- NREL: Drs. Bryan Pivovar and Shaun Alia

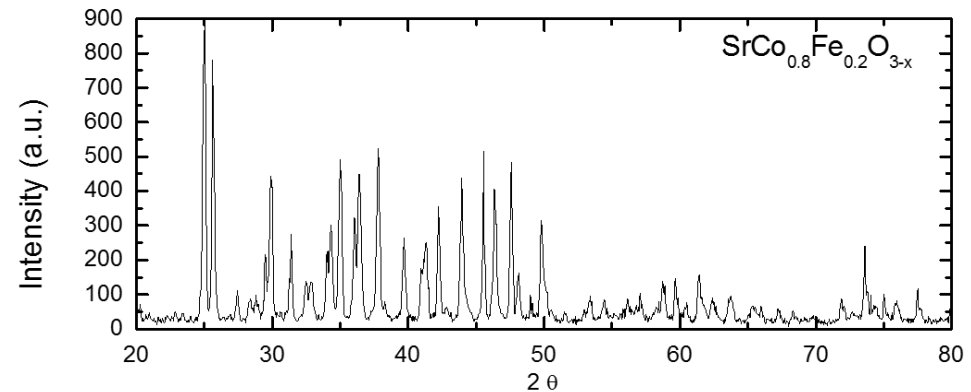
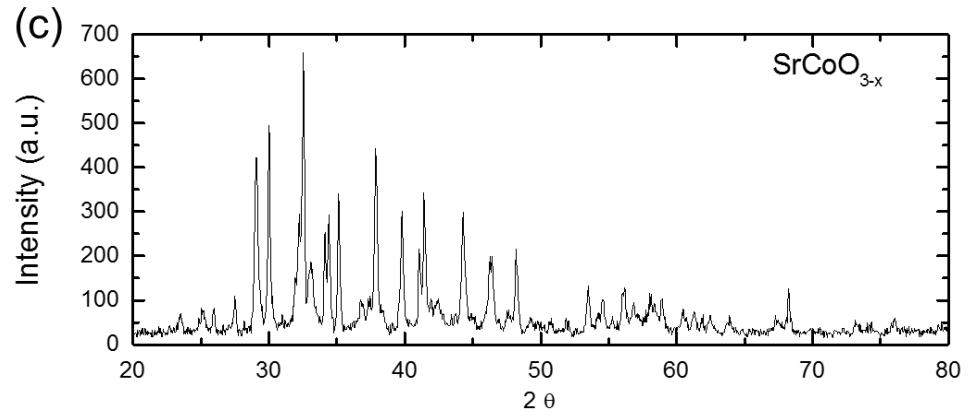
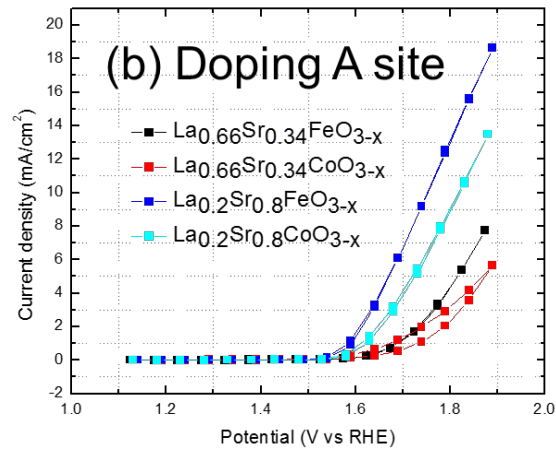
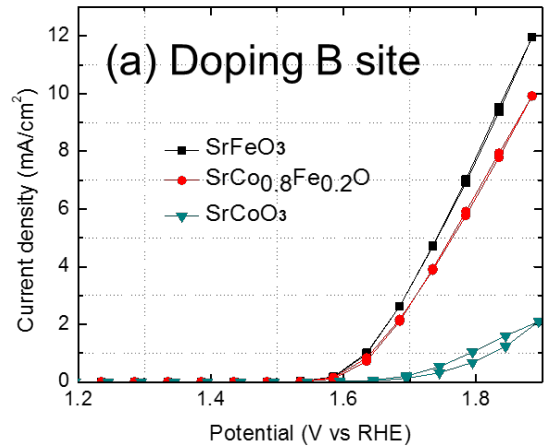
Appendix

XPS Characterization of Co_3O_4 -oCNT Catalysts



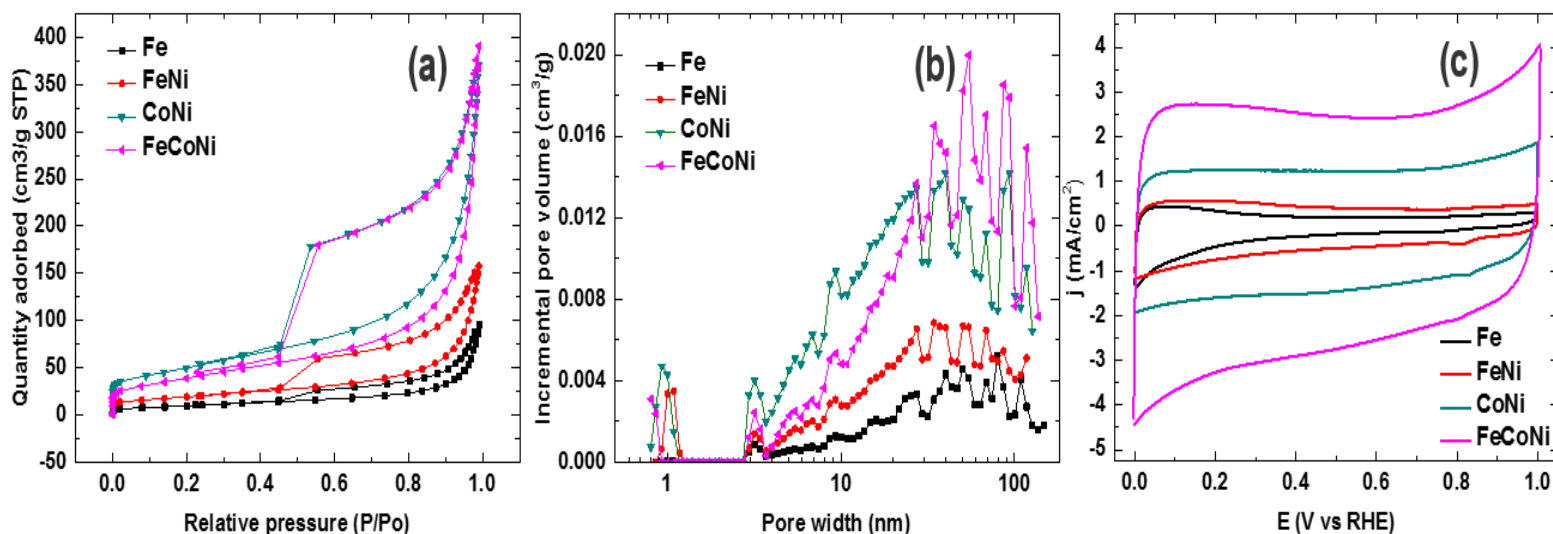
- Oxide or hydroxide in Co intermediate forms single bonds with neighboring C
- Oxidized C were significantly reduced to be stabilized after NH_3 -treatment
- Increase of satellite peaks for CoO indicates increase of the +2 state Co in metal oxides after NH_3 -treatment

Oxygen-deficient Perovskite Catalysts



BET, Pore Size and Electrochemical Surface Area of Graphene Tube Catalysts

Catalysts name	BET Surface Area (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (nm)	EASA (m ² /g)
N-nGT(Fe)	35.34	0.12	13.98	33.32
N-nGT(FeNi)	67.8	0.22	13.33	49.9
N-nGT(CoNi)	177.15	0.51	11.93	99.96
N-nGT(FeCoNi)	144.84	0.53	14.76	221



Publications

- Wang, X.; Pan, H.; Ke, Y.; Sheng, H.; Swihart, M. T.; Wu, G. “Size-controlled large-diameter and few-walled carbon nanotube catalysts for oxygen reduction”. *Nanoscale*, **7**, 20290-20298 (2015).
- 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*, **11**(1), 10–21 (2016).
- 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, doi:10.1016/j.nanoen.2015.12.032.
- Zhao, S., Rasimick, B, Mustain, W., and Xu, H. “Highly Durable and Active Co_3O_4 Nanocrystals Supported on Carbon Nanotubes as Bifunctional Electrocatalysts in Alkaline Media”, submitted to *Nano Energy* (2016)
- Zhao, S. and Xu, H., “*Metal Oxides Supported on Carbon Nanotubes as Bifunctional Electrolysts for Reversible Alkaline Membrane Fuel Cells*”, to be presented in the 229th ECS meeting, abstract# 1434, San Diego, May 31 (2016)