Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

HydroGEN: Low-Temperature Electrolysis

G. Bender, H.N. Dinh

Presenter: Guido Bender, NREL

Date: 4/30/2019

Venue: 2019 DOE Annual Merit Review

Crystal City, Virginia

Project ID # P148A

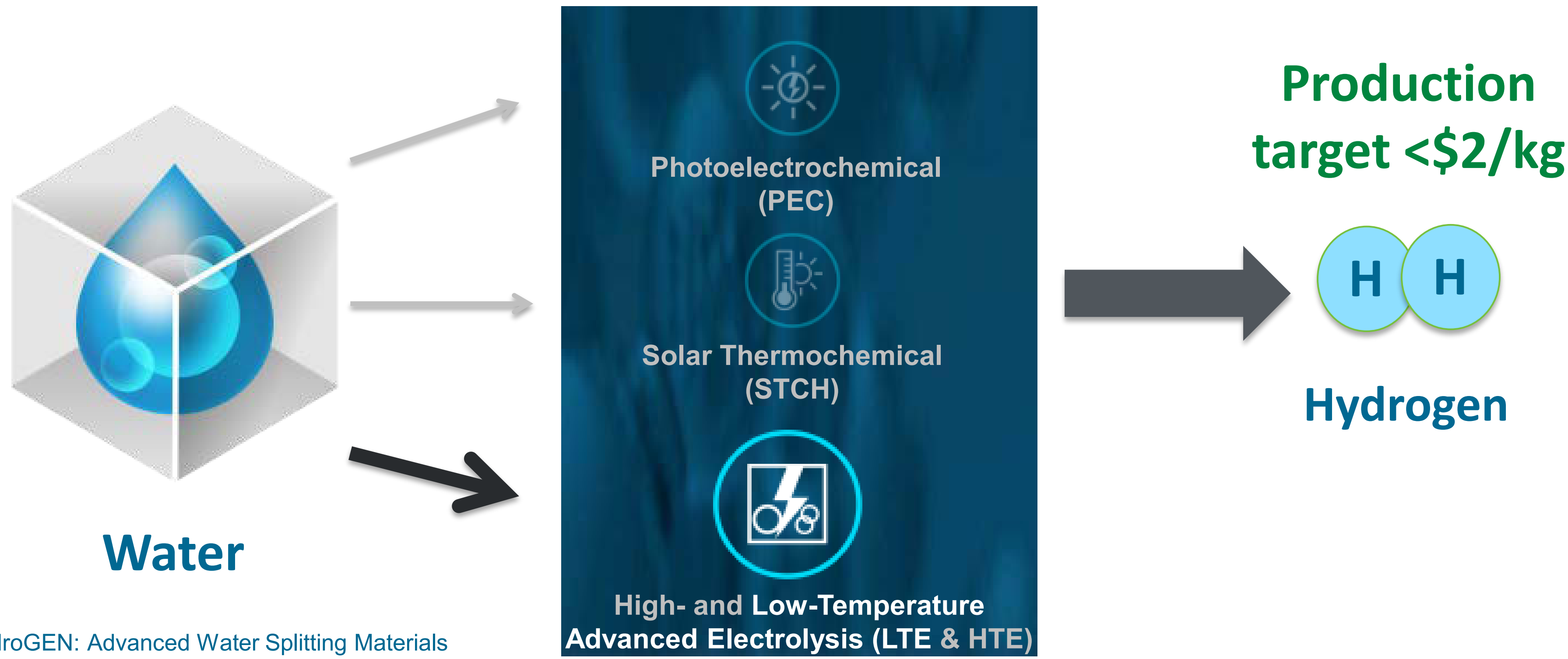
NREL · Berkeley Lab · Sandia National Laboratories · INL Idaho National Laboratory · Lawrence Livermore National Laboratory · SRNL

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

AWSM Consortium 6 Core Labs:

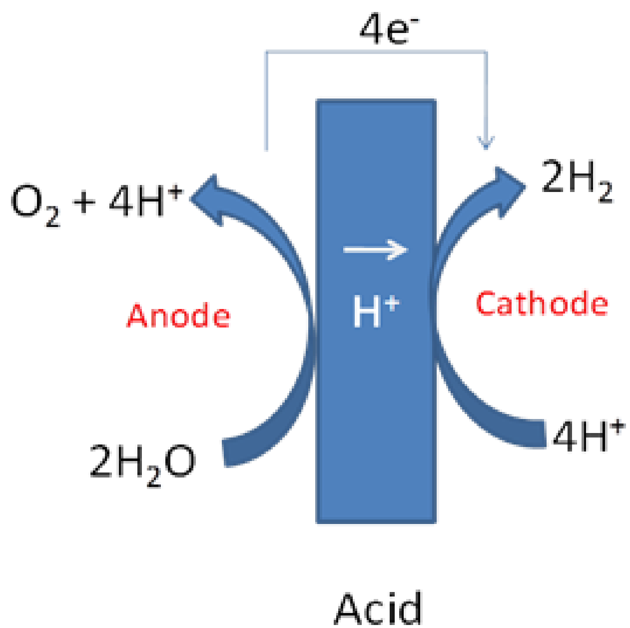
NREL, Berkeley Lab, Sandia National Laboratories, Idaho National Laboratory, Lawrence Livermore National Laboratory, SRNL

Accelerating R&D of innovative materials critical to advanced water splitting technologies for clean, sustainable & low cost H_2 production, including:



Overview - LTE Technology

Schematic PEM*

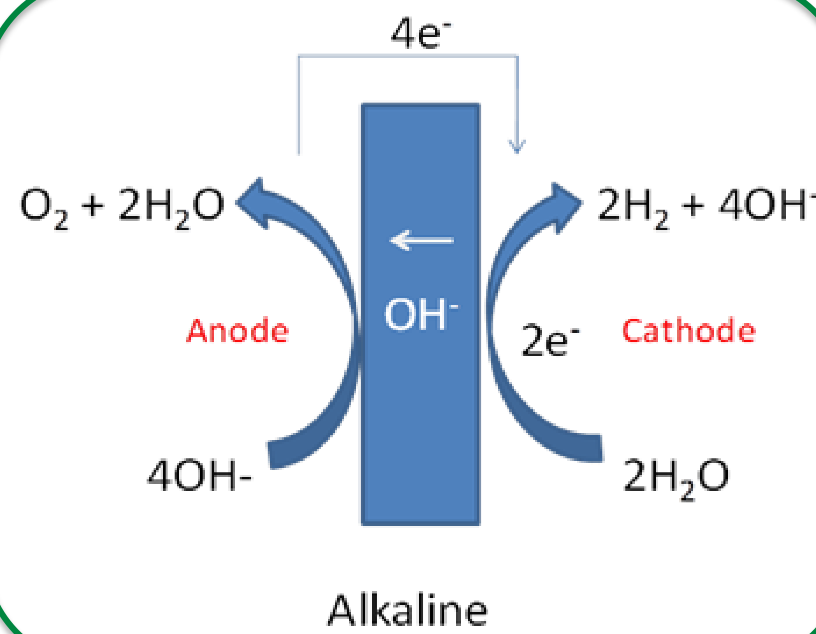


Anode: $2H_2O => O_2 + 2H^+ + 2e^-$

Cathode: $2H^+ + 2e^- => H_2$

- **Niche Application Deployment**

Schematic AEM*



Anode: $4OH^- => O_2 + 2H_2O + 4e^-$

Cathode: $4H_2O + 4e^- => 2H_2 + 4OH^-$

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

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

Overview - LTE Technology Relevance / Impact

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

BOP – Balance of Plant
PTL – Porous Transport Layers

Overview - LTE Technology Relevance / Impact

State-of-Art PEM

- 2V @ $2A/cm^2$
- 2-3 mg/cm^2 PGM catalyst loading on anode & cathode
- 60k – 80k hours in commercial units
- Niche applications
  - Life support
  - Industrial H_2
  - Power plants for cooling
- \$3.7/kg H_2 production*

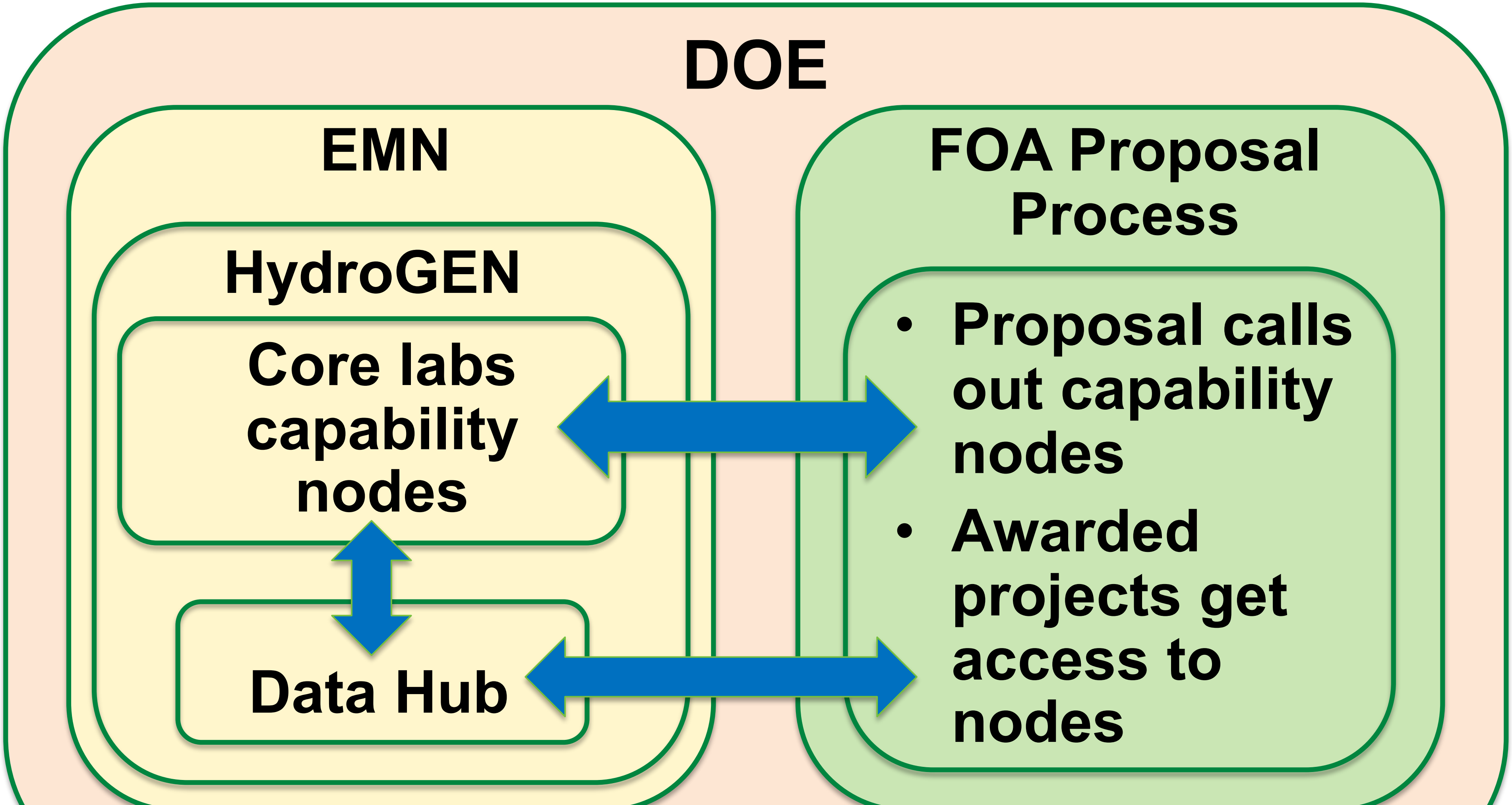
State-of-Art AEM

- 2V @ $0.2A/cm^2$ in H_2O
- Improved performance in basic solution
- 2-3 mg/cm^2 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

Approach – HydroGEN EMN



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

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

BERKELEY LAB

Sandia National Laboratories

Lawrence Livermore National Laboratory

Support through:

Personnel

Equipment

Expertise

Capability

Materials

Data

LTE Projects

PROTON ON SITE nel number one by nature
YOUR SOURCE FOR ALL THINGS HYDROGEN

Argonne NATIONAL LABORATORY

Northeastern University
Center for Renewable Energy Technology

Los Alamos NATIONAL LABORATORY EST. 1943 (2)

Accomplishments and Progress:
Established Nodes for Project Support

NREL NATIONAL RENEWABLE ENERGY LABORATORY | Lawrence Livermore National Laboratory | Sandia National Laboratories | BERKELEY LAB

45 nodes for LTE

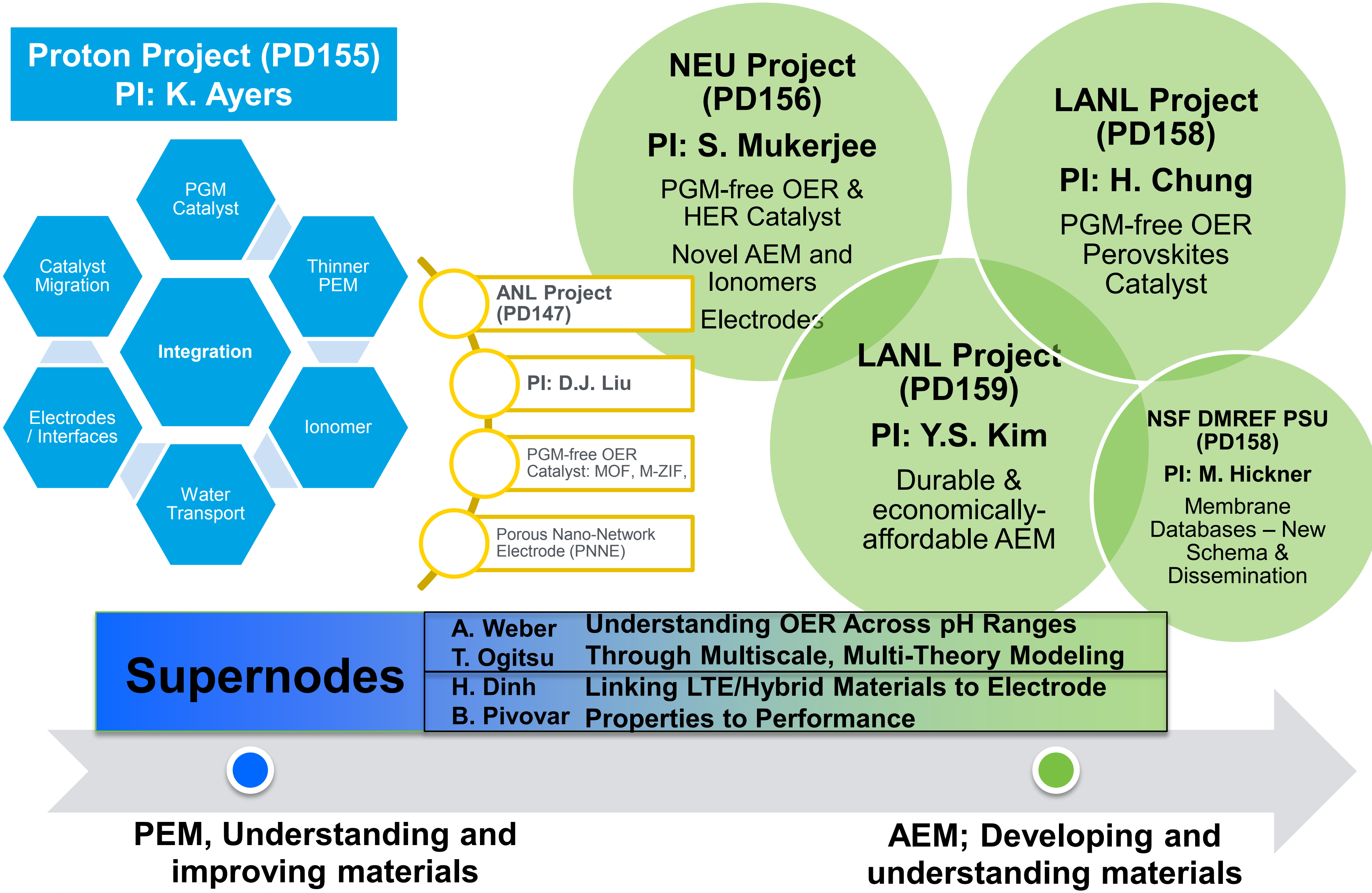
- 19x readiness level 1
- 21x readiness level 2
- 5x readiness level 3

21 nodes used by LTE projects

Node Classification

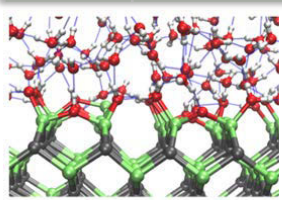
6x Analysis
13x Benchmarking
25x Characterization
14x Computation
7x Material Synthesis
7x Process and Manufacturing Scale-Up
3x System Integration

Accomplishments and Progress:
5 HydroGEN LTE Seedling Projects and Others



Collaboration and Coordination - Node Utilization

Lab	Node	Proton	ANL	NEU	LANL1	LANL2	Super	DMREF
NREL	Data Hub							✓
LLNL	Computational Materials Diagnostics and Optimization of PEC Devices		✓					
NREL	Electr. Structure Modeling of Catalysts						✓	
LLNL	Ab Initio Modeling of Electrochemical Interfaces						✓	
LBNL	DFT and Ab Initio Calculations		✓		✓			
LBNL	Multiscale Modeling of Water-Splitting Devices	✓		✓		✓	✓, ✓	
SNL	LAMMPS			✓				
SNL	Separators for Hydrogen Production				✓	✓		
NREL	Novel Membrane Fabrication and Development for LTE and PEC	✓		✓			✓	✓
NREL	Multi-Comp. Ink Development, High-Throughput Fabrication, & Scaling	✓	✓	✓			✓	



Computation

Processing & Scale Up

Material Synthesis

Collaboration and Coordination - Node Utilization

Lab	Node	Proton	ANL	NEU	LANL1	LANL2	Super	DMREF
SNL	Advanced Electron Microscopy		✓					
NREL	Catalyst Synthesis, Ex situ Characterization & Standardization	✓	✓				✓, ✓	
LBNL	Ionomer Characterization and Understanding	✓		✓		✓	✓	
NREL	In Situ Testing Capabilities	✓		✓	✓	✓	✓	✓
LBNL	Understanding Inks and Ionomer Disp.						✓	
SNL	Near Ambient Pressure E-XPS				✓			
NREL	Surface Analysis Cluster Tool		✓		✓			
LBNL	Probing and Mitigating Corrosion	✓						
LBNL	PEC In Situ Testing using X-Rays				✓		✓	
LBNL	Water Splitting Device Testing					✓	✓	
SRNL	Fabrication and Characterization of Electro-catalyst and Components for H2 Production						✓	

Characterization

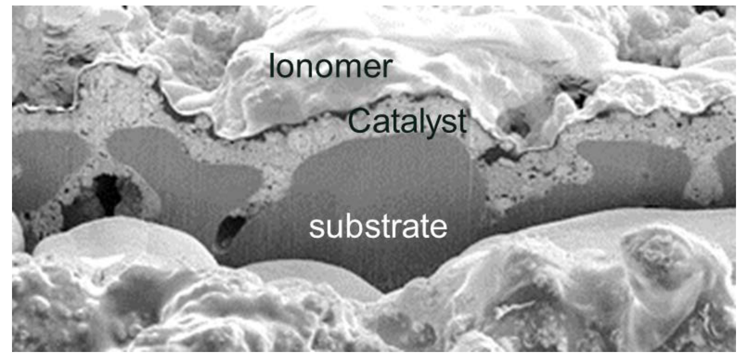
High Efficiency PEM Water Electrolysis

7 Nodes

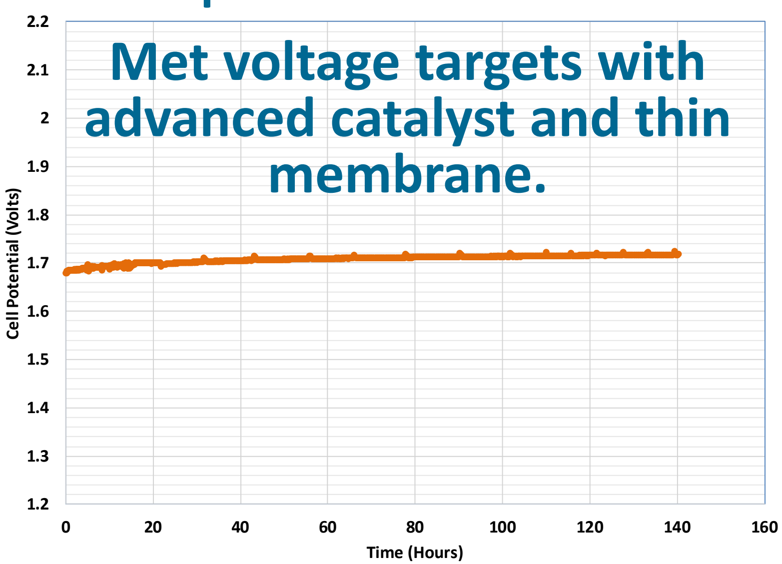
Goals: Develop ultra-efficient PEM electrode per targets below

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

Approach: Look at materials and manufacturing holistically to optimize



Accomplishments in Phase 1



Focus of Phase 2

1. Understand water management and relationship to catalyst loading and porous transport layer geometry,
2. Demonstrate electrochemical stability of Ir-Ru alloy catalysts,
3. Quantify migration of platinum group metals after accelerated stress tests.

K. Ayers, P155, 4/30/19 Tue.

PGM-free OER Catalysts for PEM Electrolyzer

Argonne National Laboratory | University at Buffalo, The State University of New York | GINER | Sandia National Laboratories | NREL National Renewable Energy Laboratory | Berkeley Lab | Lawrence Livermore National Laboratory | 5 Nodes

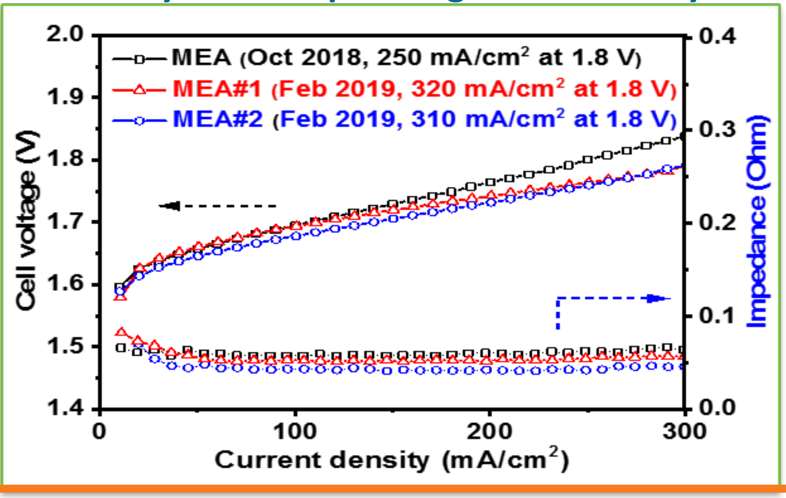
Project Vision: To lower the capital cost of proton exchange membrane water electrolyzer (PEMWE) by replacing expensive Ir with platinum group metal-free (PGM-free) electro-catalysts.

Project Impact: To reduce anode catalyst cost by removing the catalyst pricing and supply bottlenecks for the widespread implementation of PEME for H_2 production using renewable energy sources.

Project Approach: Developing metal-organic framework (MOF) based PGM-free oxygen evolution reaction (OER) catalysts with performance approaching to that of Ir and demonstrating through operating PEMWE.

Accomplishments in Phase 1

The team demonstrated, for the first time, PGM-free OER catalyst in an operating PEM electrolyzer



Focus of Phase 2

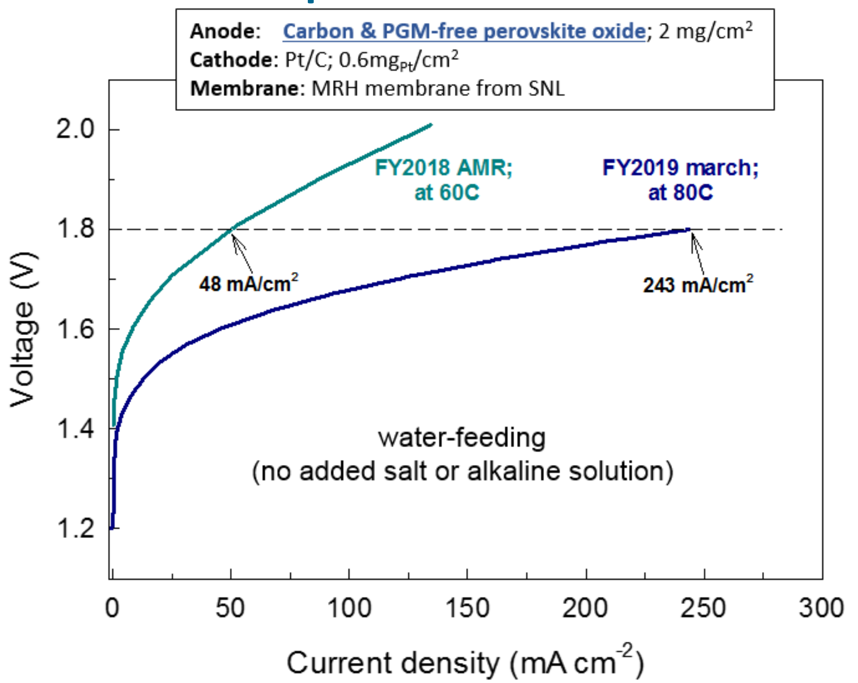
- Continue to improve PGM-free OER catalyst through multi-metallic MOF/ZIF design & synthesis
- Investigate the catalyst-structure relationship and performance improvement through collaboration with HydroGen using advanced characterizations & computational modeling
- Double PEMWE current density with new PGM-free OER catalysts over the BP1 benchmark
- Demonstrate PGM-free catalyst stability in PEMWE through cell voltage cycling test

D.J. Liu, P157, 4/30/19 Tue.

Los Alamos National Laboratory | Pajarito Powder Fuel Cell Catalysts | Sandia National Laboratories | NREL National Renewable Energy Laboratory | Berkeley Lab | 5 Nodes

Project Goal: The key challenge in anion exchange membrane (AEM) electrolyzer is to achieve high performance without feeding alkaline or salt solutions to the electrodes. In this project, LANL team is developing PGM-free catalysts demonstrating high performance in the pure-water feed AEM water electrolyzer.

Accomplishments in Phase 1



Focus of Phase 2

- Catalyst development:
  - Composition and particle size control to improve activity and durability
- Fundamental study:
  - Understanding the phenomena occurring at the catalyst-ionomer interface using in situ and ex situ AP-XPS and XAS
  - Adopting GDE electrochemical cell to explore catalyst-ionomer interaction
- Optimizing catalyst-ionomer combination to improve performance and durability of AEM water electrolyzer

H. Chung, PD158, 4/30/19 Tue.

Scalable Elastomeric Membranes for Alkaline Water Electrolysis

Los Alamos National Laboratory · Rensselaer · Proton On Site / nel · Sandia National Laboratories · NREL National Renewable Energy Laboratory · Berkeley Lab

5 Nodes

Project Goal:

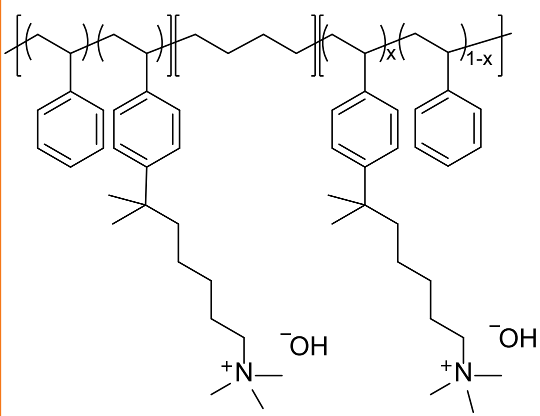
Preparing durable and economically-affordable alkaline hydroxide conducting SES materials and demonstrating the high performance and durability in AEM-based water electrolysis

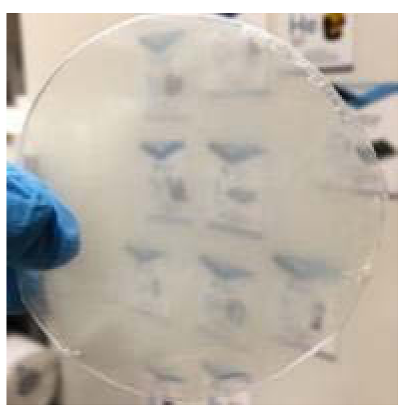
Accomplishments in Phase 1

- **Semi-crystalline SES AEM synthesized by acid catalyzed polymerization without using expensive metal catalyst.**

Properties:

- **IEC = 1.71 mequiv./g**
- **Water uptake = 144 %**
- **In-plane swelling = 30%**





Go-No-Go decision properties (Oct. 2018)

Properties	Target	Status
Hydroxide conductivity (mS cm^{-1}) at 30 °C	40	42 (30 °C) 54 (60 °C) 63 (80 °C)
Alkaline stability after 300 h in 1 M NaOH at 80 °C	< 5 % loss conductivity	0% loss
Mechanical toughness (mechanical strength (MPa) × % elongation) at 50 °C, 90% RH	> 1400	2091

Focus of Phase 2

Planned research on Phase II

- **Identify the performance and durability-limiting factors of AEM electrolysis.**
- **Further optimization of AEM and ionomeric binder for best electrolyzer performance and durability.**
- **AEM electrolyzer testing & verification**

Y. Kim, PD159, 4/30/19 Tue.

Developing Novel PGM-Free Catalysts for Alkaline HER & OER

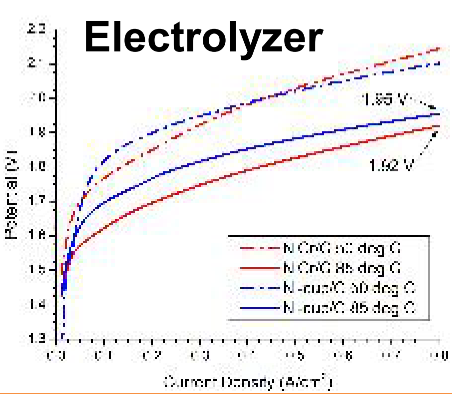
6 Nodes

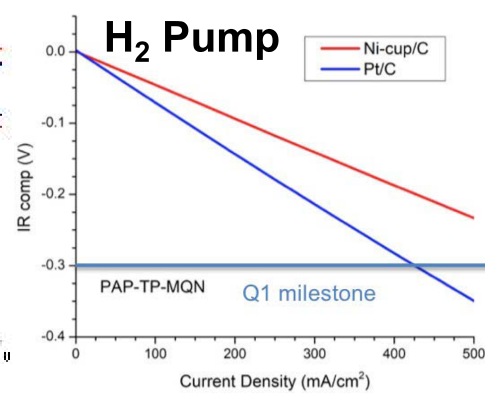
Project Vision: To develop stable, high-conductivity, and high-strength AEMs, stable and active PGM-free catalysts for hydrogen and oxygen evolution reactions.

Accomplishments in Phase 1

Catalyst development:

- HER Electrocatalysts: η of 300 mV at 500 mA/cm2 with PGM-free (Ni-Cup) HER electrocatalysts in an AEM MEA.
- OER Electrocatalysts: η of 150 mV at 500 mA/cm2 with PGM-free Ni-Fe/Raney Ni OER electrocatalysts in an AEM MEA.
- AEM MEA: Demonstrated a PGM-free AEM MEA electrolyzer performance of 0.8 A/cm2 at ≤1.92 V.





Membrane development:

- Successfully prepared and characterized single and multi-cation polyaryl piperidinyl triphenyl AEM membranes.
- ASR 0.048 Ω·cm^2 meets Phase 1 milestone
- <2% ion-exchange capacity loss at 1000 h in 95C 1M KOH

Focus of Phase 2

- Refine the HER and OER catalysts down selected in Phase 1
- Improve the durability of multiple cation AEM via cross-linking or introduction of reinforcement matrix
- Introduce high performance electrode architectures to facilitate gas evolution from the catalytic layer

Linking LTE/Hybrid Materials to Electrode Properties to Performance

Supernode

NREL NATIONAL RENEWABLE ENERGY LABORATORY | Savannah River National Laboratory | BERKELEY LAB | **8 Nodes**

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.**

Materials selection
PEM
AEM

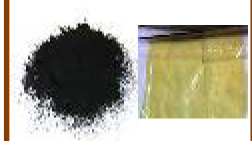
- Electrocatalyst ex-situ characterization **(NREL)**
- Ionomer thin films **(LBNL)** → Modeling **(LBNL)**
- Polymers and Membranes **(NREL)**

- Catalyst-Ionomer-solvent Interactions: Ink properties **(NREL, LBNL)**
- Electrode Fabrication **(NREL)**
- Catalyst-Ionomer Interactions: Electrode properties **(NREL)**

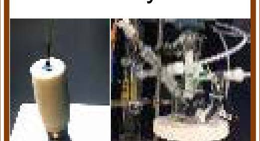
- In situ Cell testing **(NREL, SRNL)**
- Multiscale Electrolysis Model **(LBNL)**

Materials → **Devices**

Materials:
Catalyst, Ionomer & Membranes

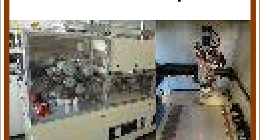


Electrochemical Characterization
Catalyst

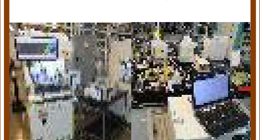


Ink Composition
Catalyst, Ionomer & Solvents

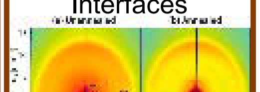
MEA Integration
Fabrication in Parameter Space



Performance Evaluation
In-Situ PEM, AEM

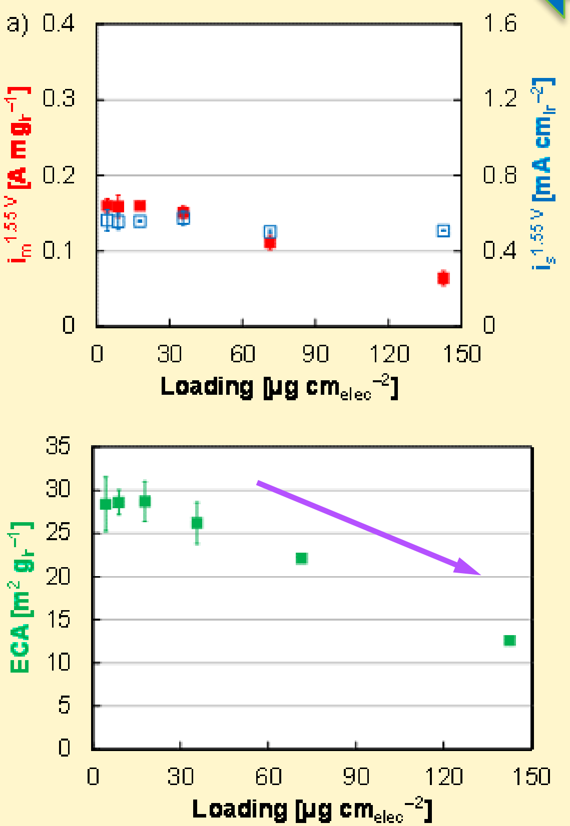


Advanced Characterization
Morphology, Material Properties, Interfaces

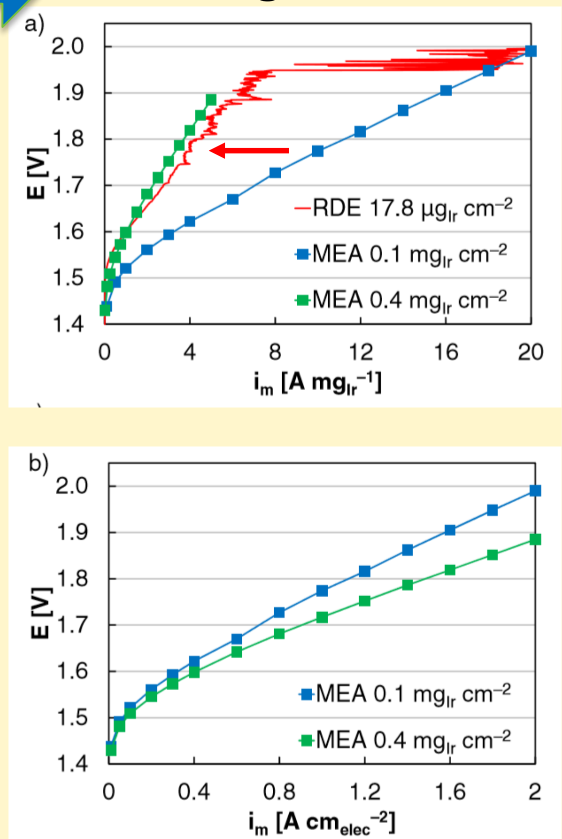


Effect of catalyst loading on performance

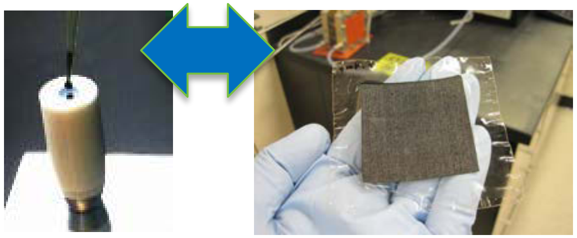
RDE Half-Cells



MEA Single-Cells



- Systematic variation of catalyst loading in RDE and MEA experiments
- Increased loading resulted in lower mass-normalized performance due to decreased utilization (surface area)

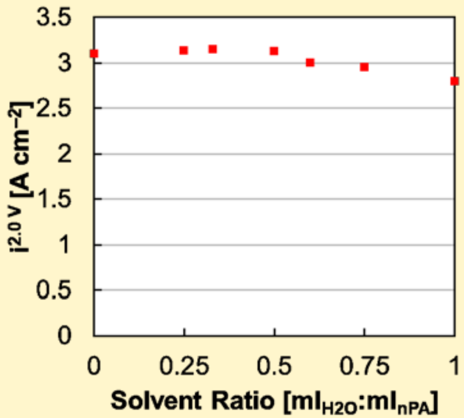


MEA data – S.M. Alia, B. Rasimick, C. Ngo, K.C. Neyerlin, S.S. Kocha, S. Pylypenko, B.S. Pivovar, *J. Electrochem. Soc.*, **2016**, *163*(11), F3105-F3112. DOI:10.1149/2.0151611jes
RDE data – S.M. Alia, G.C. Anderson, *J. Electrochem. Soc.*, **2019**, *166*(4), F282-F294. DOI:10.1149/2.0731904jes

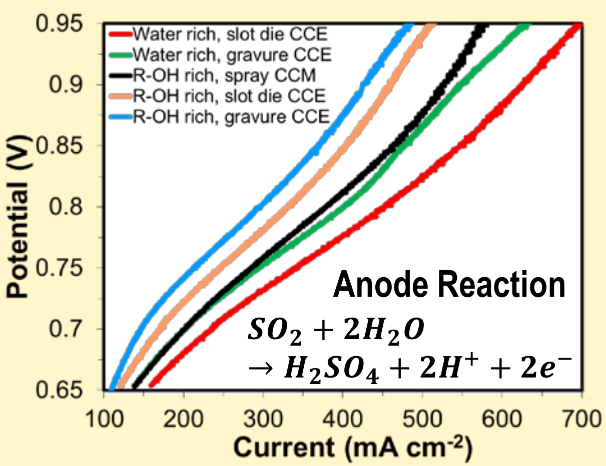
LTE Supernode MRS Poster, 4/30/19 Tue.

Supernode

LTE In-Situ Testing



Hybrid Cycle In-Situ Testing



- Performance testing of fabrication parameters
- Solvent ratio impacts performance in LTE
- Solvent choice and fabrication method impacts performance of hybrid sulfur cycle system

Proposed Future Work

1. Study the impact of coating methods on electrode morphology and PEM electrolysis performance
2. Study interaction of thin ionomer film on catalyst to understand its impact on local electrode structure and performance.
3. Correlate changes in performance due to processing & materials using modeling.
4. Develop pathway to branch studies into AEM technology

LTE Supernode MRS Poster, 4/30/19 Tue.

Accomplishments and Progress – Benchmarking

- **Collaborated with HydroGEN Benchmarking Project**
- **Point of contact for leveraging exchange with IEA Annex 30 for in-situ & ex-situ research**
- **Leadership role in developing path forward for harmonized protocols, hardware, and materials**
- **Benchmarking working groups and annual meeting**
- **Disseminated benchmarking information:**

a) G. Bender, M. Carmo, T. Smolinka, A. Gago, N. Danilovic, M. Mueller, F. Ganci, A. Fallisch, P. Lettenmeier, K. A. Friedrich, K. Ayers, B. Pivovar, J. Mergel, D. Stolten, "Initial Approaches in Benchmarking and Round Robin Testing for Proton Exchange Membrane Water Electrolyzers", International Journal of Hydrogen Energy, submitted August 2018, March 2019 in press

b) S.M. Alia, G. Anderson, "Iridium Oxygen Evolution Activity and Durability Baselines in Rotating Disk Electrode Half-Cells", J. Electrochem. Soc., **2019**, 166(4), F282-F294. DOI:10.1149/2.0731904jes

c) G. Bender, M. Carmo, S. Fischer, T. Lickert, T. Smolinka, J. Young, "Round Robin Testing for Polymer Electrolyte Membrane Water Electrolysis - Phase 2", World Hydrogen Energy Conference, Rio de Janeiro, June 19, 2018

Summary - HydroGEN LTE Projects

- **HydroGEN LTE is**
  - Supporting 5 FOA projects with 21 nodes
  - Supporting 1 NSF project with 3 nodes
  - Leading 2 Supernodes with 14 nodes
- **Projects demonstrate improvements in PEM & AEM technologies**
- **Working closely with the project participants and benchmarking activities to advance knowledge and utilize capabilities**

Future Work

- Continue to enable and support research of Phase 2 Projects through lab nodes and expertise
- Enable new FOA awarded seedling projects (Fall 2019)
- Continue to develop supernodes to help accelerate LTE research
- Work with the 2B team and LTE working group to establish testing protocols and benchmarks
- Utilize data hub for increased communication, collaboration, generalized learnings, and making digital data public

Acknowledgements

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U.S. Department of Energy

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INL Idaho National Laboratory
Lawrence Livermore National Laboratory
SRNL

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