2020 DOE Hydrogen and Fuel Cells Annual Merit Review

High-Efficiency Reversible Alkaline Membrane Fuel Cells

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Giner, Inc.

Project #: FC315

May 21, 2020

Overview

Timeline

- Project Start Date: January 1, 2019
- Project End Date: December 31, 2020

Barriers Addressed

A: Cost
B: Durability
C: Performance

Budget

- Overall $1,250.139
  - DOE share $799,503
  - Cost share $250,636
  - FFRDC $200,000 to NREL
- $579,309 spent*

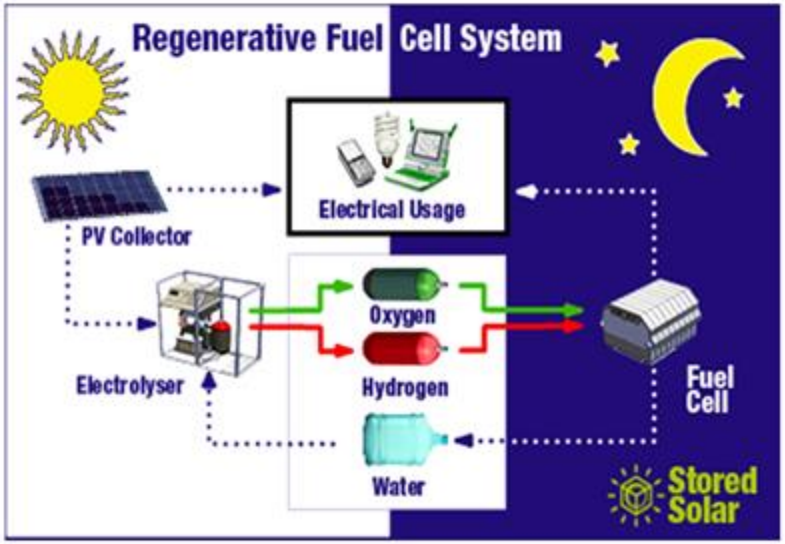
* as of 5/13/2020

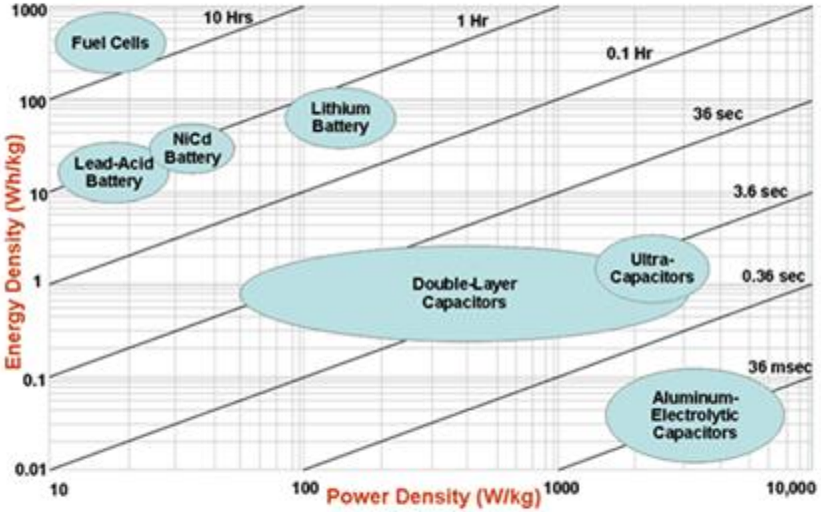
Partners

- Giner, Inc. Project lead
  Zach Green, Fan Yang and Derek Strasser
- Collaborations:
  - University at Buffalo
  - University of Delaware
  - National Renewable Energy Lab

Relevance

Demonstrate a reversible AMFC with >50% RTE at 500+ mA/cm^2 without introducing any salts or bases in the aqueous feed





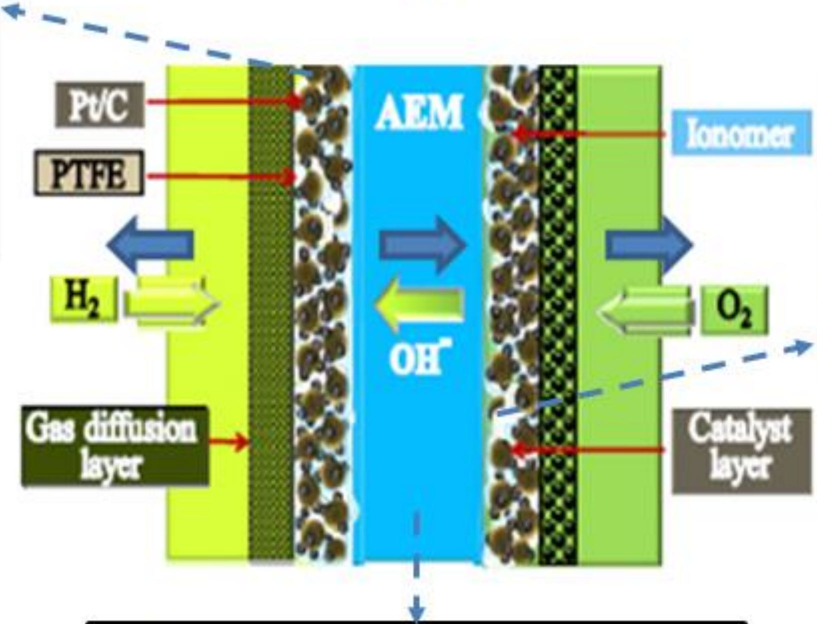
Source US Defence Logistics Agency

- RCs can store renewable energy with higher energy density than batteries
- **Unitized RFCs** use a single stack for both operating modes for substantial weight and cost savings

Technical Approaches

Reversible Anion Exchange Membrane (AEM) Fuel Cells

Bifunctional catalysts for hydrogen oxidation reaction (HOR) /hydrogen evolution reaction (HER)



Bifunctional catalysts for oxygen reduction reaction (ORR) /oxygen evolution reaction (OER)

High-performance Membrane

- High OH^- conductivity
- Oxidative resistance
- Mechanical stability

Performance Tasks

- **Task 1 Membrane and Ionomer Development**
  - Develop alkaline ionomers
  - Impregnate ionomers into dimensionally-stable membranes (DSM)
- **Task 2 Catalyst Preparation**
  - Prepare bifunctional HOR/HER and ORR/OER catalysts
  - Low PGM (baseline) and PGM-free catalysts
- **Task 3 MEA Design and Fabrication**
  - Optimize interactions of catalyst, ionomer and membrane
  - MEA water management
- **Task 4 Reversible Fuel Cell Test**
  - Charge-discharge operations
  - Salt addition Impact
- **Task 5 Techno-economical Analysis**
  - Capital cost
  - Operation efficiency and cost

Milestone Summary (Milestones are on track)

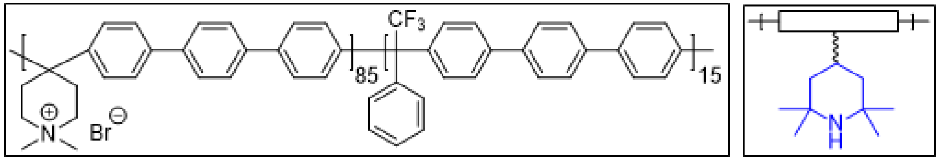
Milestone #	Milestone Description	Completion time	Completion percentage
Milestone 1.1	Demonstrate 30-50 µm self-supporting membranes with conductivity >100 mS/cm (80 °C), tensile strength > 50 MPa, elongation at break > 100%	June 2019	**100%**
Milestone 1.2	Deliver 400 cm^2 of PAP-TP-TMP membranes w/ superoxide disproportionation activity and 50 % improved oxidation resistance	December 2019	100%
Milestone 1.3	Demonstrate PAP membranes and ionomers w/ half-life in $KO_2/DMSO/D_2O$ 10x longer than commercial ionomer	June 2020	100%
Milestone 1.4	Prepare reinforced PAP membranes with through-plane ASR < 0.15 Ohm cm^2, ≥60 MPa tensile strength, ≥150% elongation at break	September 2020	50%
Milestone 2.1	15 g $Co3O_4$ or $NiCoO_4$ ORR/OER catalyst	March 2019	100%
Milestone 2.2	Produce 5 g MoS_2/RGO HER catalyst	September 2019	100%
Milestone 2.3	5 g chevrel-phase $NiMo_3S_4$ HER catalyst	December 2019	100%
Milestone 3.1	Identify three most impactful parameters for reversible fuel cell electrode design and fabrication	December 2019	100%
Milestone 4.1	**GO/NO GO Achieve a round trip efficiency of 50% at 500 mA/cm^2 in both fuel cell and electrolyzer modes**	**December 2019**	100%
Milestone 4.2	**With a reversible AEM fuel cell MEA, achieve round trip efficiency of 40% at 400 mA/cm^2 with pure water as feedstock**	**March 2020**	100%
Milestone 4.3	**With a low-PGM reversible AEM fuel cell MEA, achieve round trip efficiency of 45% at 500 mA/cm^2 with pure water as feedstock or 50% at 600 mA/cm^2 with allowed salts in water feedstock**	**June 2020**	100%
Milestone 4.4	Achieve a degradation rate <1 % over 200 hours with operation in both fuel and electrolyzer modes	September 2020	30%
Overall project	Obtain reversible AEM fuel cell round trip efficiency of 50% @ 1000 mA/cm^2	December 2020	50%

Accomplishment #1: Oxidation-resistant AEM

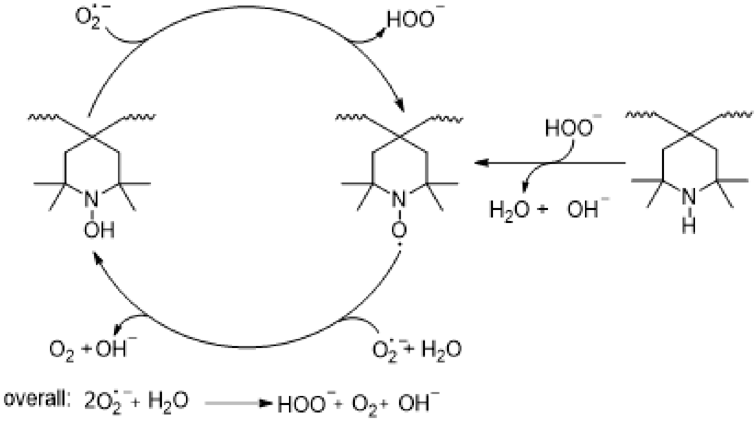
Goal: Develop oxidation-resistant alkaline ionomer/membrane for reversible AEMFC without the addition of any salts or bases

Strategy: Introduce stable C-H bonds with high BDE (bond dissociation energy) to mitigate hydrogen abstraction

- BDE: vinyl > aryl > aliphatic (prim. > sec. > tert.) > benzyl > allyl
- Introduce TMP type scavenge radicals to minimize oxide radical amount

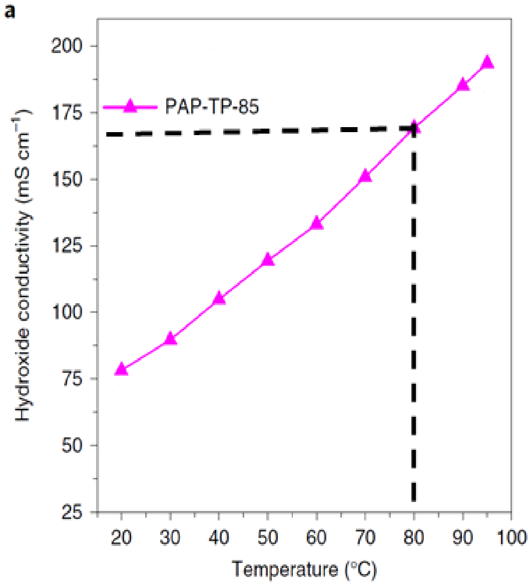


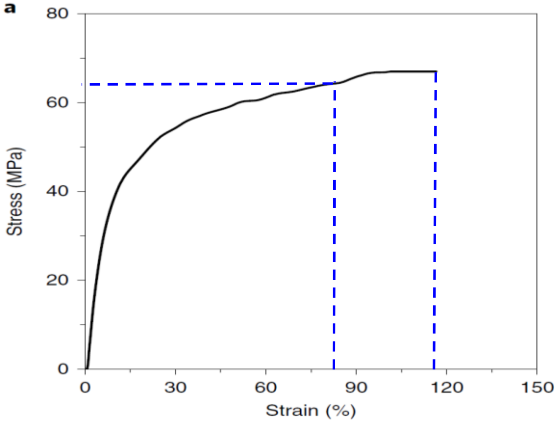
PAP-TP-85: aryl and aliphatic C-H bonds



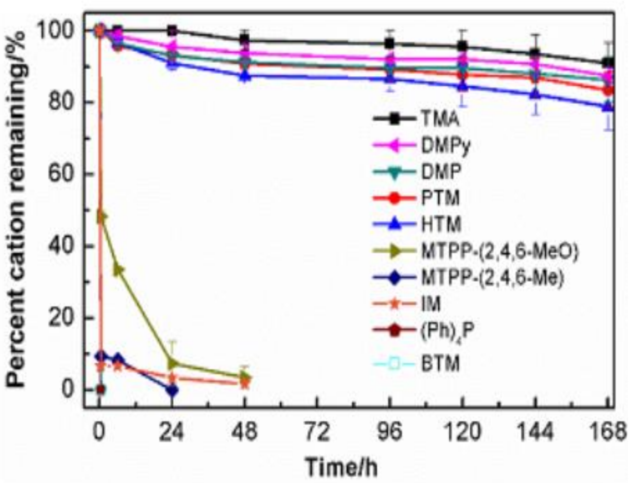
PAP-TP-85 Membrane Properties

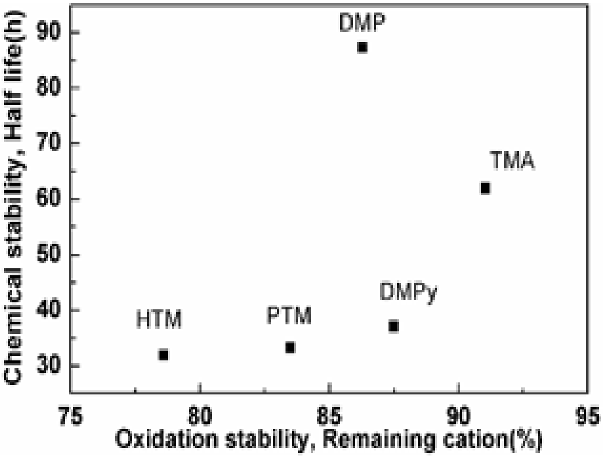
Conductivity: 157 mS/cm (80°C)
Tensile strength: 62 Mpa
Elongation at break: 115%





***N*, *N*-dimethylpiperidinium (DMP) is more stable than several common cations to superoxide radical species:**

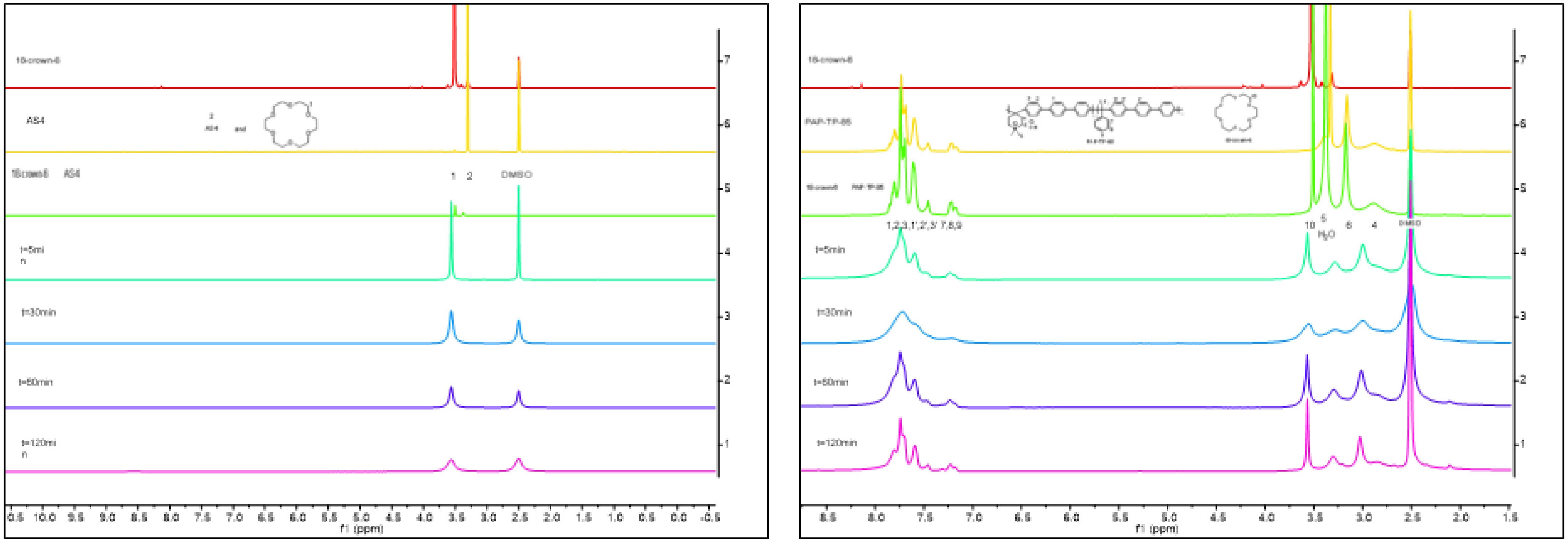




TMA = tetramethylammonium	DMPy = dimethylpyrrolidinium	DMP = dimethylpyrrolidinium
PTM = propyltrimethylammonium	HTM = hexytrimethylammonium	MTPP = trimethyphenylphosphonium
IM = imidazolium	$(Ph)_4P$ = tetraphenylphosphonium	BTM = benzyltrimethylammonium

PAP-TP-85 shows considerable improvements over commercial ionomers

PAP-TP-85 Membrane Stability

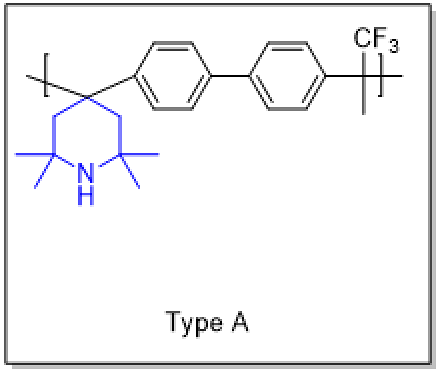


Time series of ^{1}H NMR spectra for oxidation stability test of AS-4 (left) and PAP-TP-85 (right)

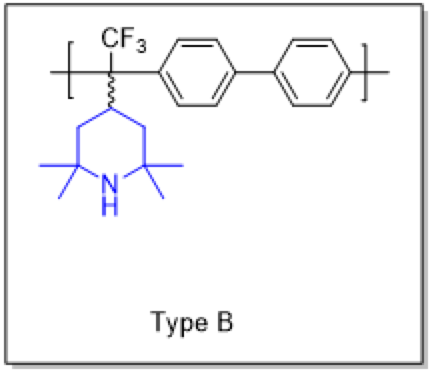
- The commercial ionomer AS-4 degraded in 5 min in KO_2/DMSO
- PAP-TP-85 survived longer than 120 min in KO_2/DMSO

✓ PAP-TP-85 is at least 24 times more stable than Tokuyama AS-4

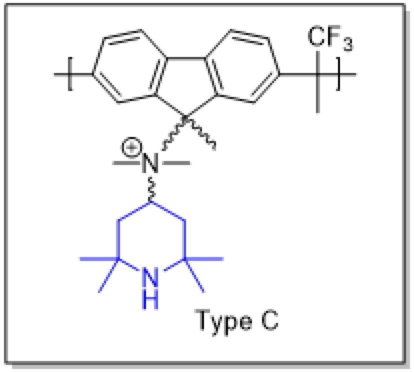
Next Generation of AEMs: Target Structures



Type A

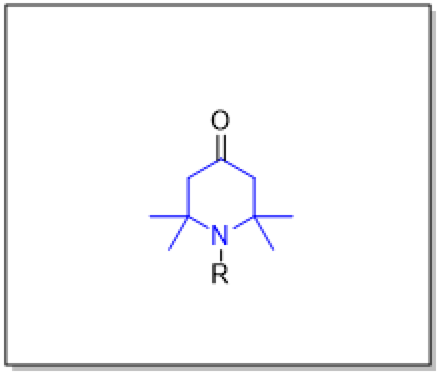


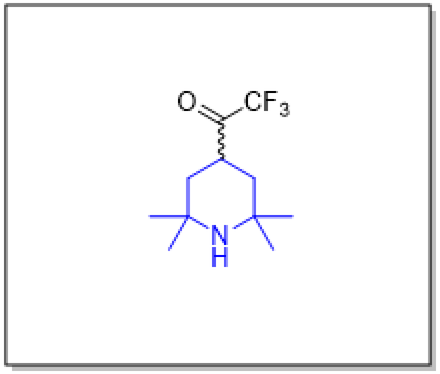
Type B

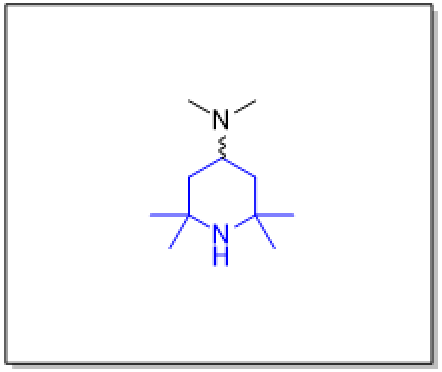


Type C

Corresponding amine monomer



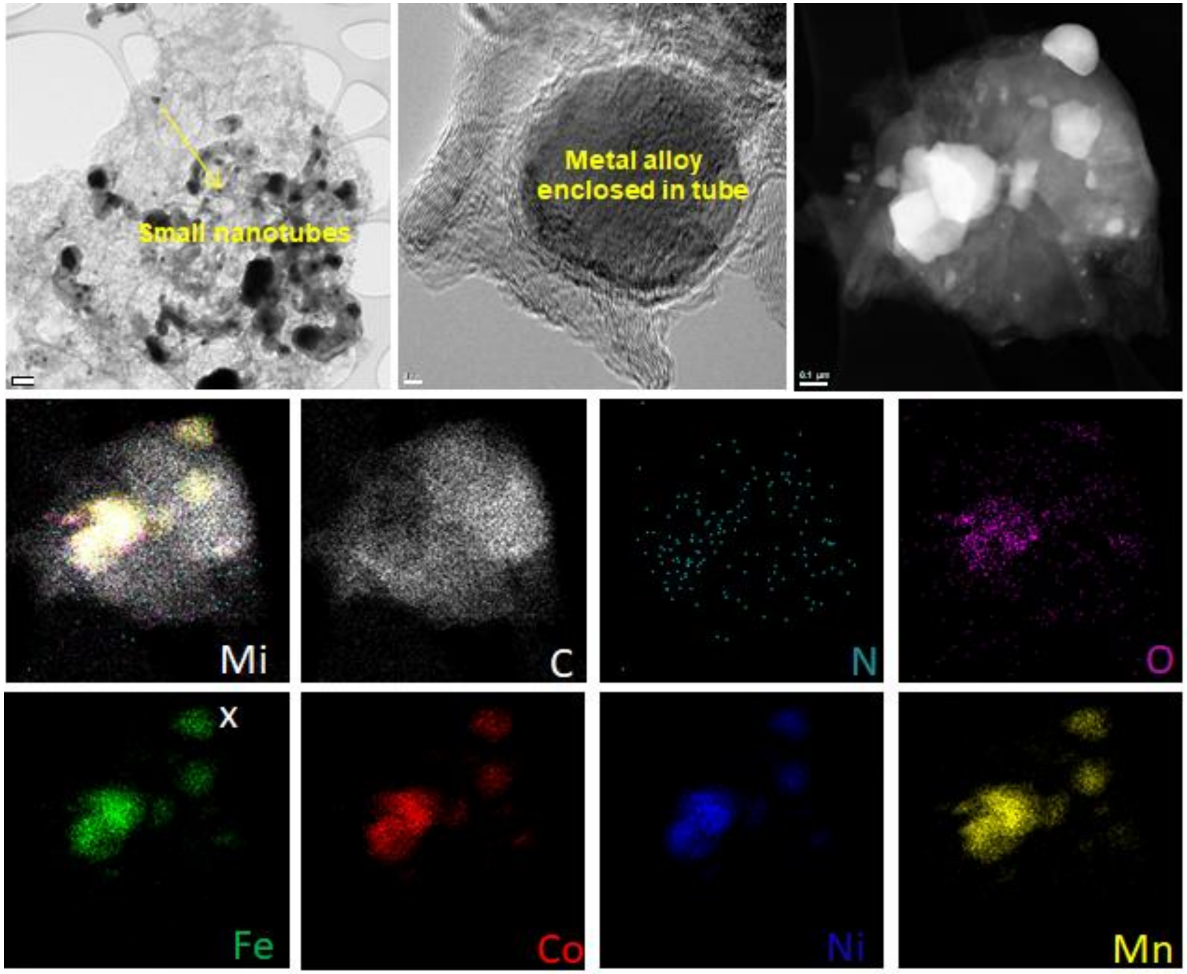




Accomplishment 2: Bifunctional O_2 Catalysts

- n Co-ZIF-8 (n=0, 0.2, 0.4, 0.6, 0.8, 1.0), where n is defined as the molar percentage of Co against total Zn and Co in the starting materials

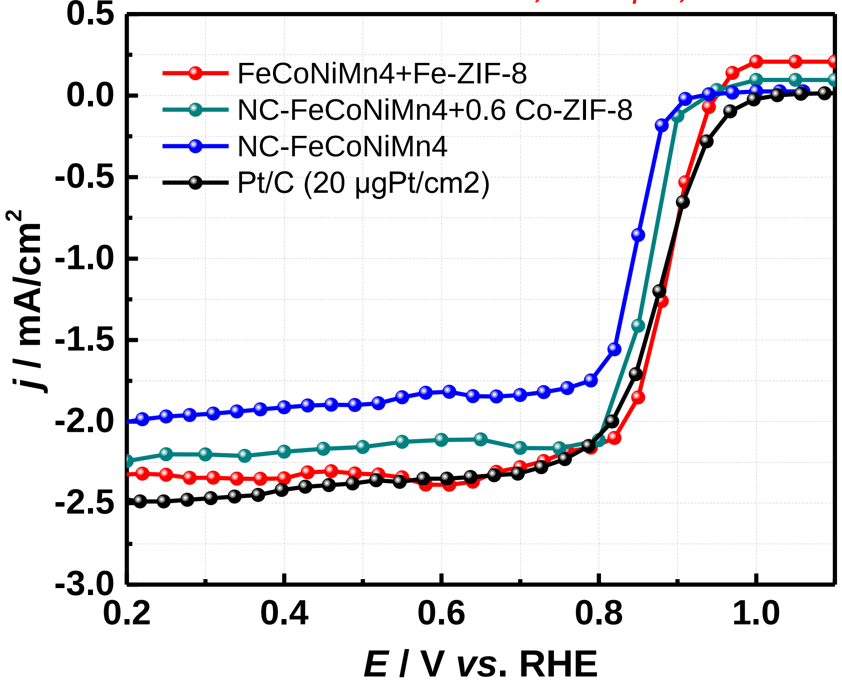
Novel Bifunctional O_2 Catalysts: TEM



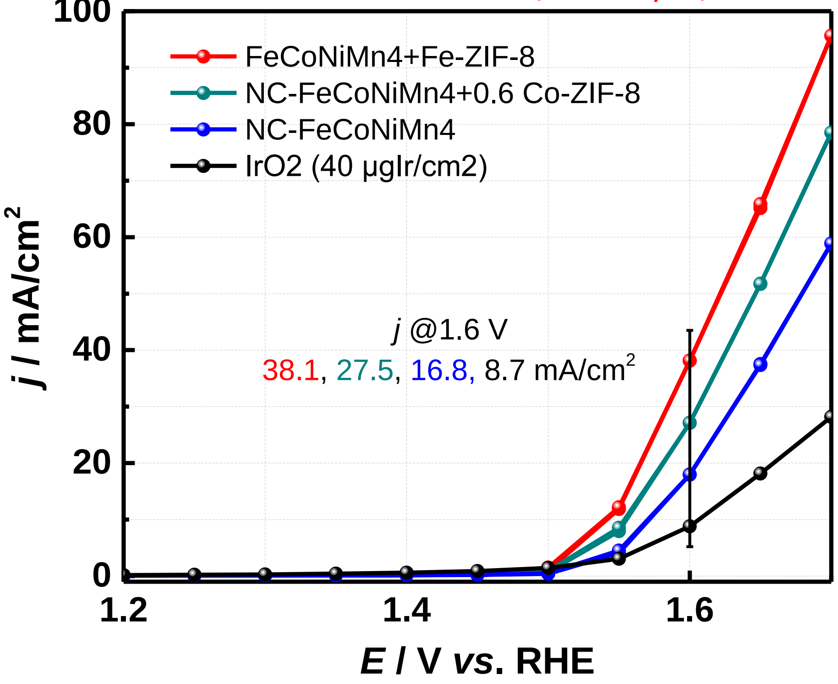
- Most of the metal particles are clearly enclosed by the carbon layers at the tip of the carbon tubes.
- Fe-ZIF-8 derived carbon (50 nm) can not be identified clearly due to low magnification.

Catalyst Activity

RDE tests in 1.0 M NaOH, 900 rpm, 25°C



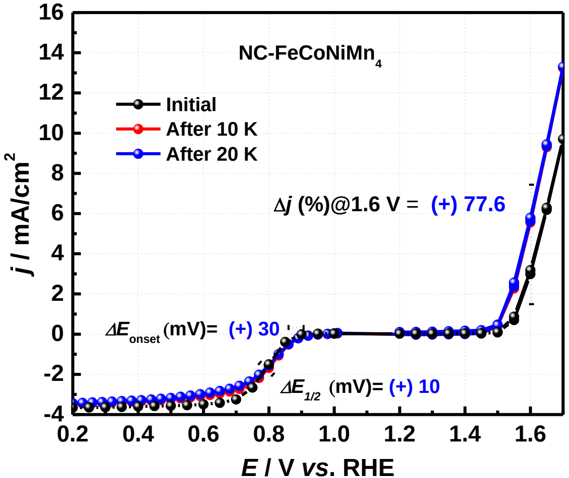
RDE tests in 1.0 M NaOH, 1600 rpm, 25°C

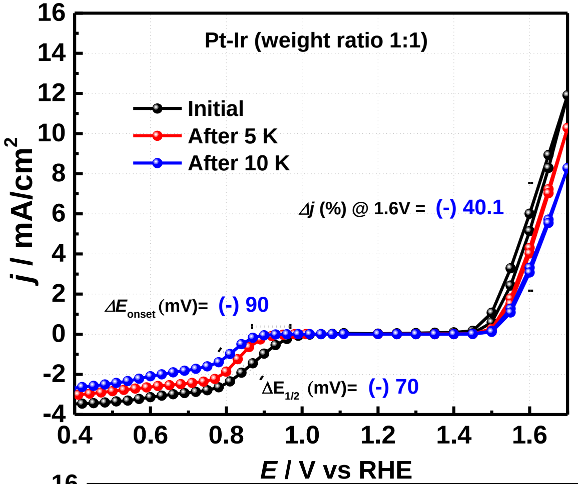


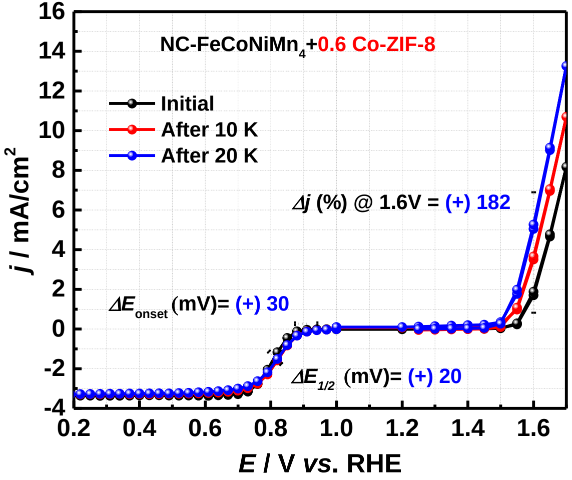
- Significant activity improvement for both ORR and OER was achieved on the new composite oxide/nanocarbon catalysts through tuning their morphology by adding Co- and Fe-ZIF-8-derived carbon.
- It is proved an effective strategy to integrate ZIF-derived carbon with FeCoNiMn-based graphene tube

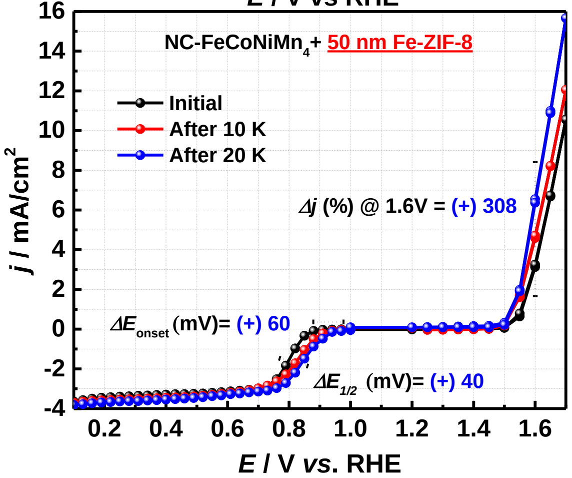
Catalyst Stability

Potential cycling from 0 to 1.9 V in 0.1 M NaOH, 500 mV/s, 25°C



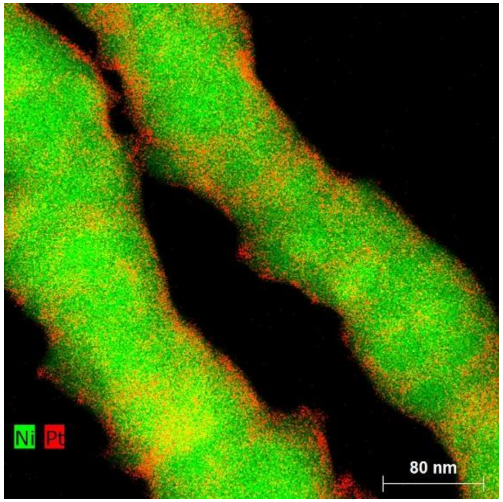


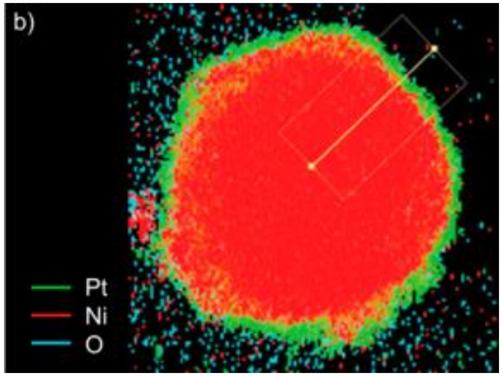




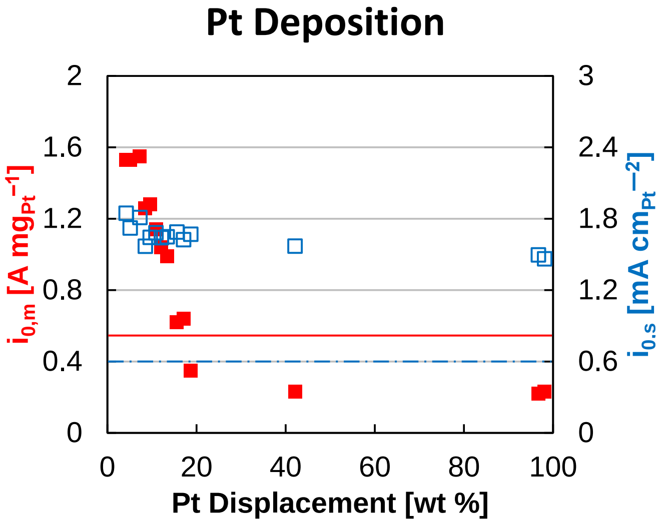
- Remarkable bifunctional ORR/OER stability is achieved in a wide potential window
- Fe-ZIF-8 derived catalysts show better stability than the Co-ZIF-8 derived catalysts.

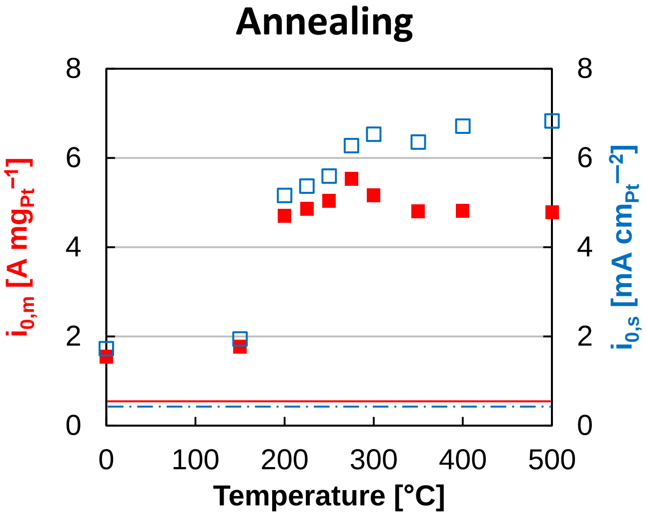
Accomplishment #3: H_2 Catalysts





Microscopy courtesy of Chilan Ngo, Svitlana Pylypenko, Colorado School of Mines


Pt Deposition

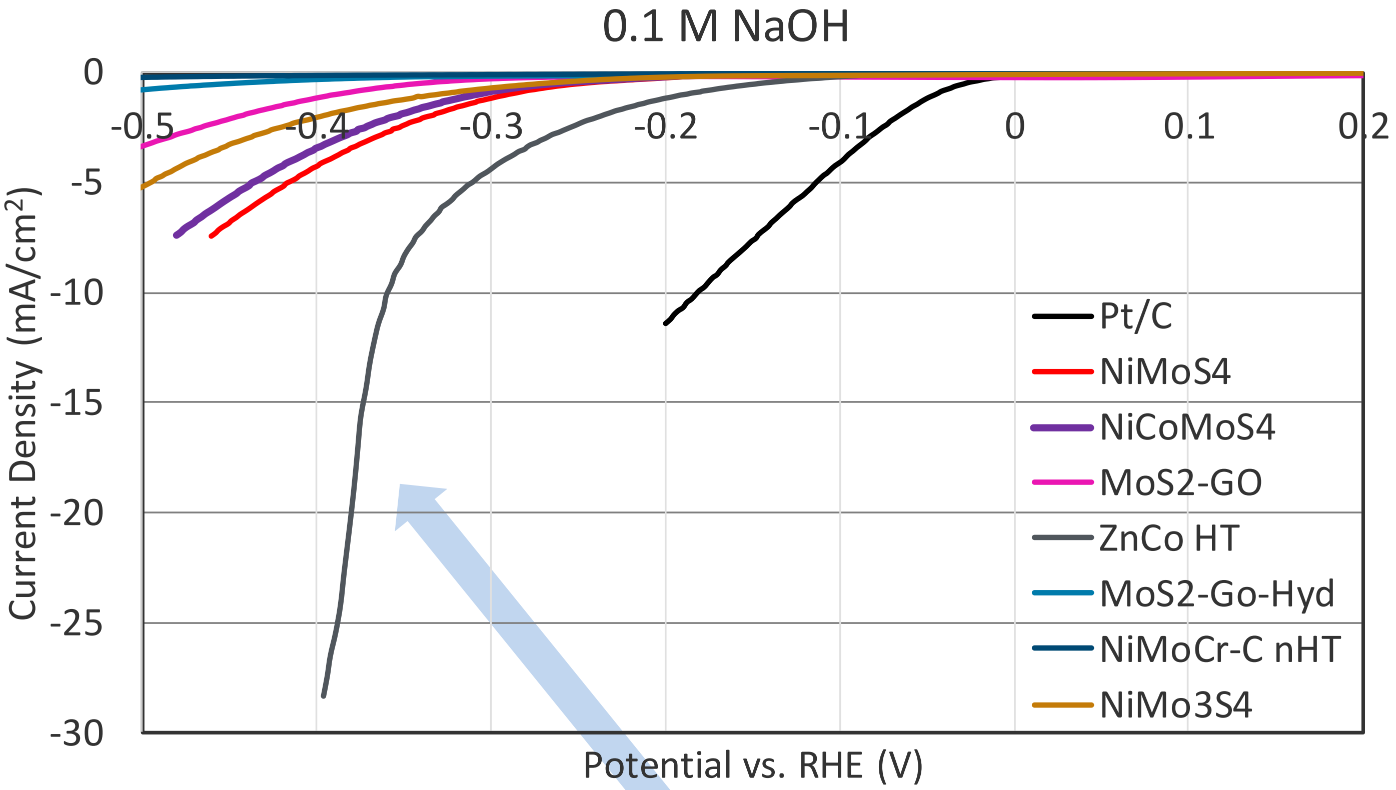

Annealing

Lower displacement levels improves ECA (90 $m^2\ g_{Pt}^{-1}$) due to thinner Pt layers, higher utilization

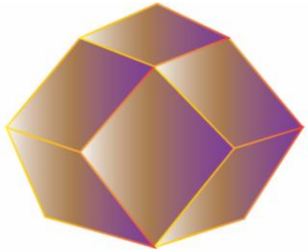
Hydrogen annealing

- Increasing lattice compression with higher annealing temperatures improved activity
- Likely due to lattice compression weakening Pt-H, Pt-OH binding

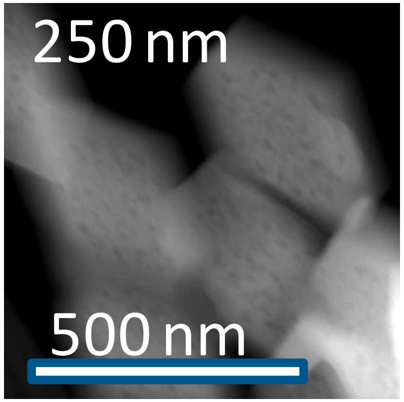
Non-PGM Options: RDE Performance



N$_2$ saturated 0.1 M NaOH used as electrolyte.
Glassy carbon as WE, Gold mesh as CE and Hg/HgO as RE. WE was rotated at 2500 rpm to remove gas bubbles.
Polycrystalline Pt was used to calibrate Hg/HgO prior each set of catalyst test.

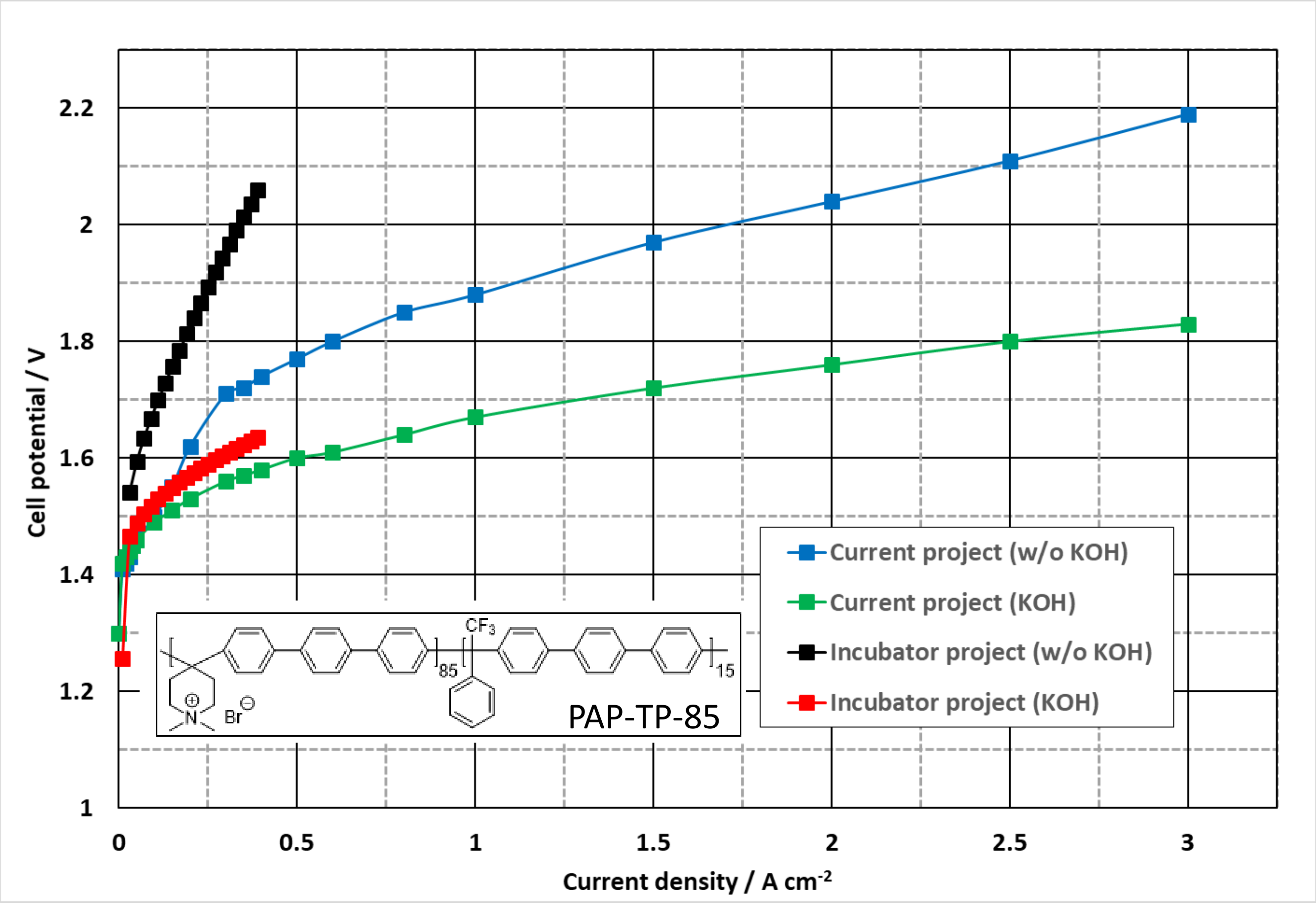

ZnCo ZIF

High surface area and porous framework of ZnCO ZIF manages gas bubbles in efficient manner



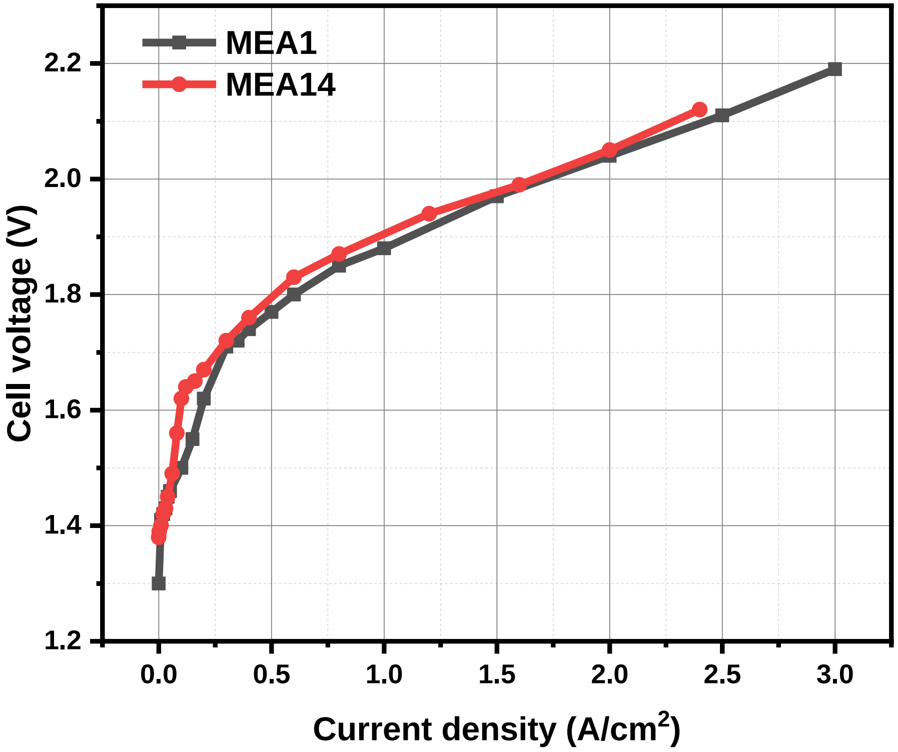
Accomplishment #4: AEM Electrolysis

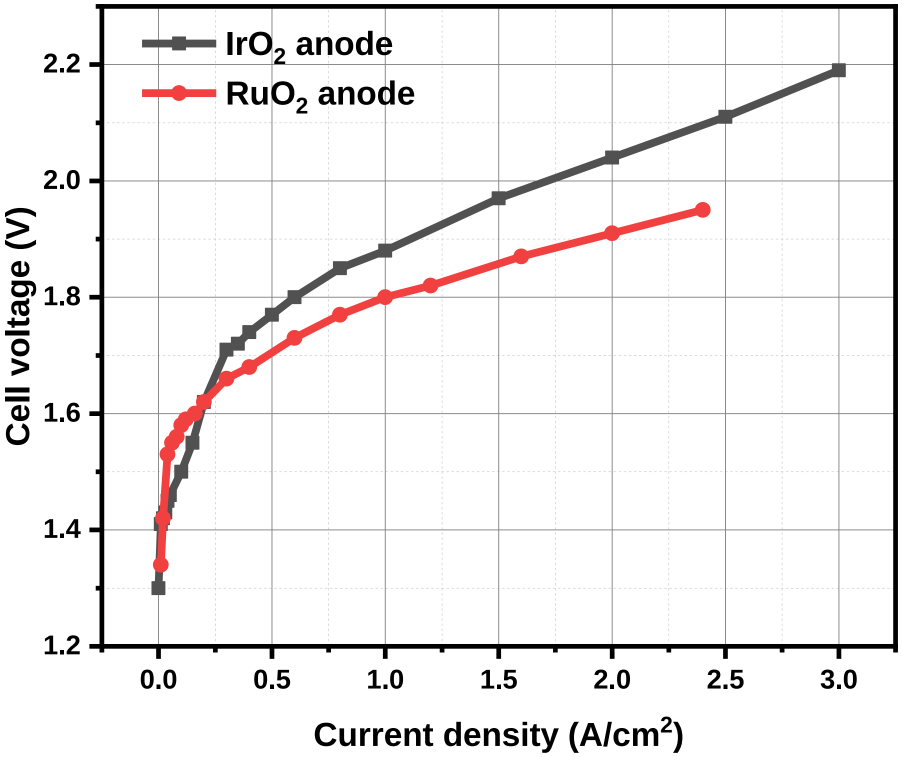
- Direct-spray MEA fabrication process developed at Giner in collaboration with UD
- Substantial improvement over previous AEM studies at Giner



UD AEMs enable substantial increase in electrolyzer performance without added OH

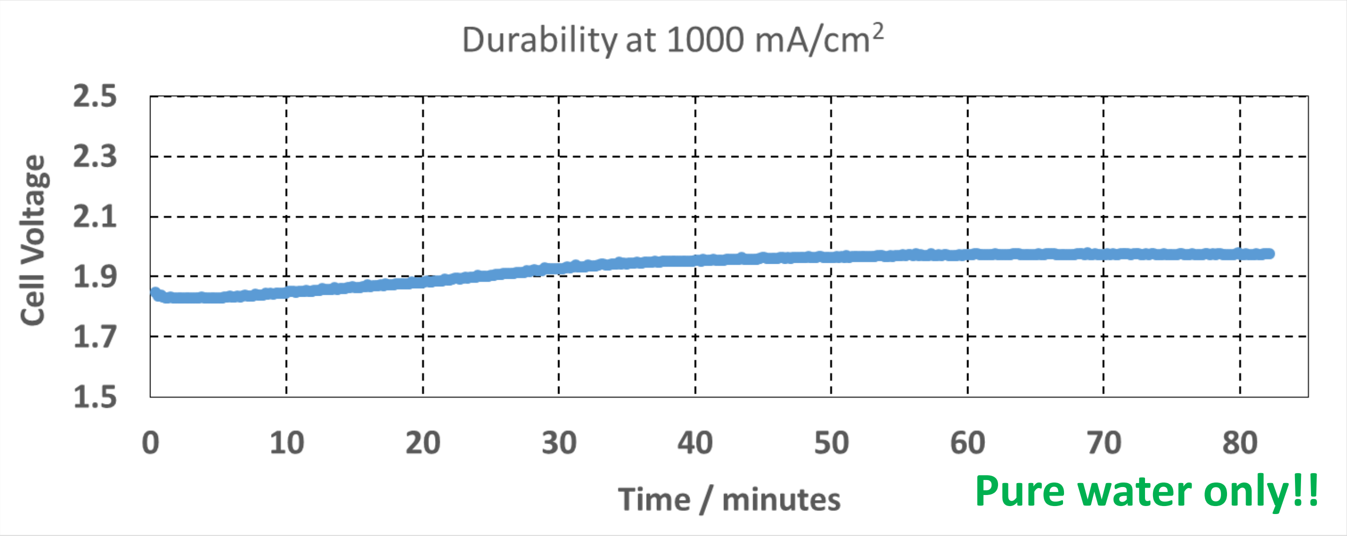
Accomplishment #4: AEM Electrolysis





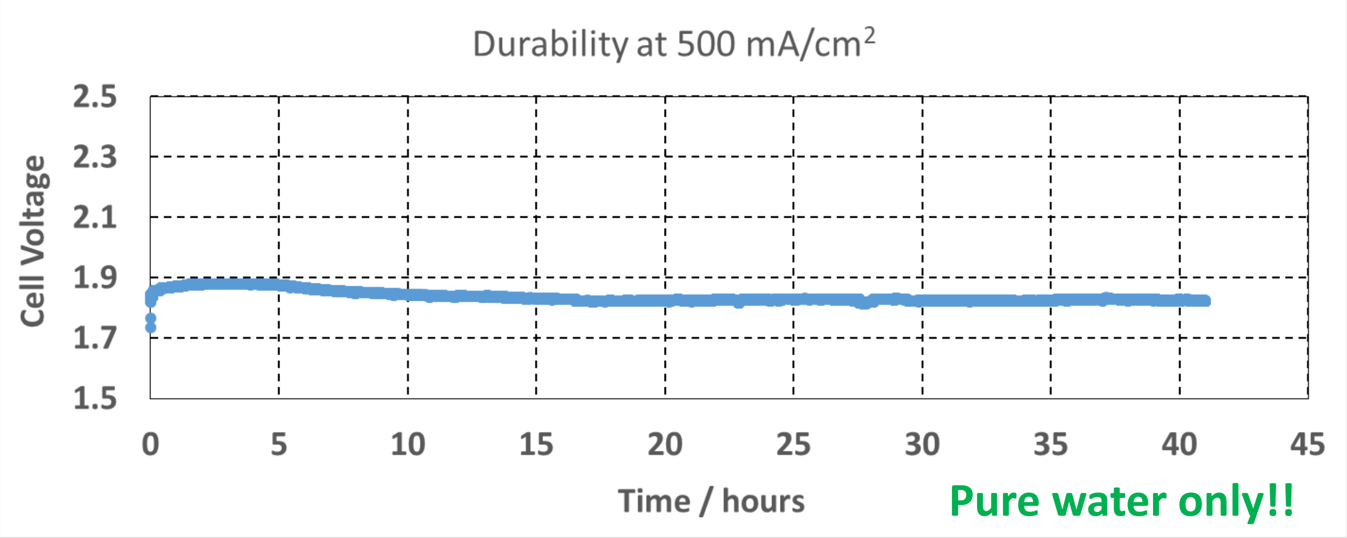
- **Consistent MEA-to-MEA repeatability**
- **Further performance boost with RuO_2 anode: approaching PEM**
- **No added salts to electrolyte moving forward**

Electrolyzer Durability



Pure water only!!

Short-term stability at high current density



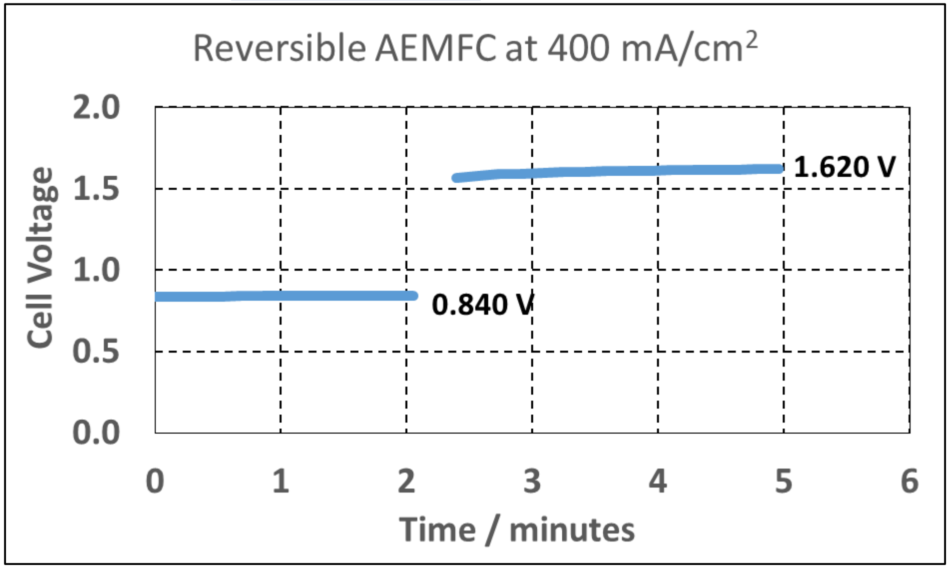
Pure water only!!

Stable performance for 40+ hours at 0.5 A/cm^2 with IrO_2 catalyst

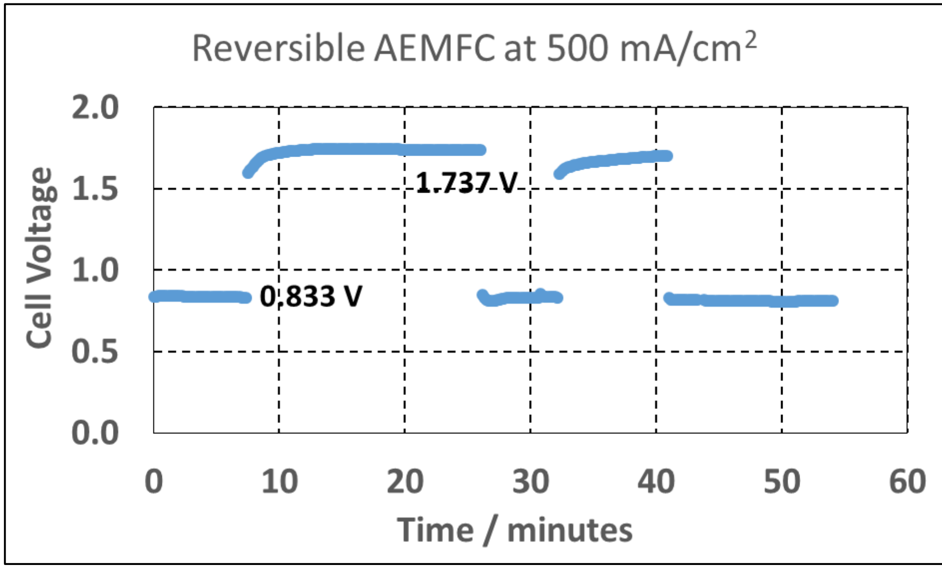
Accomplishment #5: Reversible AEMFC

Oxygen catalyst	Hydrogen Catalyst
IrO_2 / Pt (1:1)	PtRu/C

Pure Water Only!!



= 52% RTE @ 400 mA/cm²



= 48% RTE @ 500 mA/cm²

- High round trip efficiency seen at modest current densities
- Controlling dew points of feed gases critical for stable fuel cell operation
- Maintaining durability during reversible cycling presents substantial challenge

Responses to Previous Year Reviewers’ Comments

“It would be desirable to see some more focus on explaining the concerns about AEM oxidation within the reversible fuel cell concept.” “The reduction–oxidation (redox) reaction cycle and oxidation concerns in AEMs is a new idea, and the materials did not explain well why it is important.”

> We have addressed this in the approach section: previous AEM electrolyzer work at Giner has identified commercial ionomer stability under electrolyzer operating conditions as a critical weakness. Materials from UD have demonstrated remarkable oxidative stability, and this has translated to vastly improved electrolysis performance in the absence of added salt/hydroxide.

“There is little value in combining a fuel cell and an electrolyzer, that device is called a metal hydride battery…”

> The great advantage which this reviewer must appreciate is whereas batteries might reach a very low storage cost of \$100/kWh in the future, hydrogen storage can be accomplished today for below \$20/kWh in tanks, and below \$1/kWh when stored underground. It is then easy to see as we seek energy storage applications for larger and longer applications it will not be hard for regenerative fuel cells to be the lowest cost when competing for a storage cost of \$1/kWh vs \$100/kWh.

“The go/no-go milestone needs some more description. For example, it needs to be known if the reversible fuel cell will use caustic solvent and, if not, what voltage limit it will have, what the target temperature is, and how many cycles will be analyzed. Milestone 4.2 should also carefully define the degradation rate of <1%... “

> We have revised the SOPO to add clarification on the durability milestone. The intent of the go/no-go was to allow for the use of hydroxide, however in discussions with the DOE we decided to commit to pure water for the remainder of the program. This has the added benefit of simplifying test station balance of plant.

Collaboration & Coordination

Giner (prime)

- **PI: Dr. Hui Xu**
- Project management / reporting
- Catalyst selection
- MEA fabrication
- Device testing
- Economic analysis

Delaware

- **PI: Dr. Yushan Yan**
- Novel AEM membrane & ionomer development
- Membrane characterization (IEC, conductivity, mechanical properties)

Buffalo

- **PI: Dr. Gang Wu**
- ORR/OER catalyst development and synthesis

NREL

- **PI: Dr. Shaun Alia**
- EPFE based ionomer and membrane
- HER/HOR bifunctional catalysts

Future Work

- ❑ Start testing devices with PGM-free catalysts
- ❑ Investigate reinforced membranes to address reversible durability concerns
  - UD has developed some PTFE-reinforced membranes; will also explore separately at Giner
- ❑ Study and improve electrode design
  - Microscopy studies currently underway
  - Electrode design critical to optimize water management and prevent catalyst, ionomer washout during electrolysis and reversible operation

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

Summary

- Novel AEM materials from UD have shown remarkable chemical stability: 24x increase in oxidative stability compared to commercial ionomer
- Highly active, stable metal oxide/nanocarbon composite bifunctional O_2 catalysts have been developed at UB, and several low-PGM and PGM free H_2 catalysts are being studied at NREL
- At Giner, record-breaking AEM electrolyzer performance of 1.8V at 1000 mA/cm^2 has been achieved in **pure water** with no added OH- or other salts
- We have demonstrated reversible alkaline MEAs with ~50% round trip efficiency at 500 mA/cm^2 in both fuel cell and electrolyzer modes in **pure water**

Acknowledgements

- Financial support from DOE EERE Hydrogen and Fuel Cell Technologies Office (HFTO) under Award # DE-EE0008438
- DOE Program Manager

  \- Dr. David Peterson
- **University of Delaware**: Yushan Yan, Wenjuan Shi, Santiago Rojas-Carbonell, Brian Setzler
- **University of Buffalo**: Gang Wu, Huanhuan Wang
- **NREL**: Shaun Alia, Brian Pivovar
- **Giner**: Zach Green, Zach Lynn, Bongjin Seo, Derek Strasser, Teddy Wang, Fan Yang