



# HydroGEN: Low-Temperature Electrolysis (LTE) and LTE/Hybrid Supernode

G. Bender, H.N. Dinh

Presenter: Guido Bender, NREL

Date: 5/20/2020

Venue: 2020 DOE Annual Merit Review

Project ID # P148A

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

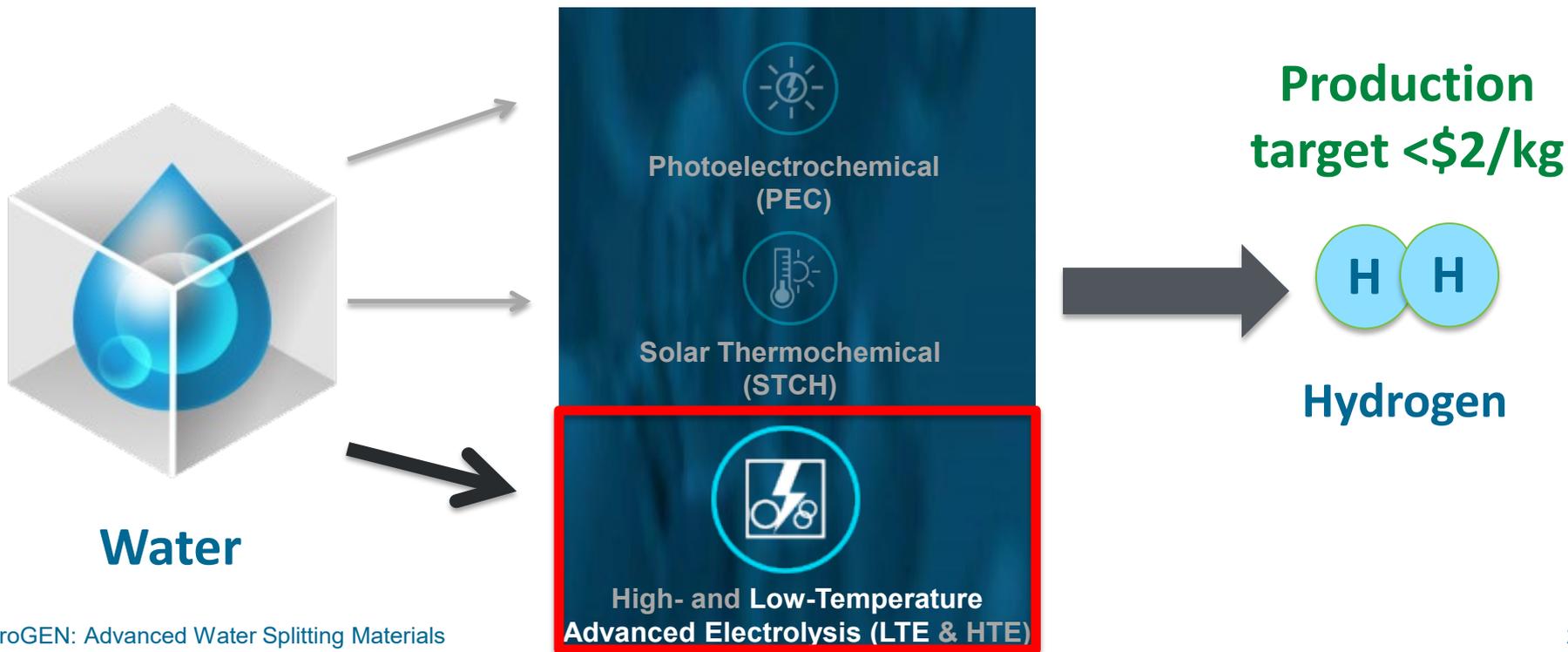


# Advanced Water-Splitting Materials (AWSM) Relevance, Overall Objective, and Impact

## AWSM Consortium 6 Core Labs:



Accelerating R&D of innovative materials critical to advanced water splitting technologies for clean, sustainable & low cost H<sub>2</sub> production, including:





# Relevance – Impact on LTE Technology

## PEM

- **Gas Crossover**
- **Membranes**
- **Catalyst Materials**
- **Catalyst Loading**
- **PTL Materials**

## AEM

- **Membranes**
- **Catalyst**
- **Ionomer**
- **Electrolyte feed required?**
- **BOP Materials**

## Common Barriers

- **Material Integration**
- **Material Cost**
- **Understanding Interfaces and Interactions**



# Approach – HydroGEN EMN

**DOE**

**EMN**

**HydroGEN**

**Core labs  
capability  
nodes**

**Data Hub**

**FOA Proposal  
Process**

- **Proposal calls out capability nodes**
- **Awarded projects get access to nodes**

<https://www.h2awsm.org/capabilities>



# Approach – HydroGEN EMN

## Low Temperature Electrolysis (LTE)

- Proton Exchange Membrane (PEM)
- Alkaline Exchange Membrane (AEM)

## Barriers

- Cost
- Efficiency
- Durability

## LTE Node Labs



Support  
through:



Personnel  
Equipment  
Expertise  
Capability  
Materials  
Data

## LTE FOA Projects



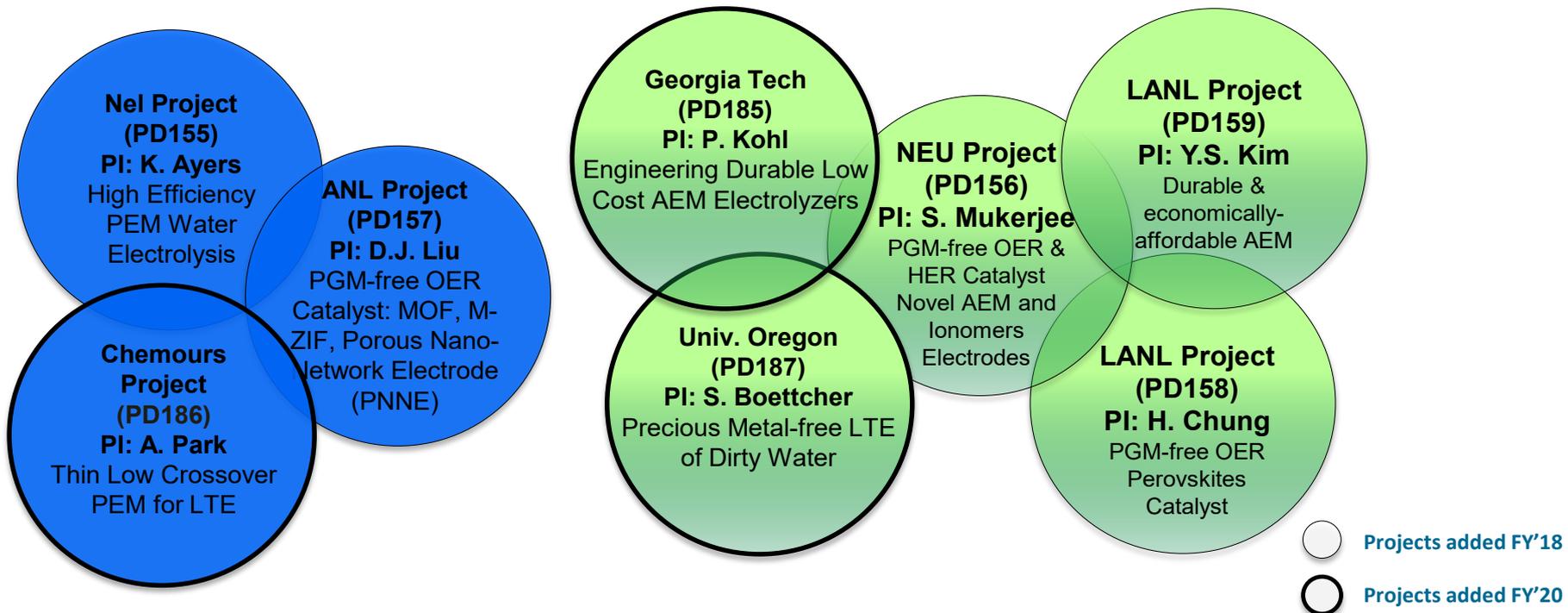
Northeastern University  
*Center for Renewable Energy Technology*



UNIVERSITY OF  
OREGON



# Accomplishments and Progress: 3x Seedling Projects Added to LTE Activities



<b>Supernodes</b>	A. Weber	Understanding OER Across pH Ranges
	T. Ogitsu	Through Multiscale, Multi-Theory Modeling
	H. Dinh	Linking LTE/Hybrid Materials to Electrode
	B. Pivovar	Properties to Performance

Discussed in PEC, P148A

Discussed here in LTE, P148C

**PEM: Understanding and improving materials**

**AEM: Developing and understanding materials**



# Accomplishments and Progress: Node Utilization for Project Support



**49 nodes requests  
for LTE**



**19 nodes used by  
LTE projects**



## Node Classification

**27x Characterization**

**10x Computation**

**7x Material Synthesis**

**5x Process and  
Manufacturing  
Scale-Up**





# Collaboration and Coordination - Node Utilization

## FY'20 Projects

Lab	Node	LTE Super	Chem	UO	GT	NeI	ANL	NEU	LANL 1	LANL 2
NREL	Data Hub									
LLNL	Computational Materials Diagnostics and Optimization						✓			
LBNL	DFT and Ab Initio Calculations						✓		✓	
LBNL	Multiscale Modeling	✓	✓		✓	✓		✓		✓
SNL	LAMMPS							✓		
NREL	Novel Membrane Fabrication	✓		✓		✓		✓		
SNL	Separators for Hydrogen Production			✓					✓	✓
NREL	Multi-Comp. Ink Development, High-Throughput Fabrication, & Scaling	✓			✓	✓	✓	✓		

**Computation**

**Processing & Scale Up**

**Material Synthesis**





# Collaboration and Coordination - Node Utilization

Lab	Node	LTE Super	FY'20 Projects							
			Chem	UO	GT	NeI	ANL	NEU	LANL 1	LANL 2
SNL	Advanced Electron Microscopy						✓			
NREL	Catalyst Synthesis, Ex situ Characterization & Standardization	✓				✓	✓			
LBNL	Ionomer Characterization and Understanding	✓	✓	✓		✓		✓		✓
NREL	In Situ Testing Capabilities	✓	✓	✓	✓	✓		✓	✓	✓
LBNL	Understanding Inks & Ionomer Disp.	✓		✓						
SNL	Near Ambient Pressure E-XPS								✓	
NREL	Surface Analysis Cluster Tool						✓		✓	
LBNL	Probing & Mitigating Corrosion					✓				
LBNL	PEC In Situ Testing using X-Rays								✓	
LBNL	Water Splitting Device Testing									✓
SRNL	Fabrication & Characterization of Electro-catalyst & Components for H2 Production	✓								

**Characterization**

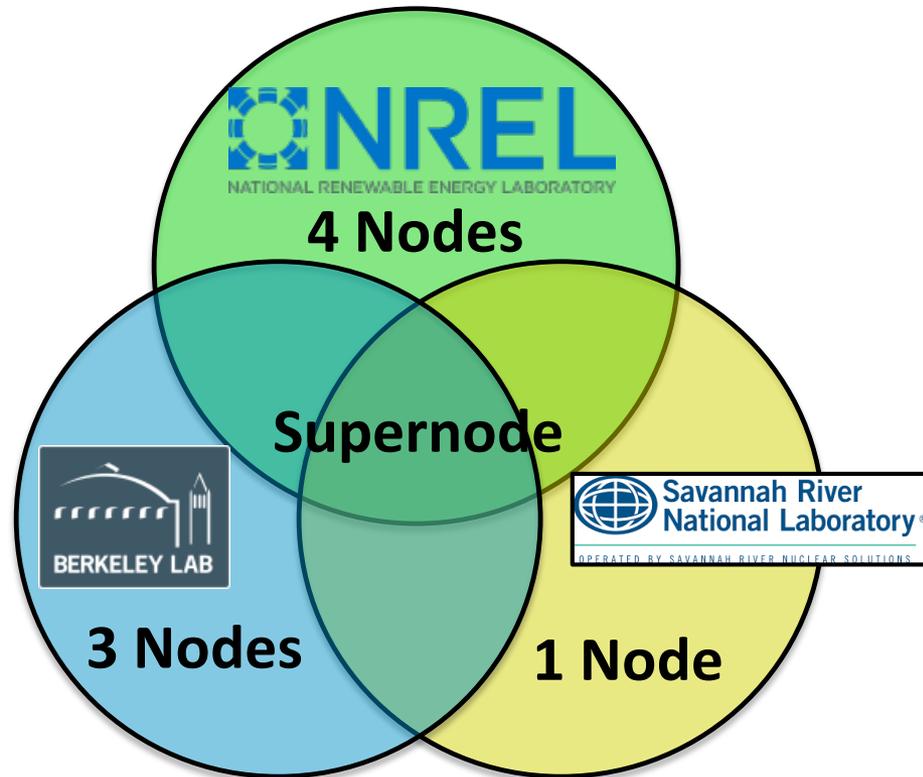


# Project Accomplishment LTE Supernode



# Supernode – Accelerate Science through Collaboration

## LTE Supernode



## Supernodes Objectives:

- Combine/integrate nodes to demonstrate value when connected (sum greater than combination of individual parts)
- Increase collaboration across core labs
- Provide core research for EMN labs, beyond just project support
- Phase 1 measurable objective: Confirm that ex-situ characterization approaches can be validated for their applicability to device performance and durability

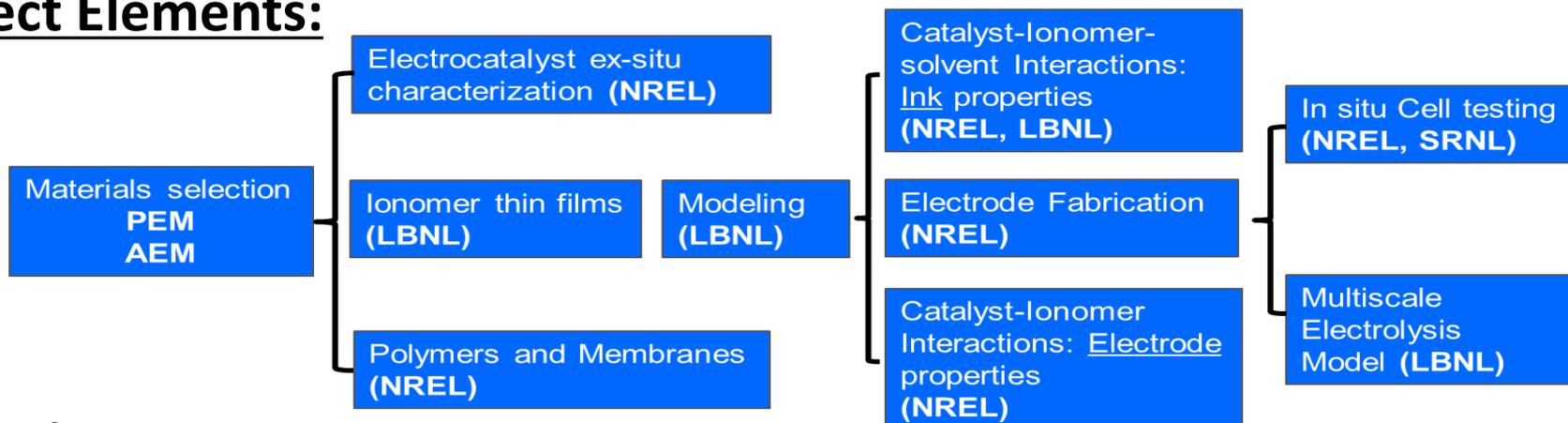


## Supernode Goals

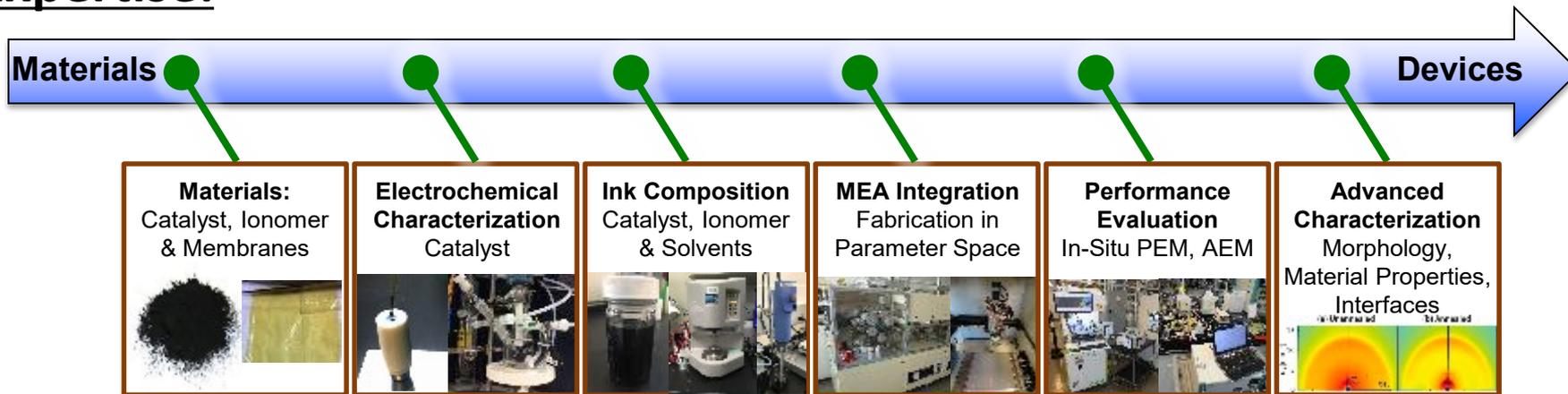


**Goals:** Create true understanding between ex-situ and in-situ performance. Identify how material properties are linked to electrode properties and how these are linked to electrolyzer performance.

### Project Elements:



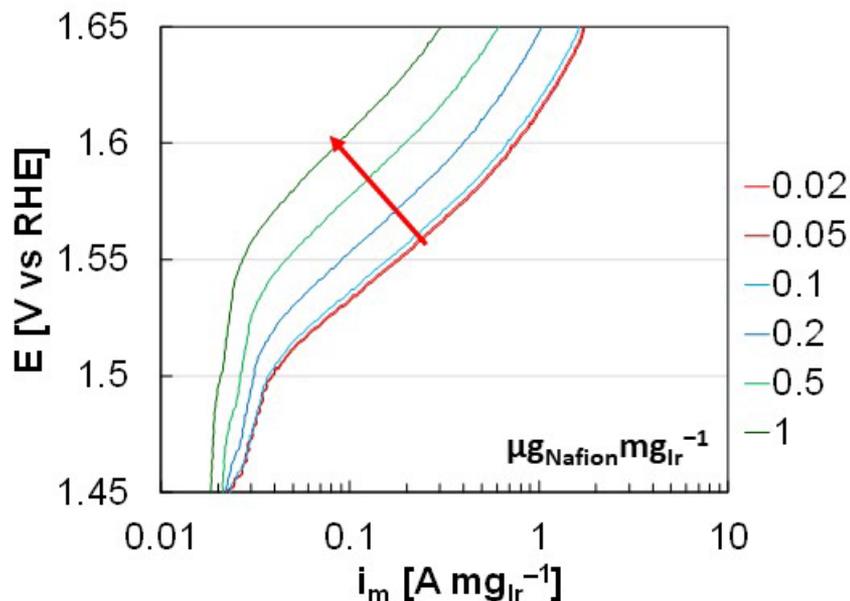
### Expertise:



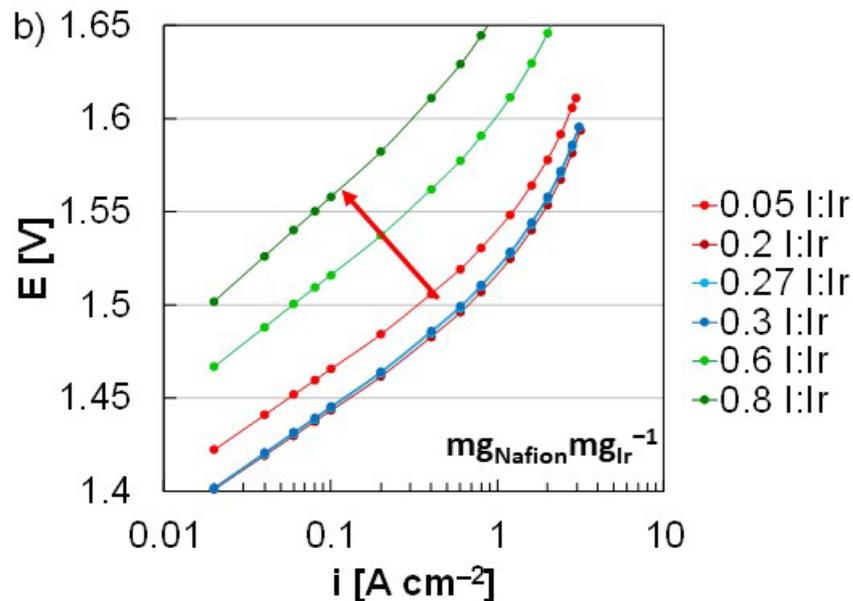


# Supernode Accomplishments: RDE/MEA Correlation

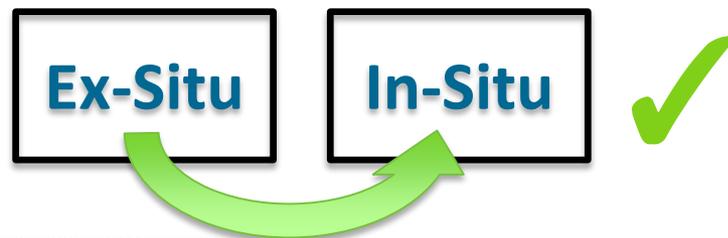
### RDE Ex-Situ



### MEA In-Situ



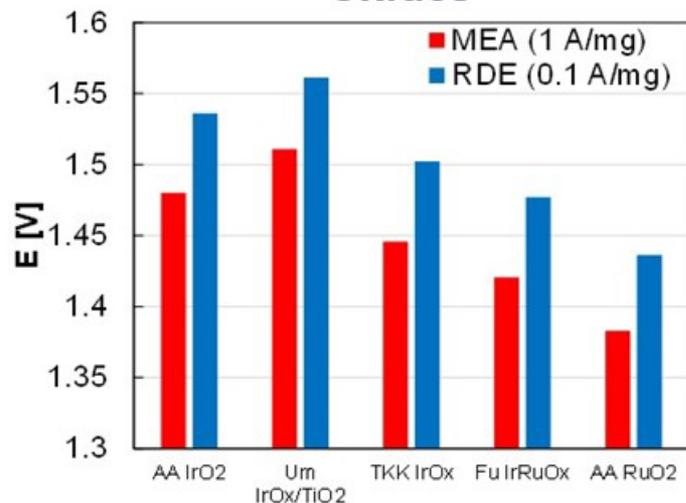
- **Correlation between RDE and MEA systems confirmed**
- **Same trend in RDE observed in MEA for effects of:**
  - **Catalyst loading**
  - **Ionomer content**
  - **Catalyst used**



S.M. Alia, G.C. Anderson, *J. Electrochem. Soc.*, **2019**, 166(4), F282-F294. DOI:10.1149/2.0731904jes

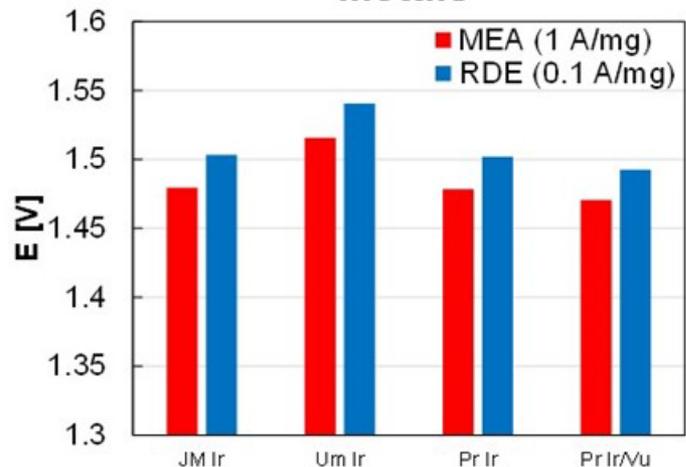
S. M. Alia, S. Stariha and R. L. Borup, *J. Electrochem. Soc.*, **2019**, 166(15), F1164. DOI: 10.1149/2.0231915jes

## Oxides

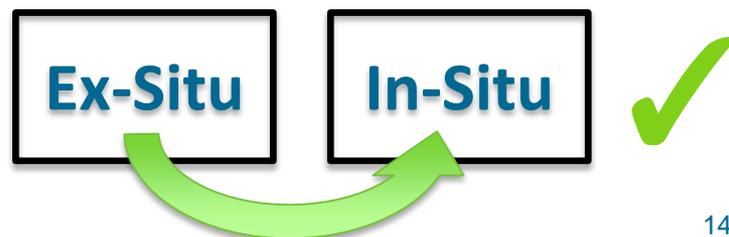


		$E^{MEA}$ [V]	$\Delta E$ [mV]	$E^{RDE}$ [V]	$\Delta E$ [mV]	$\Delta E$ [%]
Alfa Aesar	IrO <sub>2</sub>	1.480	–	1.536	–	–
Umicore	IrO <sub>x</sub> /TiO <sub>2</sub>	1.511	30.5	1.561	25.4	-16.7
TKK	IrO <sub>x</sub>	1.446	-34.5	1.502	-33.6	-2.6
Furuya	IrRuO <sub>x</sub>	1.421	-59.6	1.477	-58.8	-1.3
Alfa Aesar	RuO <sub>2</sub>	1.383	-97.4	1.436	-99.5	2.2
Johnson Matthey	Ir	1.480	–	1.503	–	–
Umicore	Ir	1.516	36.0	1.541	37.4	3.9
Premetek	Ir	1.479	-1.1	1.502	-1.2	9.1
Premetek	Ir/Vu	1.471	-9.1	1.493	-10.6	16.5

## Metals



LTE/Hybrid Supernode GNG: Demonstrate that the catalyst performance (overpotential in the kinetic region) measured via ex-situ RDE (at 0.1 A/mg) can be linked to in-situ MEA single cell performance (overpotential at 1 A/mg) within  $\pm 20\%$  for 5 commercial catalysts. This success will demonstrate that **ex-situ RDE characterization**, which is simpler and quicker than in-situ MEA testing, can be relevant and a good predictor of catalyst performance in the device. As a result, the development of electrolysis material components can be accelerated.

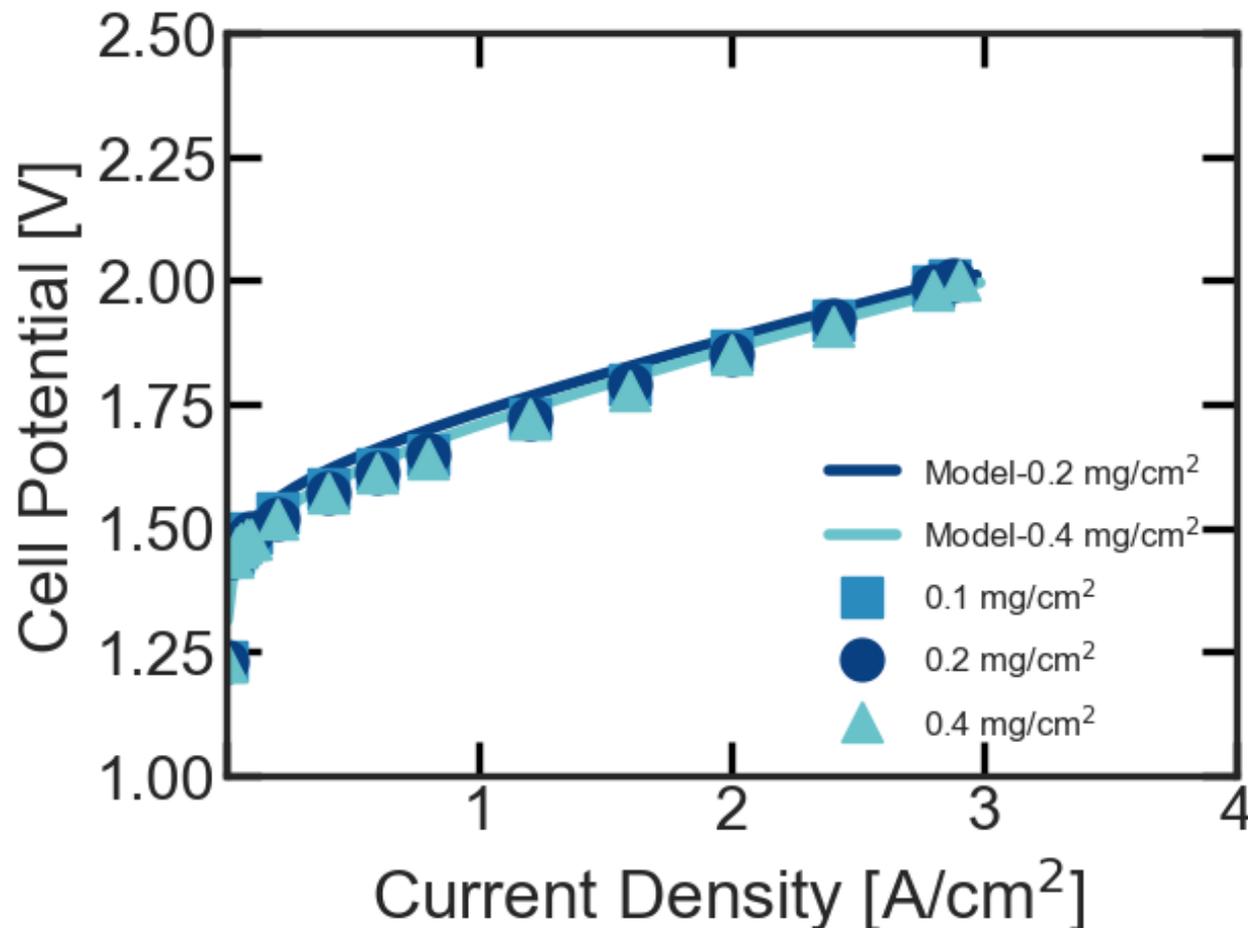


S.M. Alia, M.-A. Ha, G.C. Anderson, C. Ngo, S. Pylypenko, R.E. Larsen, *J. Electrochem. Soc.*, **2019**, 166(15), F1243-F1252. DOI:10.1149/2.0771915jes

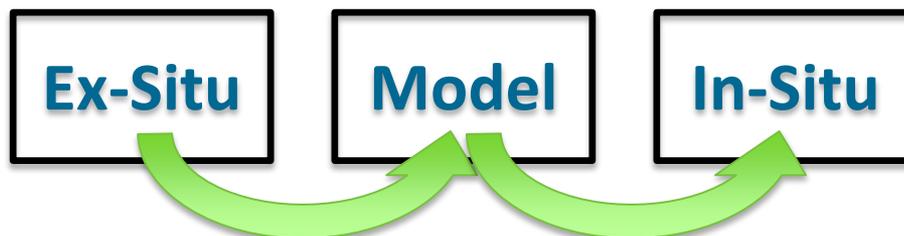


# Supernode Accomplishments: Multiscale Modeling

## Agrees with Experimental Data

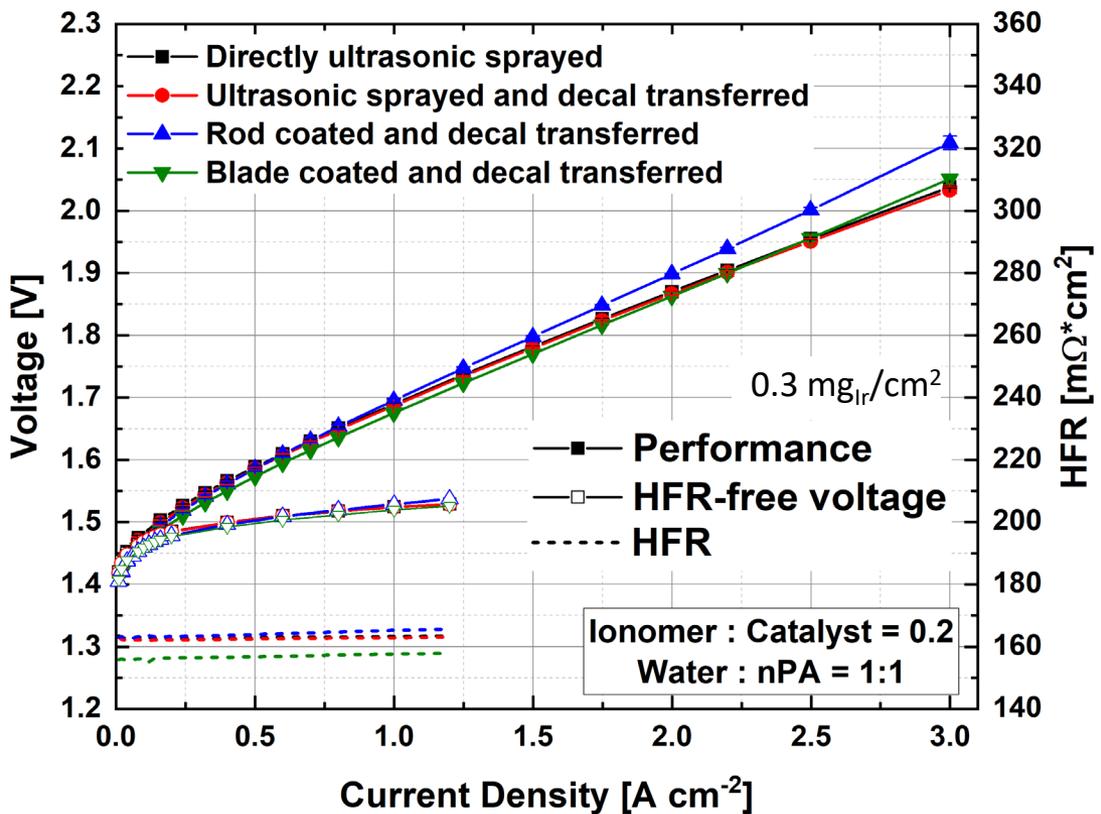


- Kinetic results determined with *ex-situ* RDE were used as inputs into cell model
- Modeling results show good agreement with experimental *in-situ* results
- Minimal loading effect also reproduced by model



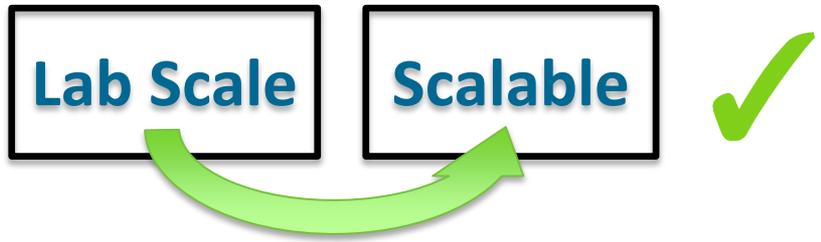


# Supernode Accomplishments: Doctor Blade and Mayer Rod Comparisons



- Demonstrated a wide range of loading possible using scalable coating methods
- Decal transfer does not limit performance compared to directly sprayed electrodes
- Doctor blade coated electrode performs better than rod coated
- **Scalable coating methods (doctor blade) show comparable performance to lab-scale coatings (ultrasonic spray)**

- Ionomer : catalyst ratio from 0.1 to 0.3 did not significantly impact performance for blade- or rod-coated methods.
- Ink composition found to be less impactful at higher loading. Thicker catalyst layers may mask nonuniformities.

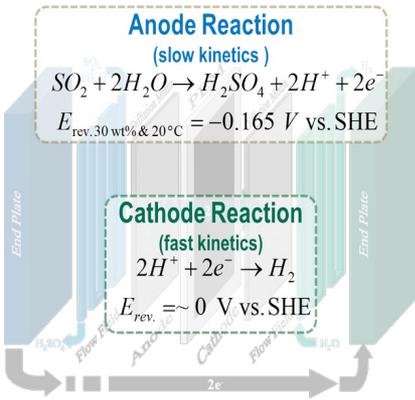




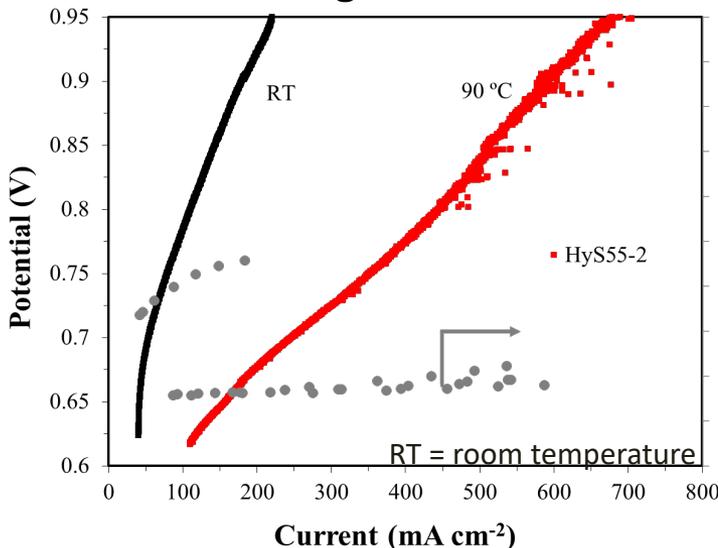
# Supernode Accomplishments: Hybrid Cycle

## Correlating Ex- & In-situ Testing

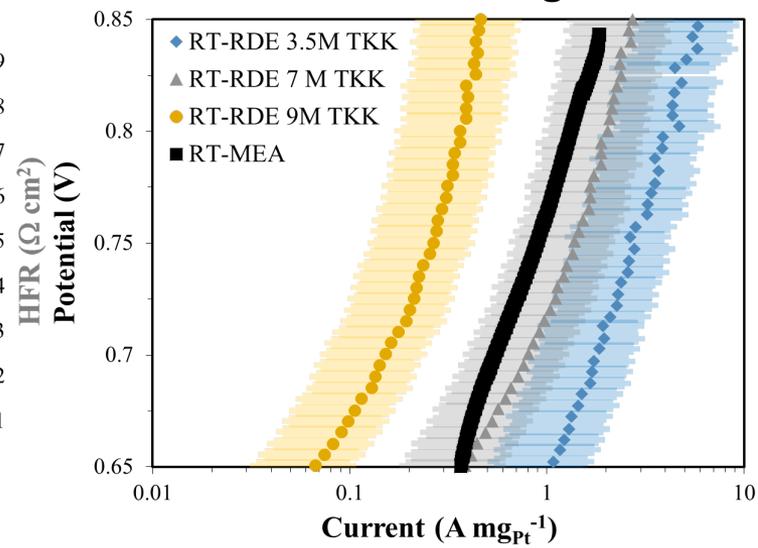
### Hybrid Cycle



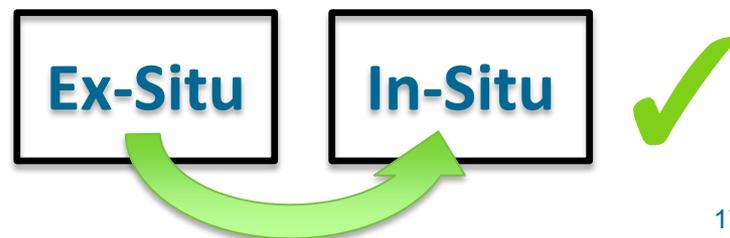
### MEA testing



### RDE vs MEA testing



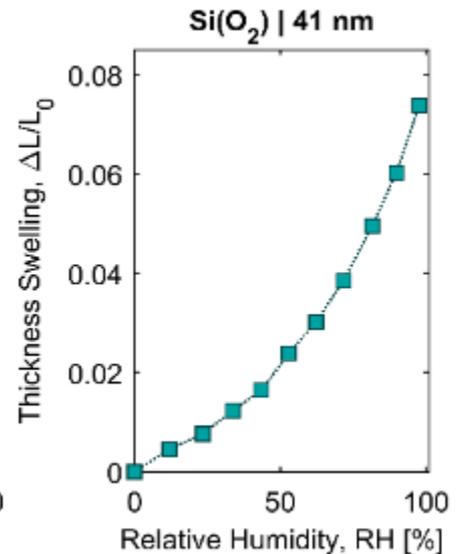
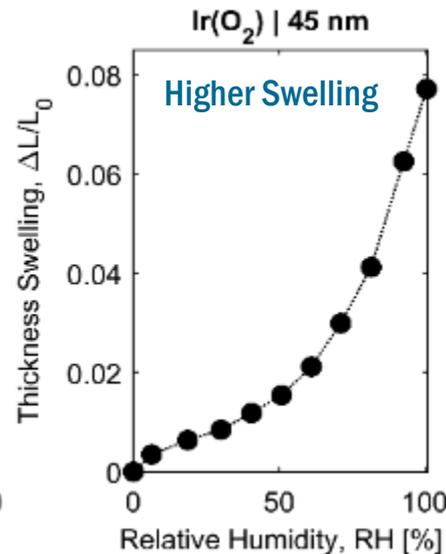
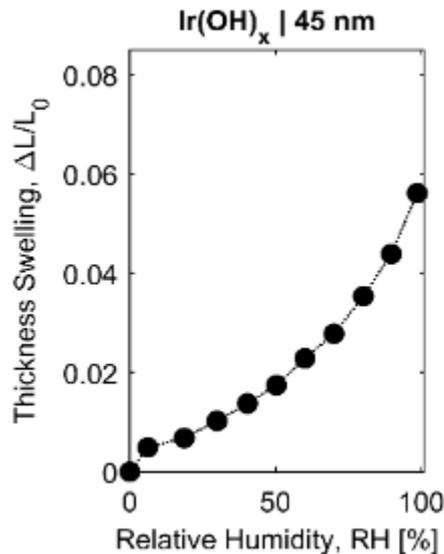
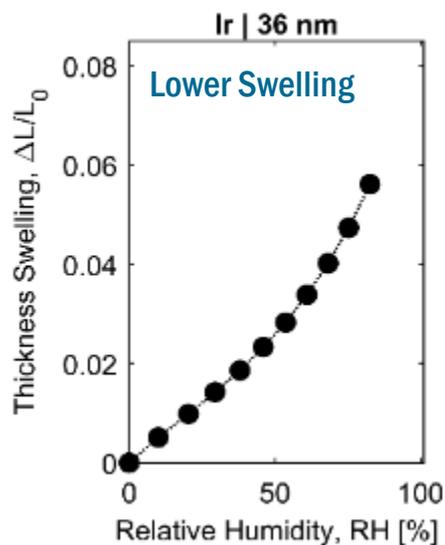
- Met Go/No Go milestone criteria of 50 % agreement between RDE and MEA testing (indicated by shaded area)
- Good agreement between in-situ and ex-situ measurements at acid concentration of 7 M
- Performance sensitivity to coating method and catalyst ink formulation is similar to that observed in fuel cells, but different from LTE
- Sensitivities differ between gas fed and liquid fed systems





# Supernode Accomplishments: Thin Film Morphology: GISAXS

- **Swelling behavior** of 40 nm Nafion film on substrates studied
- $\text{Si}(\text{O}_2) \approx \text{Ir}(\text{O}_2)$  [Bulk Oxide] >  $\text{Ir}(\text{OH})$  [functionalized]  $\gtrsim$   $\text{Ir}$  [Metal]
  - Metal oxide has lower swelling but comparable structure
  - Functionalized OH lower swelling but no phase-separated structure
  - $\text{Ir}(\text{O}_2)$  is most similar to Si, both structurally and hydration wise





# Project Accomplishment Summary Slides



# Example Project Accomplishment Slide



Rensselaer

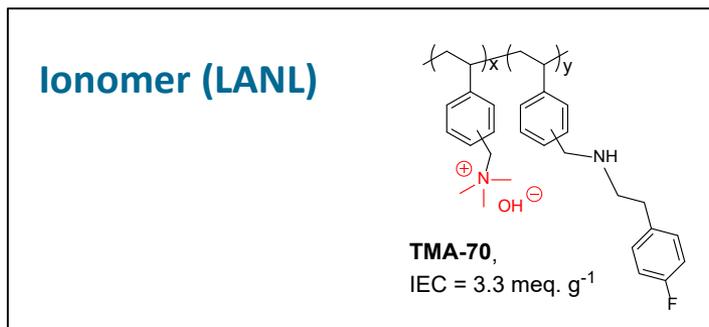
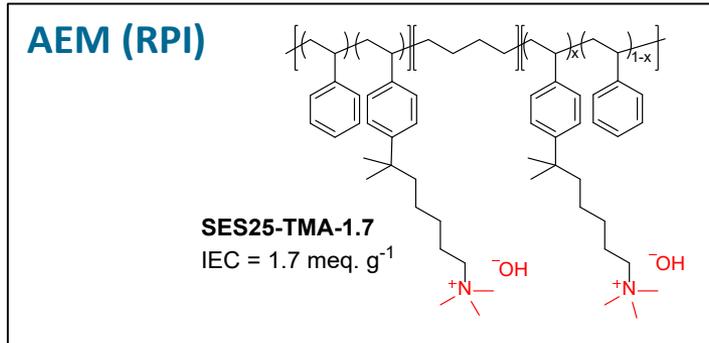
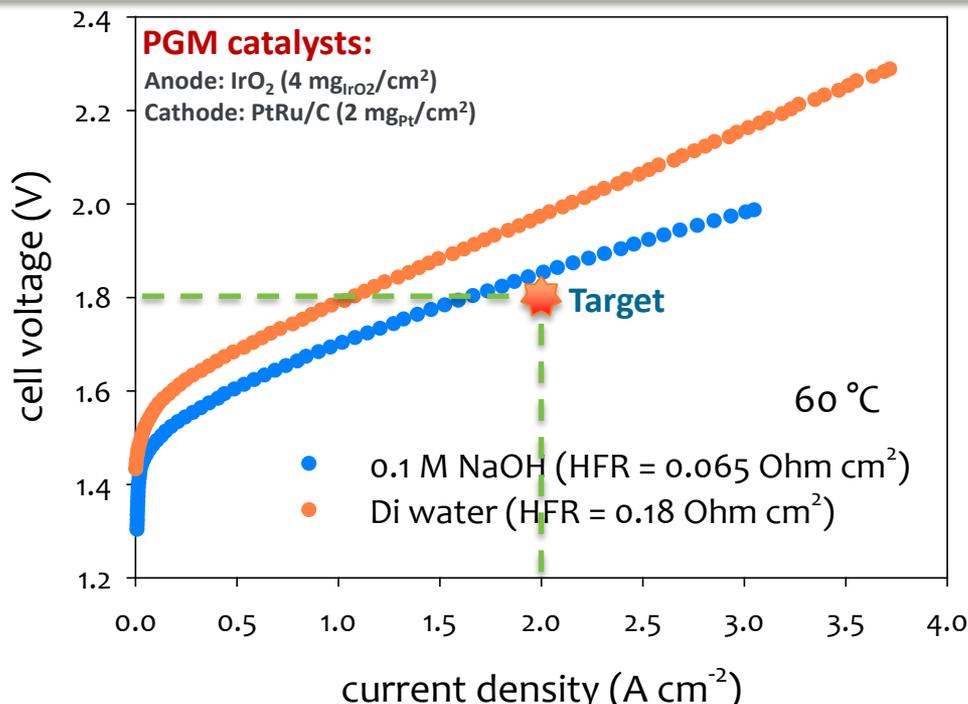


5 Nodes

## Scalable Elastomeric Membranes for Alkaline Water Electrolysis

**Project Goal:** Preparing durable and economically-affordable alkaline hydroxide conducting SES materials and demonstrating the high performance and durability in AEM-based water electrolysis

**Highlight:** The project team developed polystyrene based alkaline polymers that approach the 2020 target performance (2 A/cm<sup>2</sup> at 1.8 V) for AEM electrolyzer





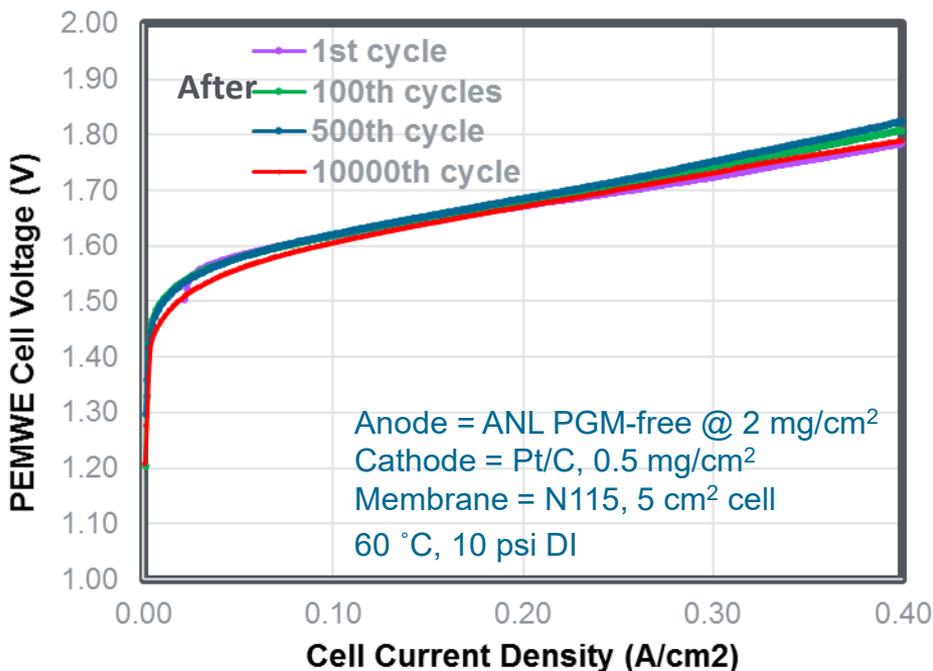
# PGM-free OER Catalysts for PEM Electrolyzer



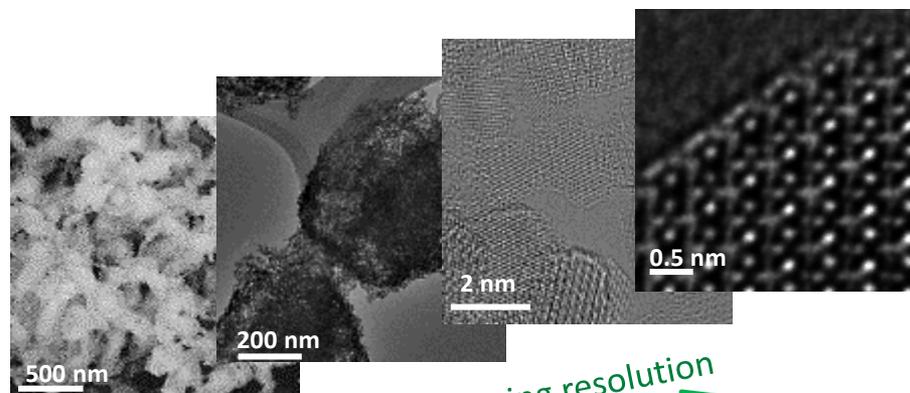
5 Nodes

**Project Goal:** To develop platinum group metal-free (PGM-free) oxygen evolution reaction (OER) electro-catalysts as viable replacement for Ir in proton exchange membrane water electrolyzer (PEMWE)

**Highlight:** An ANL PGM-free OER catalyst demonstrated an unprecedented current density of 400 mA/cm<sup>2</sup> @ 1.8 V and stability over 10,000 voltage cycles in PEMWE.



High resolution electron microscopy shows ANL PGM-free catalyst contains interconnected nanocrystallite aggregates with morphology similar to its MOF precursor



Increasing catalyst imaging resolution

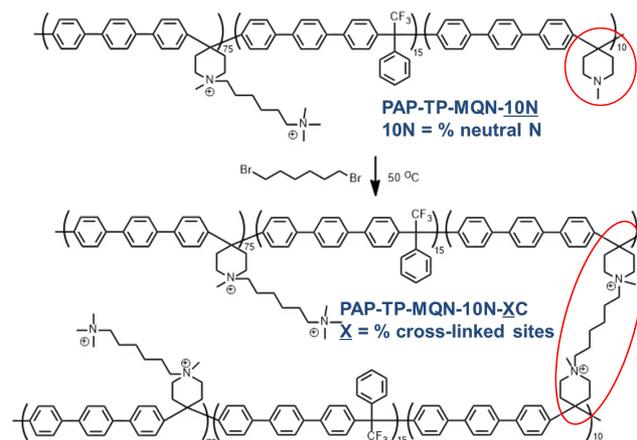
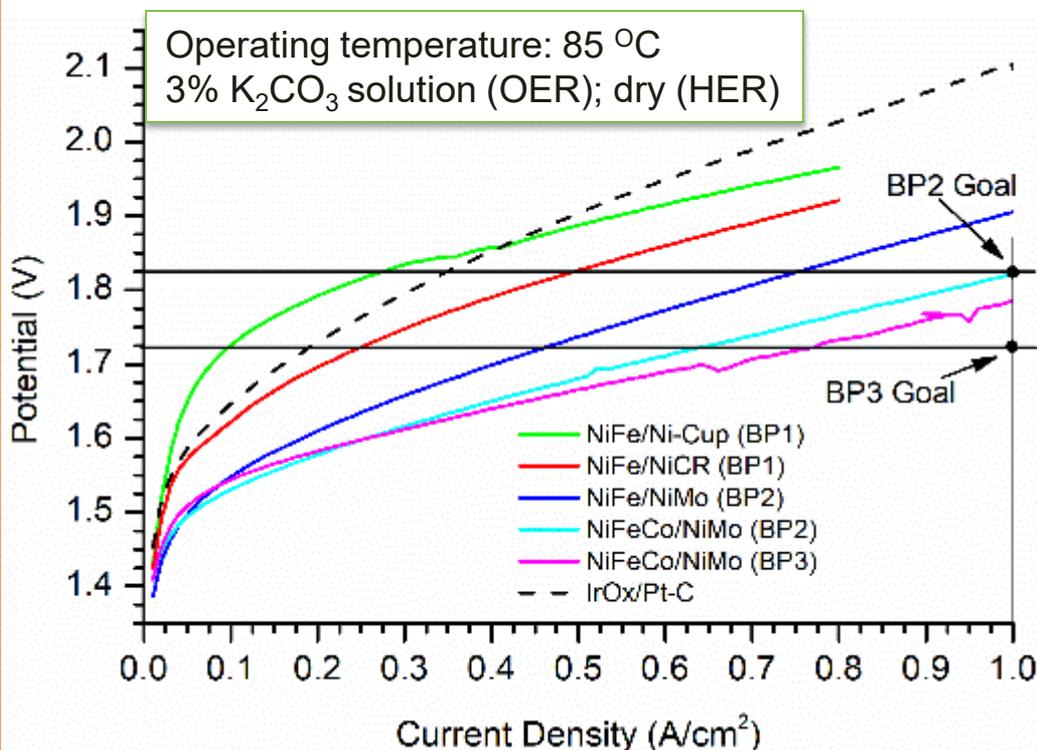
# Novel PGM-free Catalysts for Alkaline HER and OER



3  
Nodes

**Project Goal:** Decrease the cost of hydrogen production via water electrolysis using high-performing PGM-free catalysts and a novel, temperature-stable anion exchange membrane.

**Highlight:** AEM electrolysis cell that achieved a potential of 1.78 V @ 1A/cm<sup>2</sup> with a net decay rate of 1 mV/hr measured over 65 hours. The end of project goal is 1.72 V @ 1 A/cm<sup>2</sup>.



Crosslinking membranes improves mechanical stability with minimum loss of performance

**10% Crosslinked:**

IEC: 2.7 mequiv/g

Swelling @ 75°C: 12%

ASR @ 80 °C: 0.65 Ω·cm<sup>2</sup>

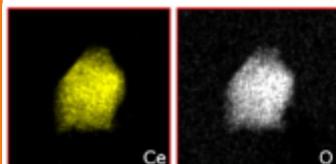
IEC loss after 1000hr in

90°C KOH: ~8.13%



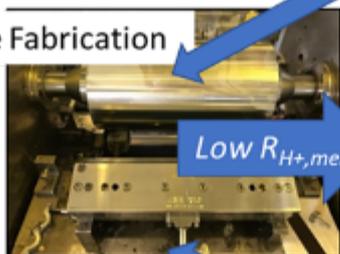
**Project Goal:** Developing thin membranes with low ohmic loss on roll-to-roll equipment for PEMWE systems, leveraging fundamental understanding of performance- and durability-enhancing additives to maximize efficiency and minimize cost of H<sub>2</sub>.

Radical Scavengers



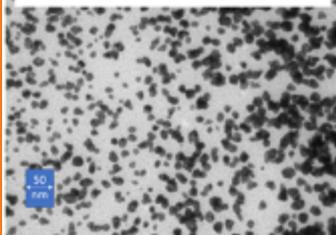
High selectivity  
Low Dissolution

Roll to Roll Membrane Fabrication

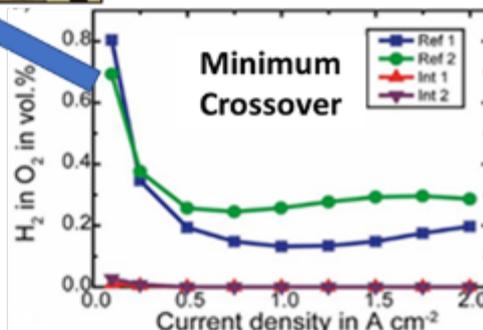
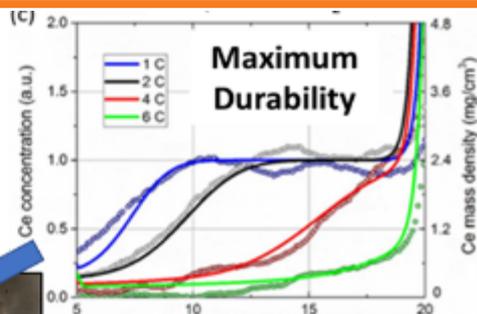


Low  $R_{H^+,mem}$

Gas Recombination Catalyst



High activity  
Low Mobility



Highlight

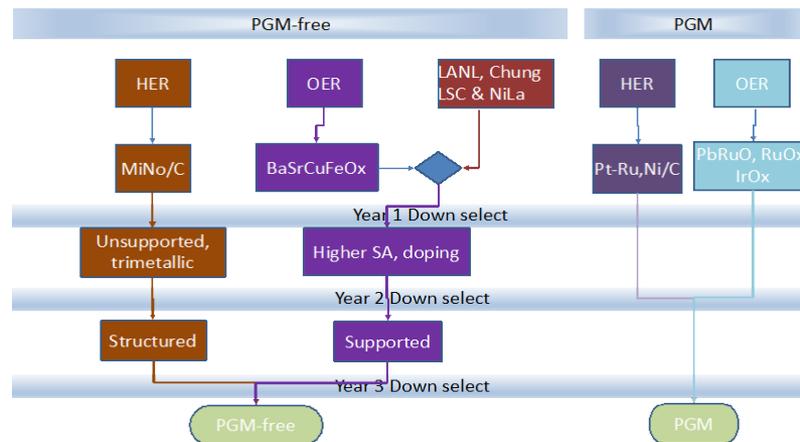
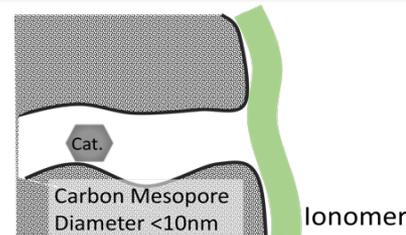
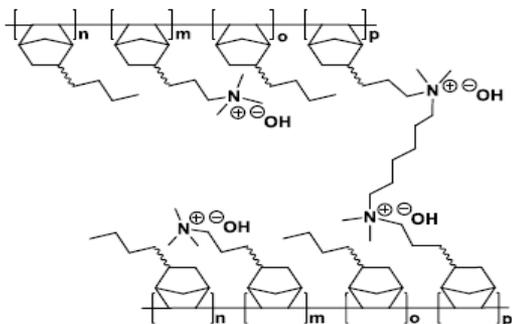
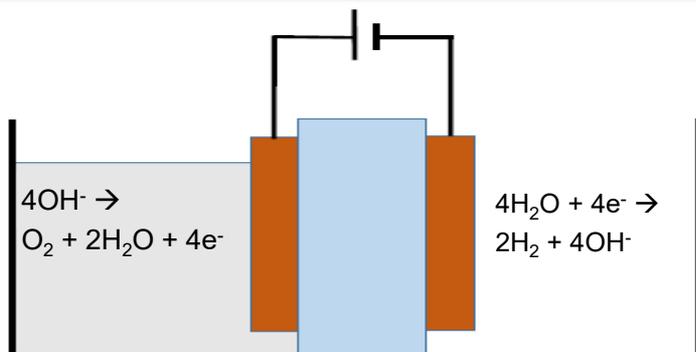
State of the art PEMWE membranes are thick (>125 μm) and unreinforced with no stabilizing additives. This project intends to improve on state of the art by:

1. Engineering a thin, reinforced membrane on roll to roll scale
2. Remediating gas crossover with recombination catalyst
3. Preventing membrane degradation with immobile radical scavengers



**Project Goal:** To enhance and combine state-of-the-art alkaline polymer electrolyzer components into one optimized membrane electrode assembly (MEA) system to achieve the DOE targets for low temperature electrolysis (LTE)

**Highlight:** Non-platinum group metal catalysts are combined with state-of-the-art anion conducting polymer membranes and ionomers to form high-performance MEAs





# PGM-free OER Catalysts for Alkaline Water Electrolysis

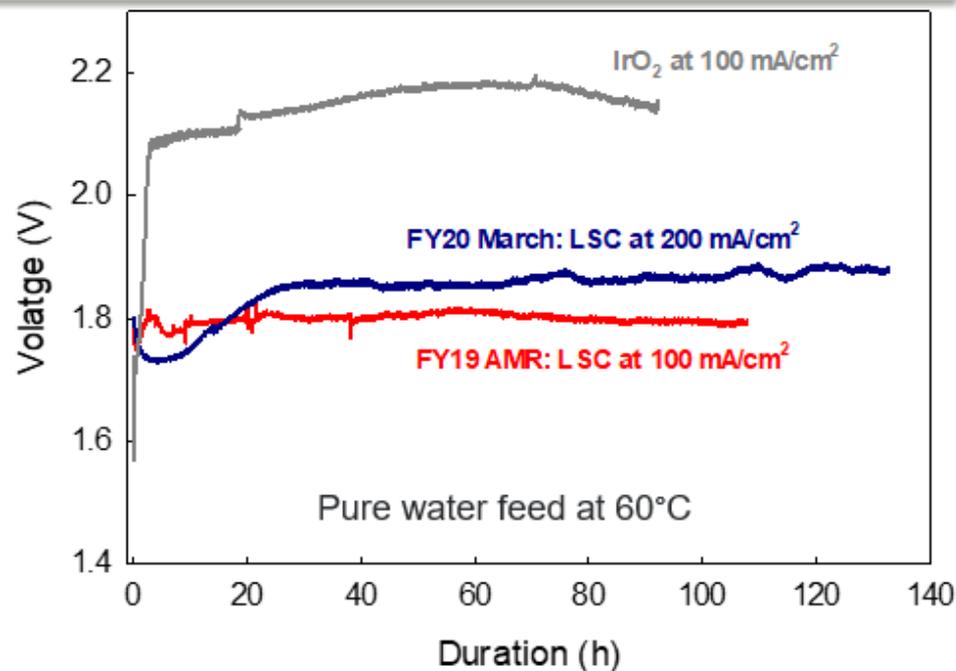
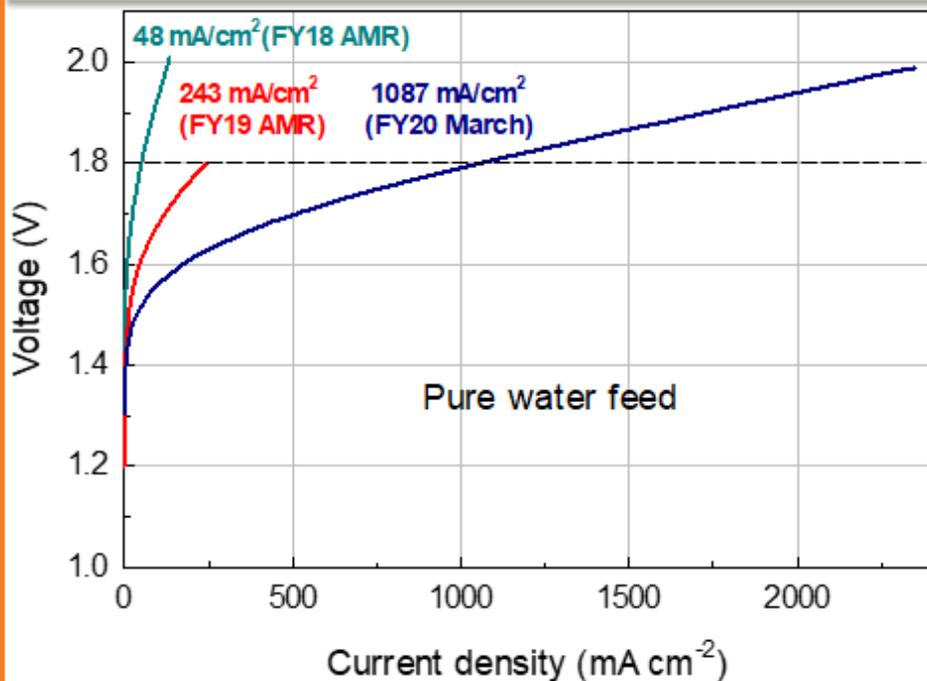


5 Nodes

## Project Goal:

Development of PGM-free Perovskite OER catalysts with high performance and durability in the alkaline solution-free pure water AEM water electrolyzer

**Highlight:** The project team achieved significant progress since FY18. It improved performance to 1.04 A/cm<sup>2</sup> at 1.8 V at 85°C and slowed degradation rates to 0.2 mV/hr at 200 mA/cm<sup>2</sup> at 60°C.





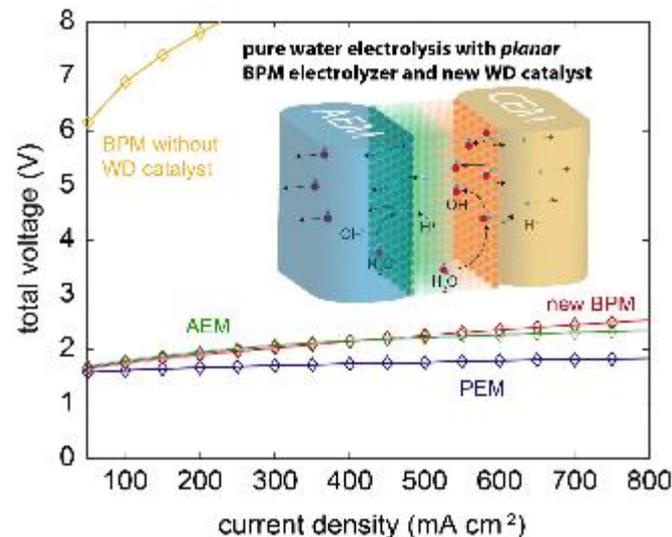
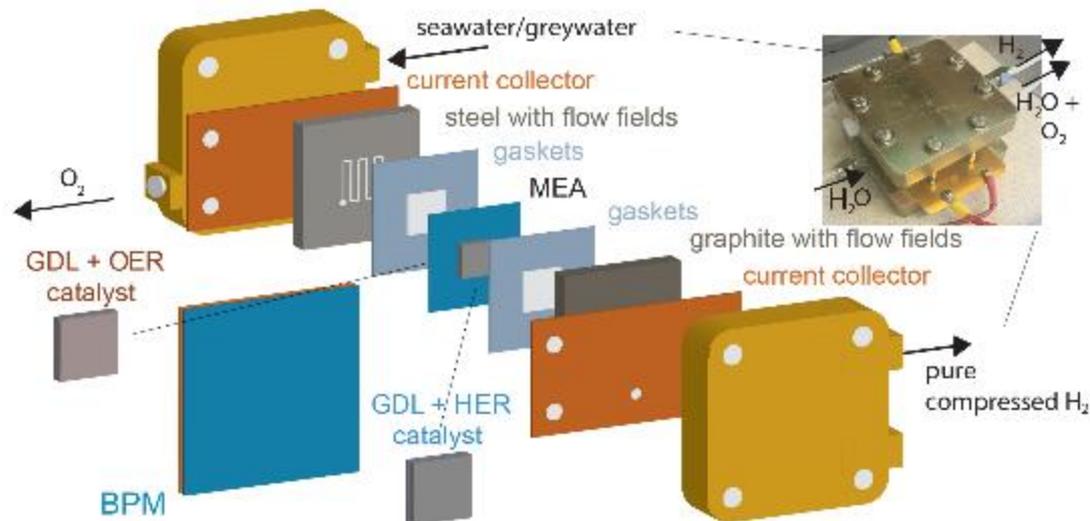
# Hydrogen From Membrane Electrolysis of Dirty Water



6  
Nodes

**Project Goal:** Develop a technical understanding of performance degradation of alkaline and bipolar membrane electrolyzers in pure and dirty water and engineer impurity tolerant systems.

**Impact:** Alkaline and bipolar membrane electrolysis systems enable PGM-free devices that may be more tolerant to impurities, if appropriately designed, which would increase system longevity, allow for less-stringent input water purity, and lower costs.





# High Efficiency PEM Water Electrolysis

nel



UCIRVINE



OAK RIDGE  
National Laboratory

NREL  
NATIONAL RENEWABLE ENERGY LABORATORY

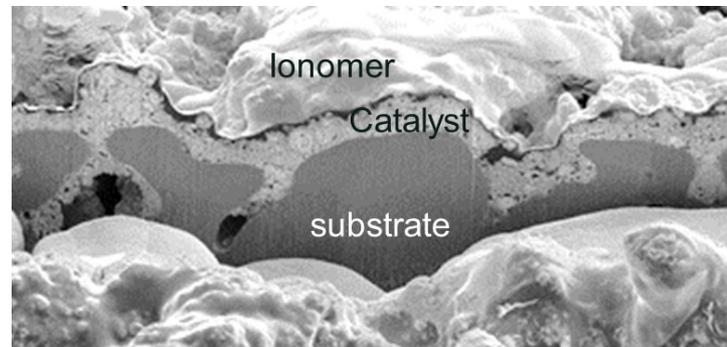


7  
Nodes

**Goals:** Develop ultra-efficient PEM electrode per targets below

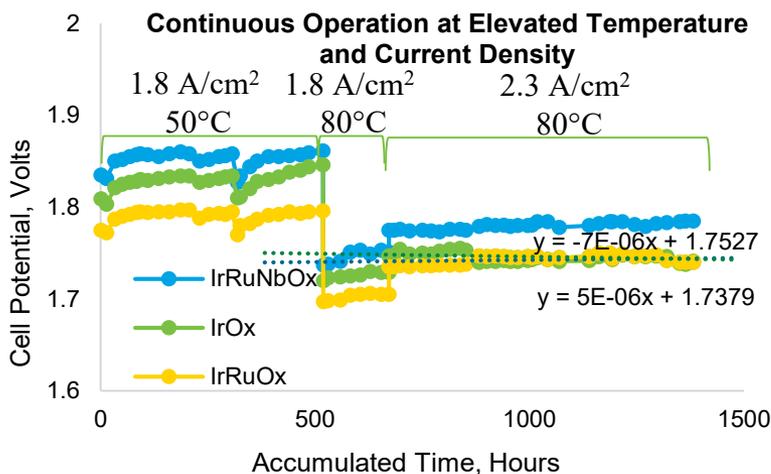
Metric	State of the Art	Proposed
Membrane thickness	175 microns	50 microns
Operating temperature	58°C	80-90°C
Cell Efficiency	53 kWh/kg	43 kWh/kg

**Approach:** Look at materials and manufacturing holistically to optimize



## Accomplishments in Phase 2

Met voltage and durability targets with advanced catalyst and thin membrane



## Focus of Phase 2

1. Development of hydrogen cross-over mitigation strategy
2. Integrate catalysts and hydrogen mitigation into integrated assembly
3. Scale-up and conduct durability tests in multi-cell stack
4. Conduct final cost analysis



- **Collaborated with HydroGEN Benchmarking Project**
  - Workshop participation
  - Session chairing
  - Progress on Protocols and Standard vocabulary & definitions
- **Interfacing HydroGEN & IEA Annex 30 Benchmarking activities**
  - Communicating RR phase II progress
  - Discussing common hardware platform
- **Contributing to Meta Data development of HydroGEN Data Center**



# Summary - HydroGEN LTE Projects

- **HydroGEN LTE is actively supporting**
  - **8 FOA projects with 41 node call outs**
  - **2 Supernodes with 14 node call outs**
- **FOA Projects demonstrate improvements in PEM & AEM technologies**
- **LTE Supernode interlinks Ex-Situ, In-Situ and Modeling Results and supports upscaling**
- **Working closely with the project participants and benchmarking activities to advance knowledge and utilize capabilities**



## Future Work

- **Fully integrate recently started FOA awarded seedling projects (~March/April 2020)**
- **Continue to enable and support research of the funded FOA Projects through lab nodes and expertise**
- **Utilize and expand Supernodes to help accelerate LTE research**
- **Work with the 2B team and LTE working group to establish testing protocols and benchmarks**
- **Continue to utilize data hub for increased communication, collaboration, generalized learnings, and making digital data public**

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

# Acknowledgements



Energy Materials Network  
U.S. Department of Energy



**HydroGEN**  
Advanced Water Splitting Materials

## Authors

Guido Bender  
Huyen Dinh

## LTE Project Leads

Kathy Ayers  
Shannon Boettcher  
Chris Capuano  
Hoon Chung  
Yu Seung Kim  
Paul Kohl  
Di-Jia Liu  
Sanjeev Mukerjee  
Andrew Park

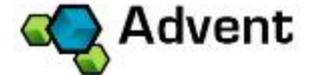
## Research Teams



Northeastern University  
*Center for Renewable Energy Technology*



Rensselaer



nel



UNIVERSITY OF OREGON



University at Buffalo  
*The State University of New York*



NATIONAL FUEL CELL  
RESEARCH CENTER  
UNIVERSITY OF CALIFORNIA - IRVINE



# Acknowledgements



Energy Materials Network  
U.S. Department of Energy



**HydroGEN**  
Advanced Water Splitting Materials

## LTE Supernode Team



Shaun Alia  
Guido Bender  
Huyen Dinh  
Allen Kang  
Scott Mauger  
Janghoon Park  
Jason Pfeilsticker  
Bryan Pivovar  
Michael Ulsh  
James Young



Elise Fox  
Héctor Colón-Mercado



Nemanja Danilovic  
Julie Fornaciari  
Ahmet Kusoglu  
Jessica Luo  
Adam Weber  
Guosong Zeng  
Jeremy Zhou



# Acknowledgements



Energy Materials Network  
U.S. Department of Energy



**HydroGEN**  
Advanced Water Splitting Materials

Publication Number: NREL/PR-5900-76549

This work was authored in part by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by U.S. Department of Energy Office of Energy Efficiency and Fuel Cell Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.



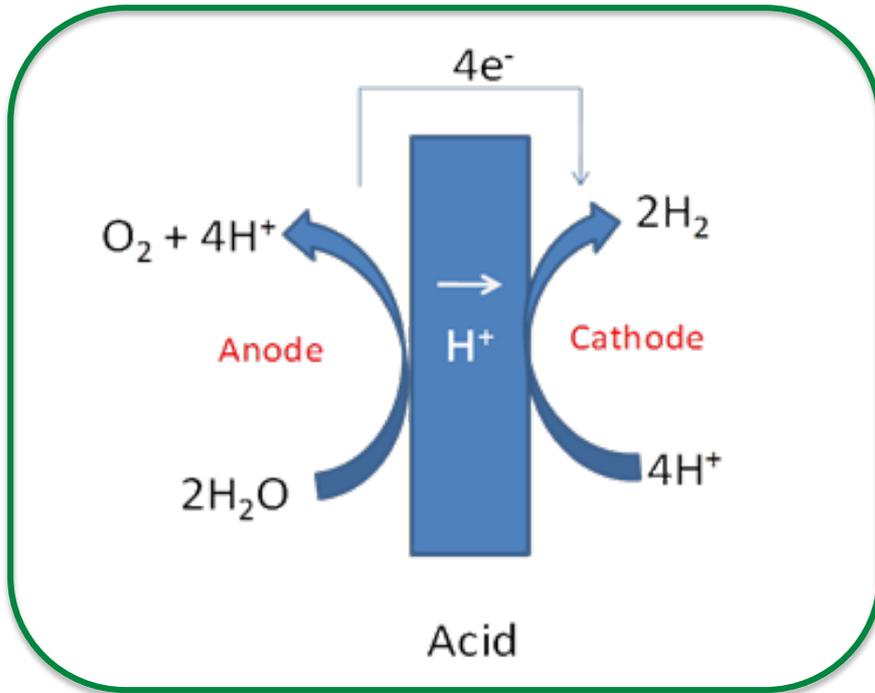


# Technical Backup Slides



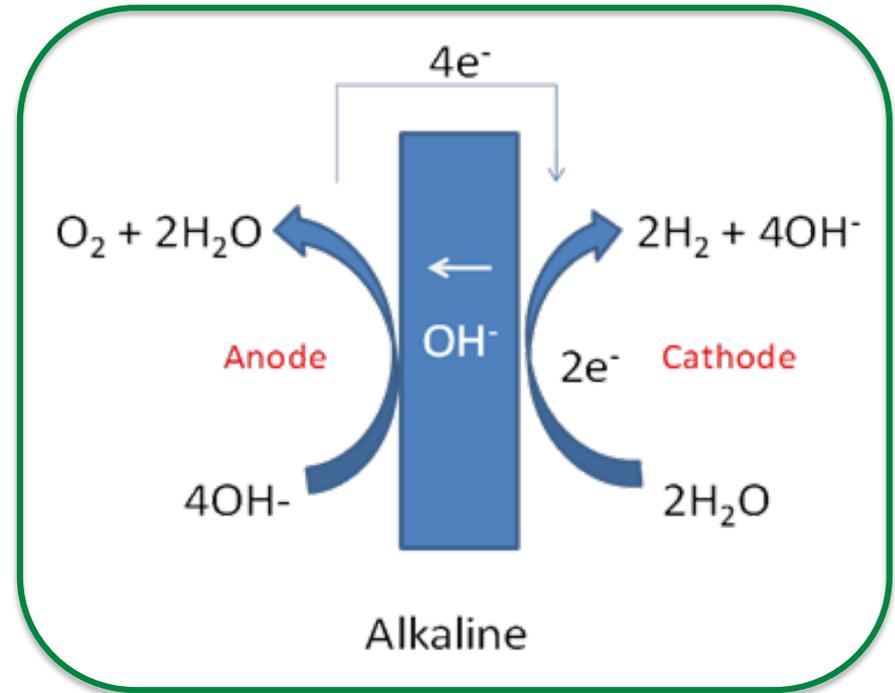
# Overview - LTE Technology

## Schematic PEM\*



- **Niche Application Deployment**

## Schematic AEM\*



- **Low TRL Technology**
- **Research Stage**



# Overview - LTE Technology Relevance / Impact

## State-of-Art PEM

- **2V @ 2A/cm<sup>2</sup>**
- **2-3 mg/cm<sup>2</sup> PGM catalyst loading on anode & cathode**
- **60k – 80k hours in commercial units**
- **Niche applications**
  - Life support
  - Industrial H<sub>2</sub>
  - Power plants for cooling
- **\$3.7/kg H<sub>2</sub> production\***

## State-of-Art AEM

- **2V @ 0.2A/cm<sup>2</sup> in H<sub>2</sub>O**
- **Improved performance in basic solution**
- **2-3 mg/cm<sup>2</sup> PGM-free catalyst loading on anode & cathode**
- **~2k hour at 27° C demonstrated \*\***
- **No commercial units**
- **\$/kg production not available**

\*High volume projection of hydrogen production for electrolysis:

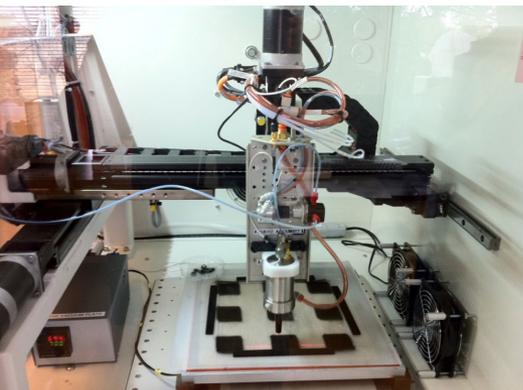
<https://www.energy.gov/sites/prod/files/2017/10/f37/fcto-progress-fact-sheet-august-2017.pdf>

\*\* K.Ayers, AMR Presentation PD094, 06/2014



# Supernode Accomplishments: Electrode Fabrication Platforms

## Ultrasonic Spray

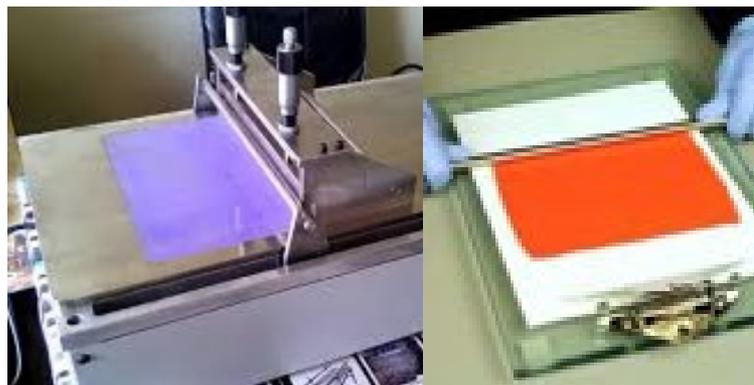


Used to demonstrate new materials and for fundamental studies

### Conditions

- Dilute ink
- Sequential build up of layers
- Heated substrate
- Vacuum substrate
- Batch Process

## Doctor Blade/Mayer Rod



Used to demonstrate new materials and for fundamental studies. Prove out ink formulations or processes prior to R2R

### Conditions

- Concentrated inks
- Single layer coating
- Heated substrate
- Vacuum substrate
- Batch Process

## Roll-to-Roll



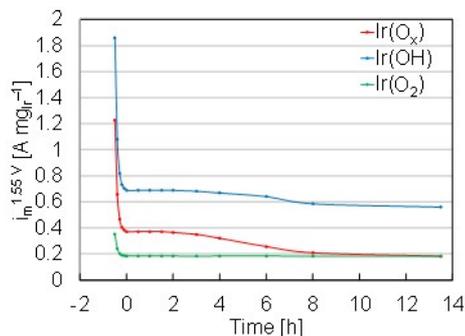
Demonstrate scalability of materials and MEA/cell designs. Studies of process variables

### Conditions

- Concentrated inks
- Single layer coating
- Room temperature substrate
- Convection drying
- Continuous Process



# Supernode Accomplishments: Thin Film Morphology: GISAXS



- Nafion morphology on Iridium substrates
  - Overall phase-separated nanostructure
  - Broader peaks and weaker phase-separation on OH
- Ir(O<sub>x</sub>) [Metal]: phase-separation (**in-plane** ordering)
- Ir(OH) [functionalized]: **no** phase-separation (both directions)
- Ir(O<sub>2</sub>) [Bulk Oxide]: phase-separation (**thickness** ordering)

