Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

HydroGEN: Low-Temperature Electrolysis

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Presenter: Guido Bender, NREL

Date: 6/13/2018

Venue: 2018 DOE Annual Merit Review

Project ID # PD148A

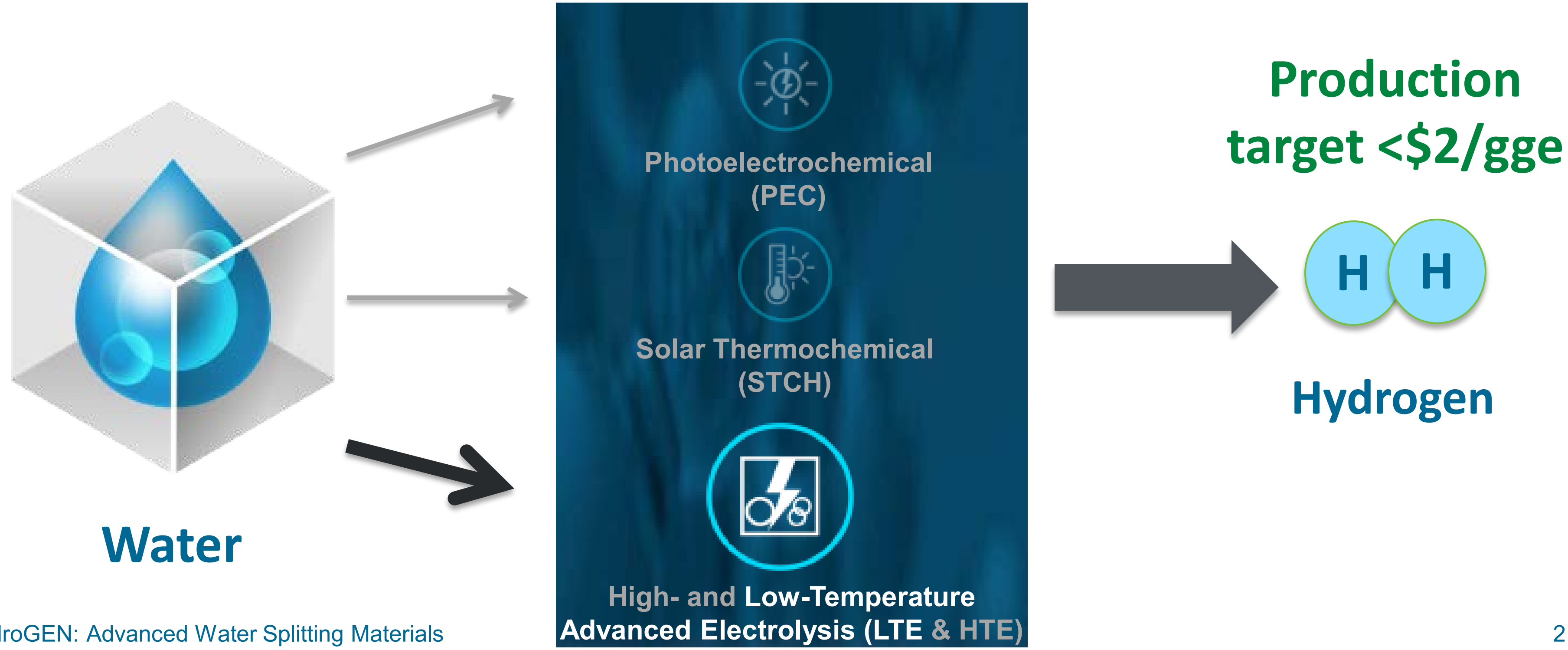
NREL · Berkeley Lab · Sandia National Laboratories · INL Idaho National Laboratory · Lawrence Livermore National Laboratory · SRNL

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

AWSM Consortium
6 Core Labs:

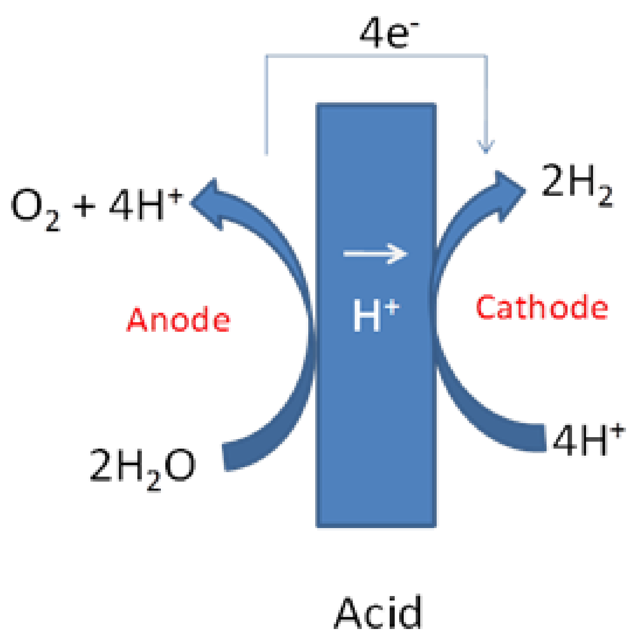
NREL National Renewable Energy Laboratory; Berkeley Lab; Sandia National Laboratories; Idaho National Laboratory; Lawrence Livermore National Laboratory; SRNL

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*

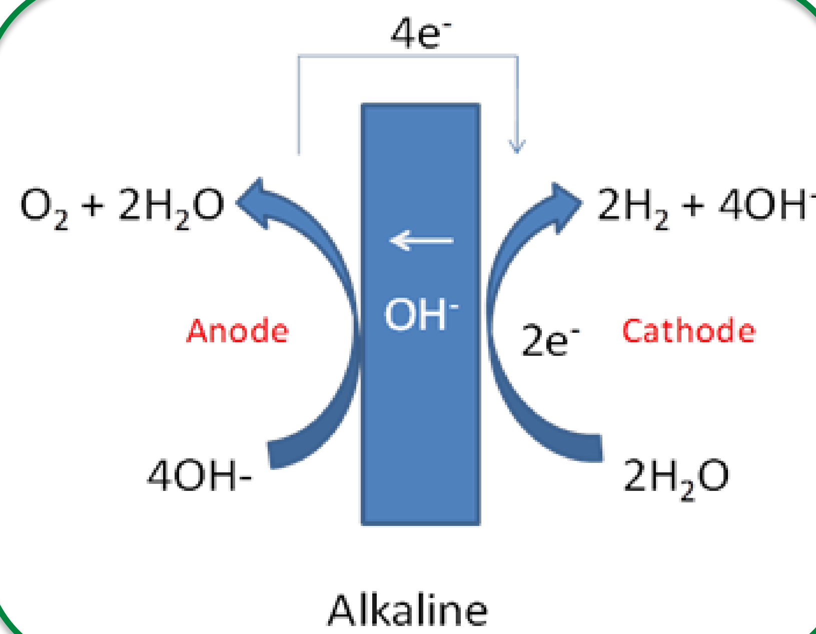


Anode: $2H_2O \Rightarrow O_2 + 2H^+ + 2e^-$

Cathode: $2H^+ + 2e^- \Rightarrow H_2$

- Niche Application Deployment

Schematic AEM*



Anode: $4OH^- \Rightarrow O_2 + 2H_2O + 4e^-$

Cathode: $4H_2O + 4e^- \Rightarrow 2H_2 + 4OH^-$

- 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*

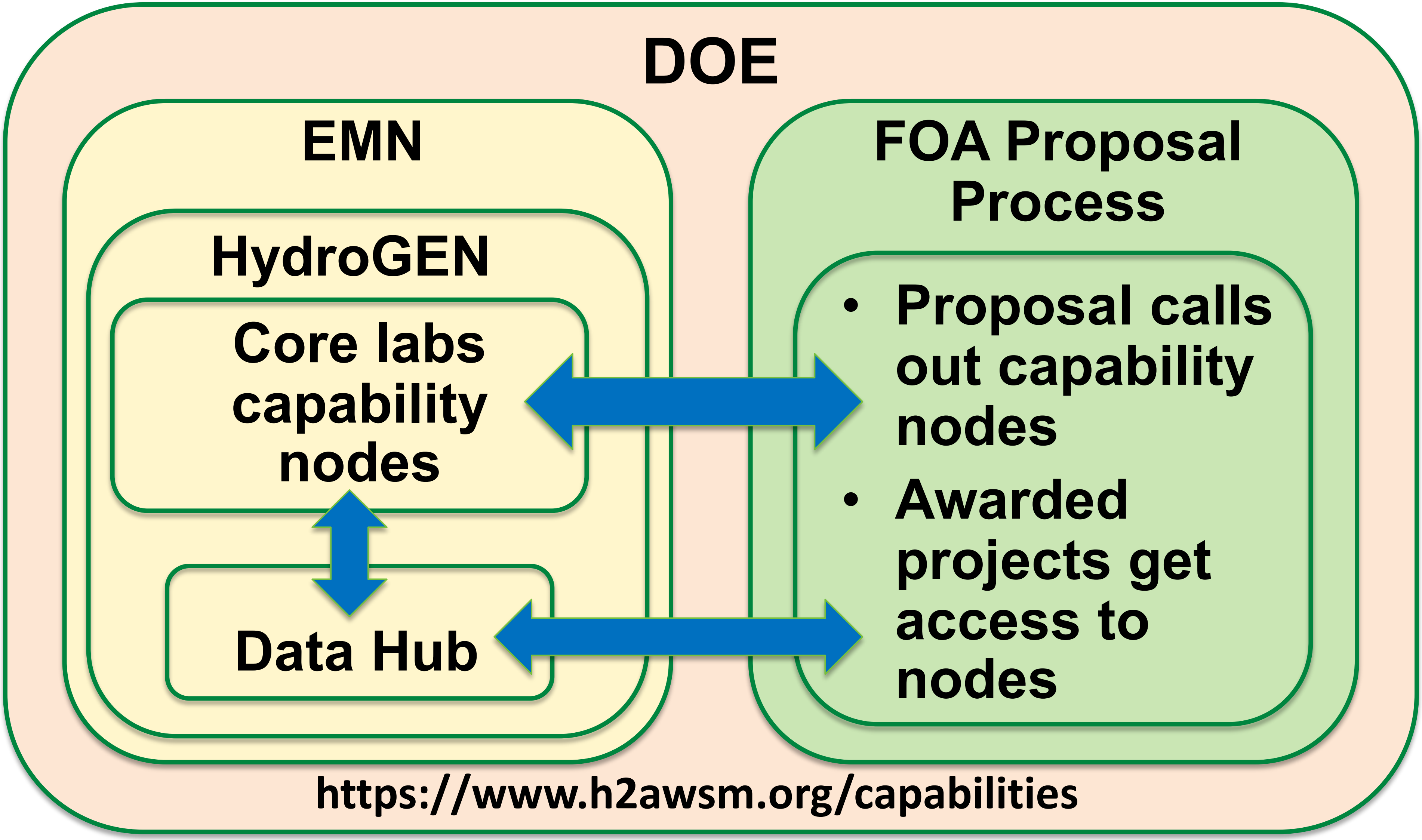
State-of-Art AEM

- 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



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 OnSite / 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

47 nodes for LTE

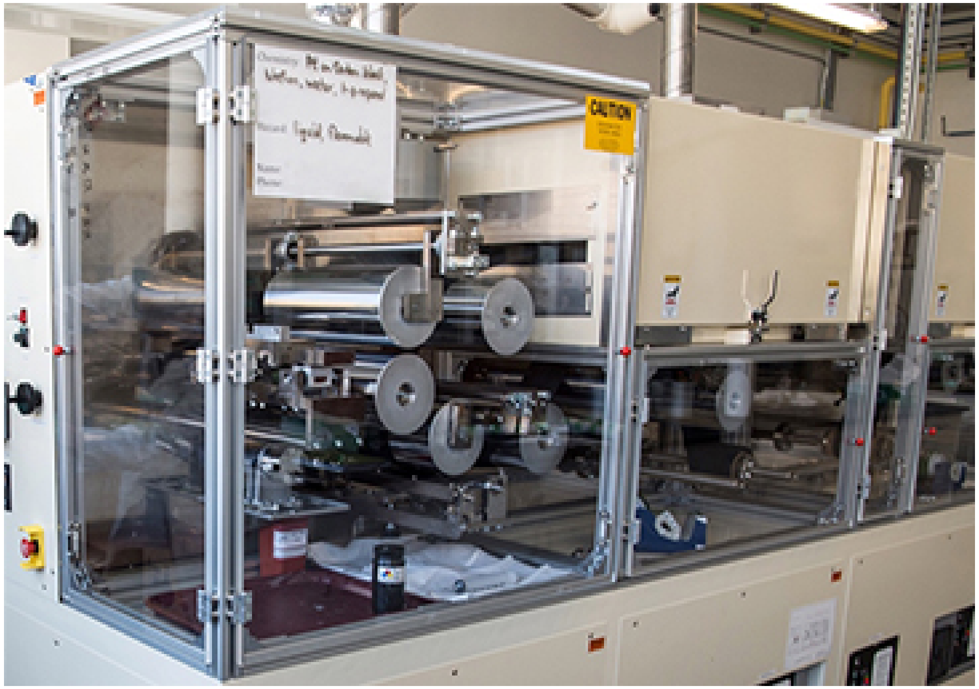
- 20x readiness level 1
- 23x readiness level 2
- 4x readiness level 3

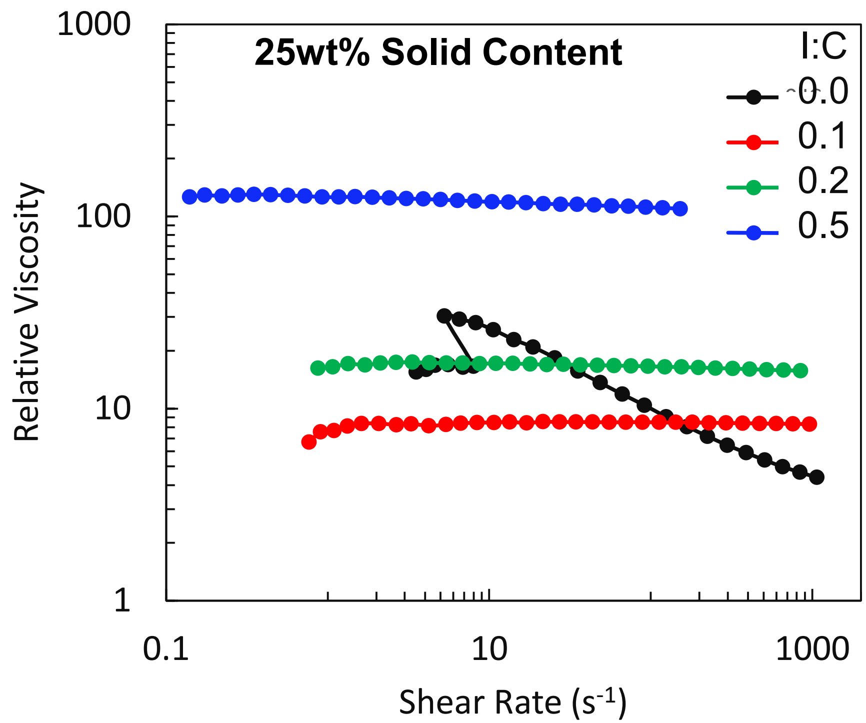
13 nodes used by current LTE projects

Node Classification

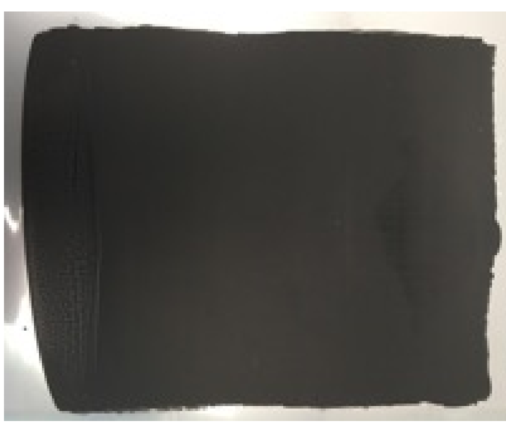
6x Analysis
14x Benchmarking
24x Characterization
13x Computation
10x Material Synthesis
10x Process and Manufacturing Scale-Up
2x System Integration

Accomplishments and Progress:
Ink Formulation Studies for Engineered Electrode Fabrication





NREL sample IrOx coating



Rheology and zeta potential measurements by NREL node show Nafion ionomer stabilizes IrO_x ink against agglomeration

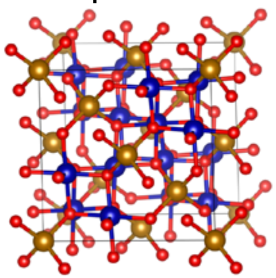
- **Node personnel interacts frequently with Proton OnSite to ensure relevance**
- **Future studies to include new materials: Pt black, high surface area IrO_x**

M. Ulsh: MN019, 6/13/18 Wed.

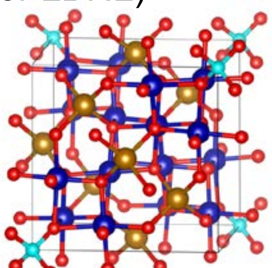
Accomplishments and Progress: Computation Nodes

- Understand factors that improve electronic conductivity of cobalt oxide
- Develop structural models of (meso-porous) cobalt oxide using a combination of DFT simulations and lattice Monte Carlo simulations.
- The developed models will be validated by characterization in future.

LLNL: study effect of defects on conductivity of Co_3O_4
(develop structural motifs for LBNL)



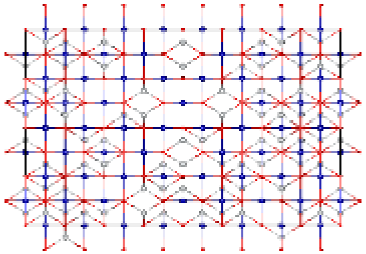
Co_3O_4 crystal

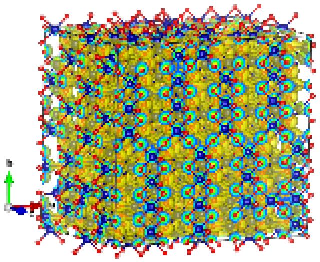


C substitution of Co

Completed:
Modeling of O vacancies, C substitution of Co and O
Ongoing:
Analysis of their electronic structures
Remaining:
C interstitials & N defects simulation being prepared

LBNL: construct realistic disordered structural models using a lattice Monte Carlo (L-MC) and classical potential





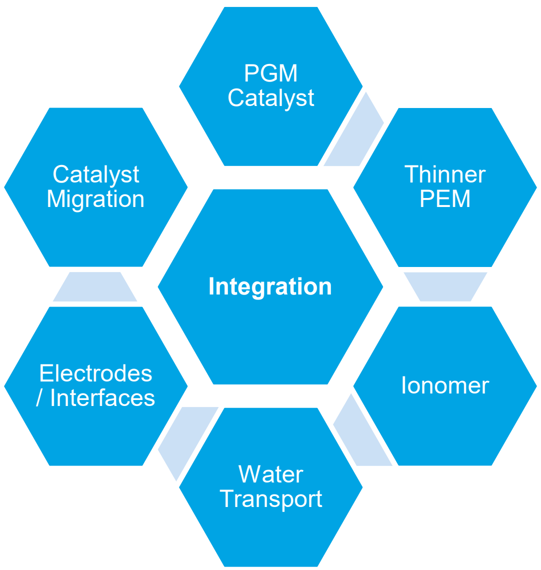
Completed:
L-MC code and potential tested for simple case (left)
Ongoing:
Analysis of the electronic structure (right)
Next:
Incorporate motifs developed by LLNL

⇒ Realistic structural models of mesoporous cobalt oxide is being developed by fully leveraging expertise at LBNL and of LLNL nodes

D.J. Liu, PD157, 6/13/18 Wed.

Accomplishments and Progress: 5 HydroGEN LTE Seedling Projects

Proton Project (PD155)
PI: K. Ayers



ANL Project (PD147)
PI: D.J. Liu
PGM-free OER Catalyst: MOF, M-ZIF,
Porous Nano-Network Electrode (PNNE)

NEU Project (PD156)
PI: S. Mukerjee
PGM-free OER & HER Catalyst
Novel AEM and Ionomers
Electrodes

LANL Project (PD158)
PI: H. Chung
PGM-free OER Perovskites Catalyst

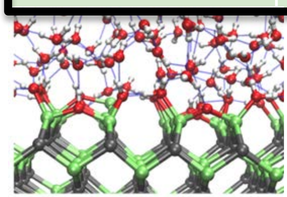
LANL Project (PD159)
PI: Y.S. Kim
Durable & economically-affordable AEM

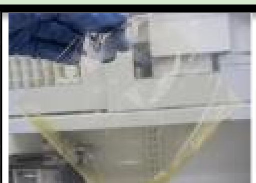
Near Term
PEM, Understanding and improving materials

Longer Term
AEM; Developing and understanding materials

Collaboration and Coordination - Node Utilization

Core Lab	Node	Proton	ANL	NEU	LANL1	LANL2
LLNL	Computational Materials Diagnostics and Optimization of Photoelectrochemical Devices		✓			
LBNL	DFT and Ab Initio Calculations for Water Splitting Including Real-Time Time-Dependent Density Functional Theory		✓		✓	
LBNL	Multiscale Modeling of Water-Splitting Devices	✓		✓		✓
SNL	LAMMPS			✓		
SNL	Separators for Hydrogen Production				✓	
NREL	Novel Membrane Fabrication and Development for Low Temperature Electrolysis and PEC	✓		✓		
NREL	Multi-Component Ink Development, High-Throughput Fabrication, and Scaling Studies	✓	✓	✓		





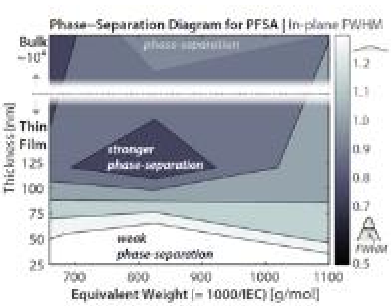
Computation

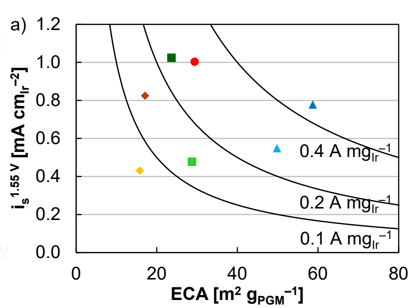
Processing & Scale Up

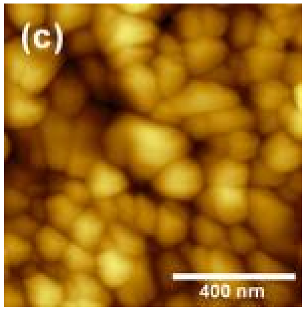
Material Synthesis

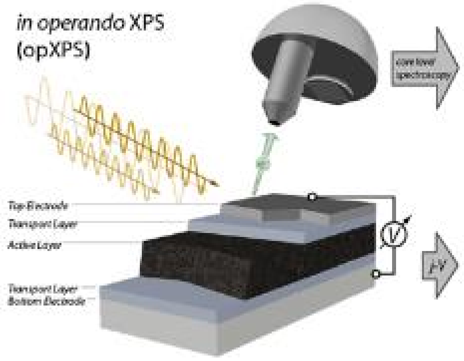
Collaboration and Coordination - Node Utilization

Core Lab	Node	Proton	ANL	NEU	LANL1	LANL2
SNL	Advanced Electron Microscopy		✓			
NREL	Electrolysis Catalyst Synthesis, Ex situ Characterization and Standardization	✓	✓			
LBNL	Ionomer Characterization and Understanding	✓		✓		✓
LBNL	In-Situ and Operando Nanoscale Characterization Capabilities for Photoelectrochemical Materials and Integrated Assemblies	✓				
NREL	In Situ Testing Capabilities for Hydrogen Generation (1kW–250 kW)	✓		✓	✓	
NREL	Surface Analysis Cluster Tool		✓		✓	







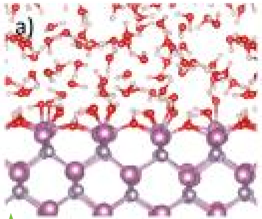


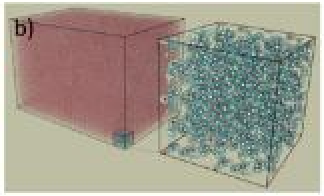
Characterization

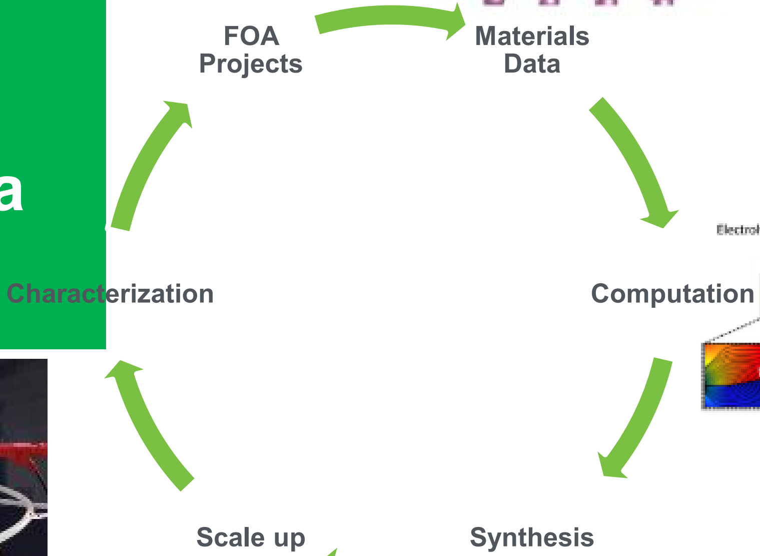
Collaboration and Coordination - Statistics

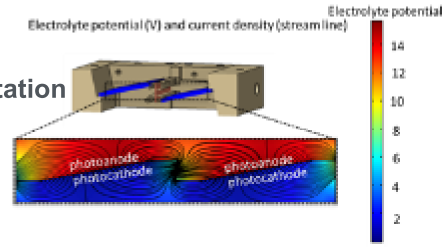
PROTON ON SITE nel number one by nature — YOUR SOURCE FOR ALL THINGS HYDROGEN | Argonne NATIONAL LABORATORY | Northeastern University Center for Renewable Energy Technology | Los Alamos NATIONAL LABORATORY EST. 1943

- Exchanged Samples: 73
- Personnel involved: 62
- Data shared through data hub:
  - 21 files
  - >20GB imaging data
  - structural model







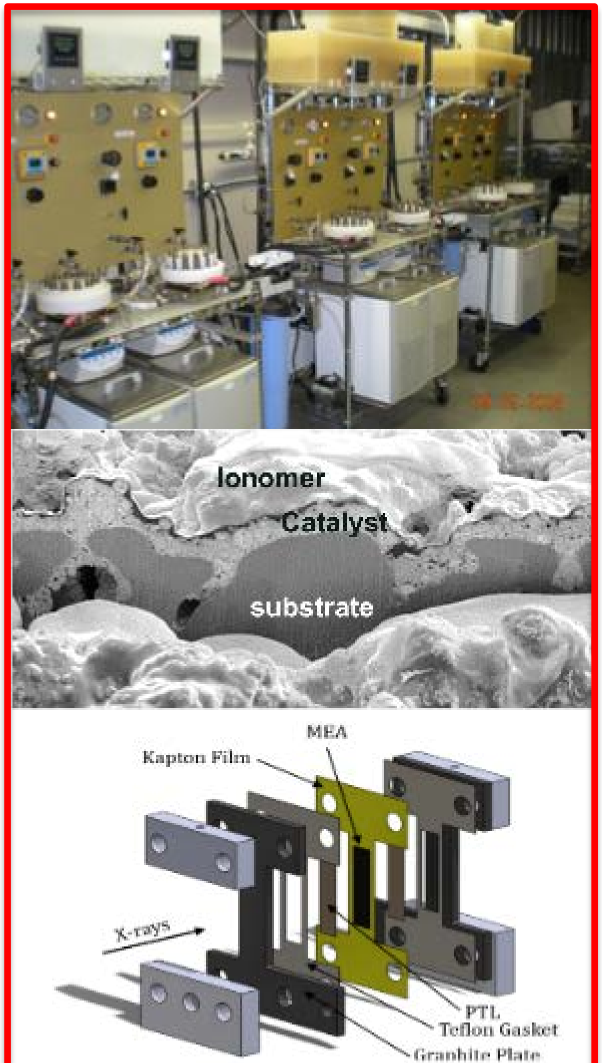


Accomplishments and Progress – Case Study

PROTON ON SITE nel · YOUR SOURCE FOR ALL THINGS HYDROGEN | Tufts University School of Engineering | Oak Ridge National Laboratory | NREL National Renewable Energy Laboratory | Berkeley Lab | 7

ProtonOnsite: High Efficiency PEM Water Electrolysis

- **Integration of advanced cell designs and materials**
  - Catalyst composition
  - Stable 3-D structures
  - Thinner membranes
  - Robust manufacturing
  - Optimized interfacial layers
- **Fundamental characterization and modeling of performance**
  - Water transport
  - Catalyst migration
- **Phase I: Define reliable MEA configuration with high efficiency through new catalyst materials and optimized membrane processing**



Statistics

- Samples Exchanged: 30
- Personnel Involved: 22
- Files shared through data hub: 6

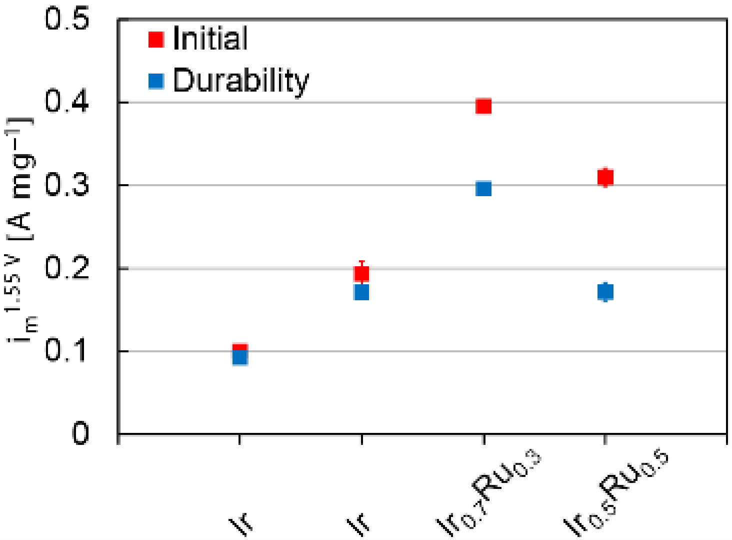
K. Ayers, PD155, 6/13/18 Wed.

Accomplishments and Progress – Case Study

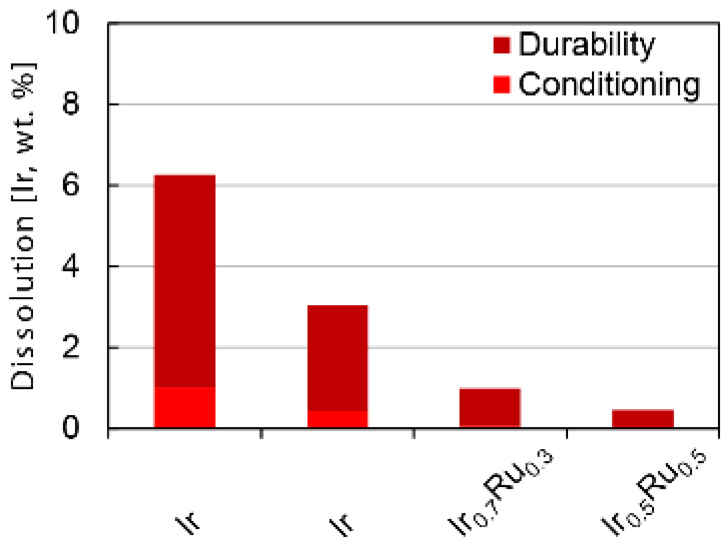
National Lab	Capability	Node Role/Task
LBNL	Multiscale Modeling of Water-Splitting Devices	Water transport modelling in cell operating with differential pressure and liquid water on the anode
NREL	Novel Membrane Fabrication and Development for Low Temperature Electrolysis and PEC	Membrane characterization, including Fenton's test for membrane durability, IEC, and Fluoride emission measurement of effluent.
NREL	Multi-Component Ink Development, High-Throughput Fabrication, and Scaling Studies	Study electrode ink formulation and mixing; ink characterization. Show pathway to scaled fabrication of advanced electrolysis electrodes.
NREL	Electrolysis Catalyst Synthesis, Ex situ Characterization and Standardization	Feasibility assessment/benchmark measurements for improved predictability of OER device performance
LBNL	Ionomer Characterization and Understanding	Development of EC-AFM to characterize catalyst dissolution and morphology degradation in-situ
LBNL	In-Situ and Operando Nanoscale Characterization Capabilities for Photoelectrochemical Materials and Integrated Assemblies	Convert water, void, and solid volumes into modeling domains. Multiphysics transport and reaction kinetics model, along with resistances and domains provided by Tufts, to assess the overall device overpotentials
NREL	In Situ Testing Capabilities for Hydrogen Generation (1kW–250 kW)	External validation and characterization of advanced MEAs and baseline MEAs

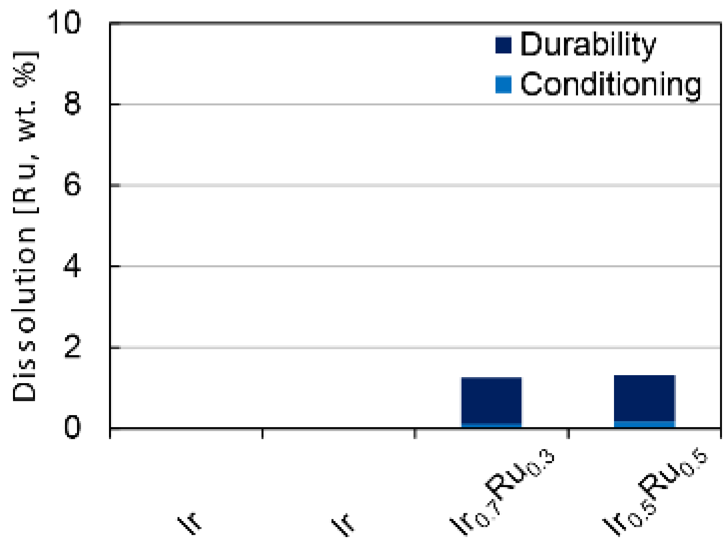
Computation | Material Synthesis | Processing & Scale Up | Characterization

Accomplishments and Progress – Case Study Advanced Catalysts: Ex-Situ Testing Node



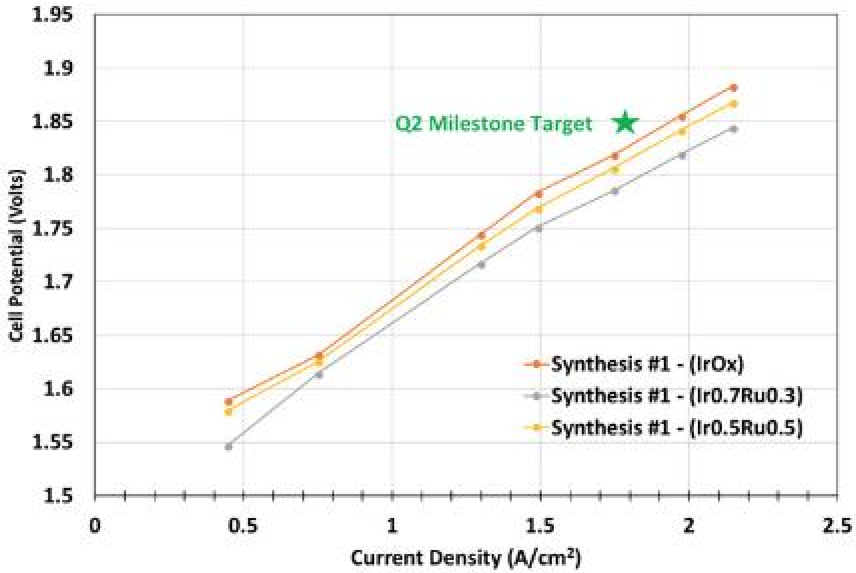
- $Ir_{0.7}Ru_{0.3}$ showed higher initial activity and durability than $Ir_{0.5}Ru_{0.5}$
- Conditioning & durability protocols impact metal dissolution
  - Weaker on IrRu alloys
  - Stronger on pure Ir
- Low metal dissolution suggests:
  - Presence of metal oxides
  - Catalysts are sufficiently stable for MEA testing

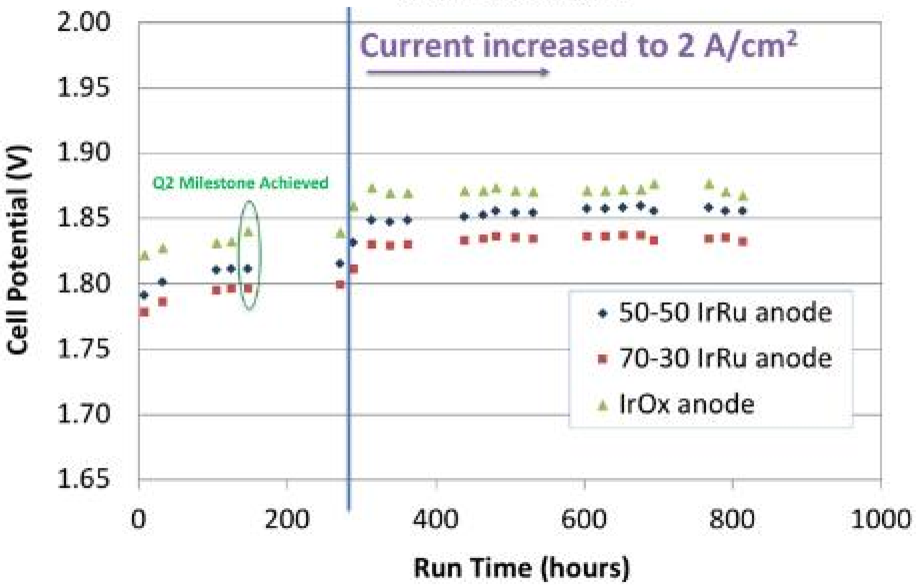




*Activities at 1.55V; ** Durability after 2.0V over 13.5h

Accomplishments and Progress – Case Study Advanced Catalysts: In-Situ Cell Testing

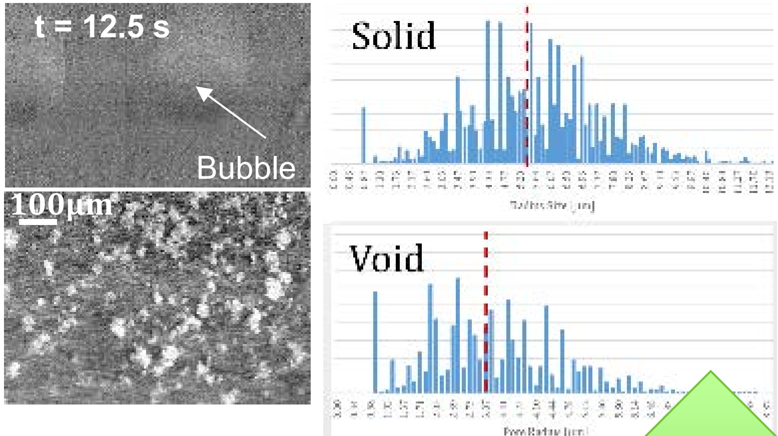




- Example Accomplishments by Project Lead
- Various synthesized catalysts met the Q2 milestone performance target (★, 1.8A/cm^2, 1.85V)
- Achieved 800 h durability at target current density (1.8 A/cm^2), and beyond
- Ex-situ (node) dissolution results correlate with the in-situ MEA performance results (project lead)

Accomplishments and Progress – Case Study Characterization Feeds Modeling

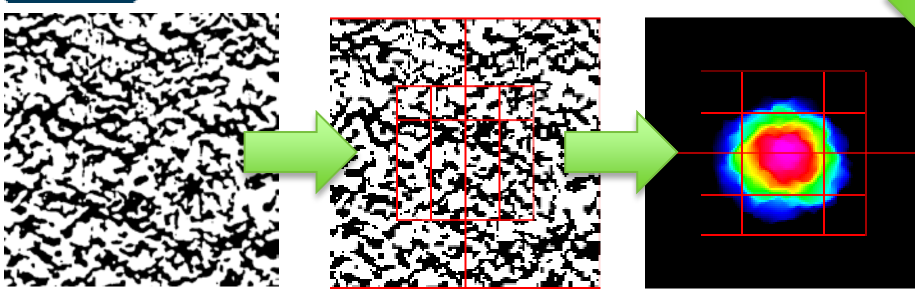
Characterization / Imaging



- **Materials Genome Initiative (MGI) Approach: Discover new materials guided by theory**
- **In-situ tomography of operating electrolysis cell**
- **In-plane and through-plane analysis of water and O_2 bubble formation**

Sample Selection / Creation

Imaging / Modeling



XCT slice data of particle-based GDL	Adaptive computational model of XCT domain	Porous media pressure from hypothetical O_2 generation site

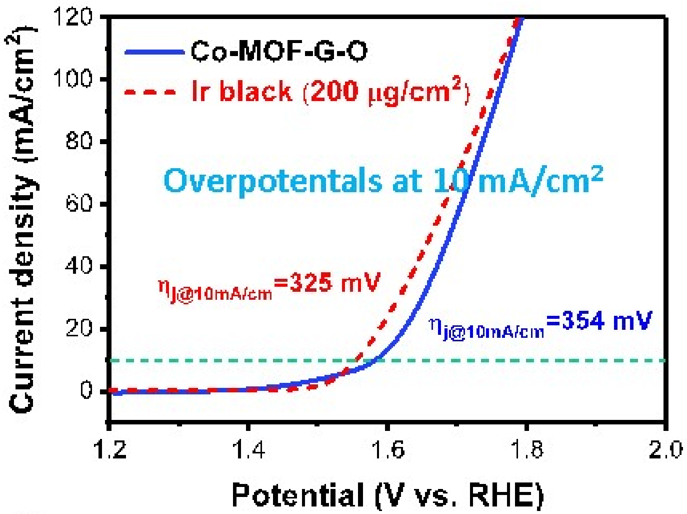
- **Effect of porous transport layer (PTL) density on water transport to catalyst layer**
- **Characterizing, modeling and optimizing transport between catalyst layer and PTL through multiscale modeling**

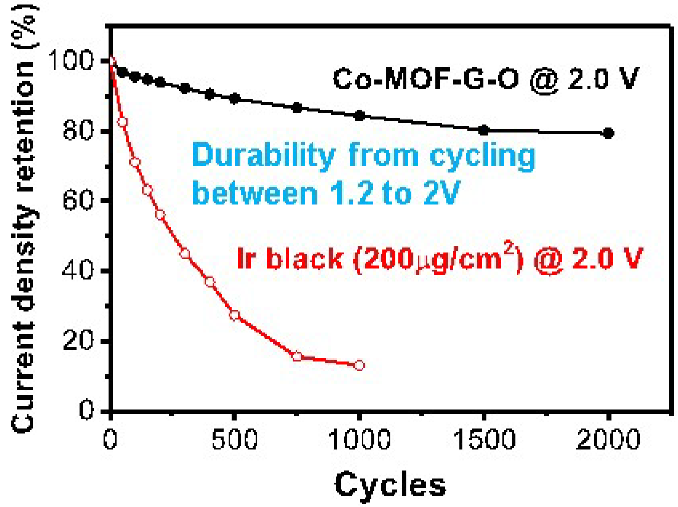
GDL –Gas Diffusion Layer; XCT – X-ray Computed Tomography

Accomplishments and Progress – Project Summary

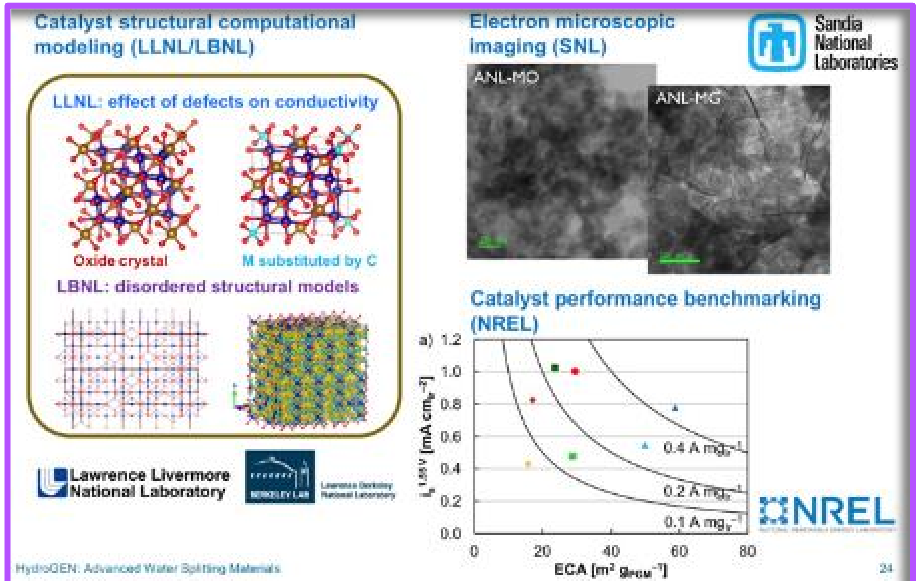
Argonne National Laboratory | University at Buffalo, The State University of New York | GINER | Sandia National Laboratories | NREL National Renewable Energy Laboratory | Berkeley Lab | Lawrence Livermore National Laboratory | 6

Developing Novel PGM-Free Catalysts for Alkaline Hydrogen and Oxygen Evolution Reactions





- **Targeting 20x reduction of anode catalyst cost by using PGM-free materials**
- **Approach based on metal-organic framework (MOF) OER catalysts**
- **Initial Co-MOF-G-O catalyst comparison with 0.2 mg/cm² loaded Ir black electrodes:**
  - **Approaching same activities (ex-situ)**
  - **Exceeds durability**

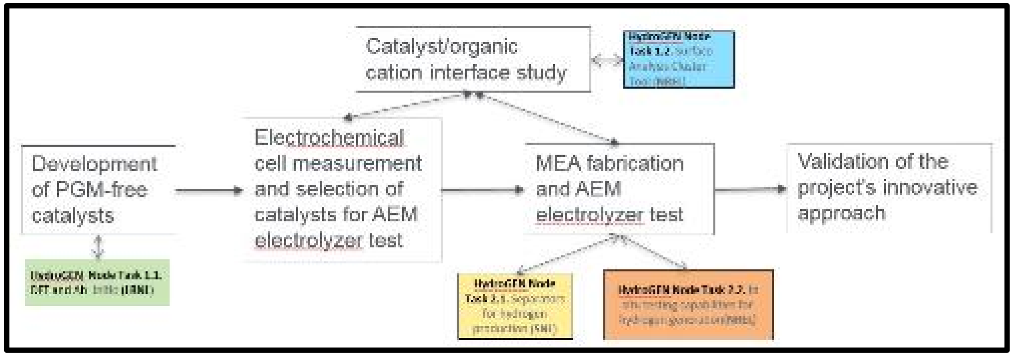


D.J. Liu, PD157, 6/13/18 Wed.

Accomplishments and Progress – Project Summary

Los Alamos NATIONAL LABORATORY | PAJARITO POWDER FUEL CELL CATALYSTS | Sandia National Laboratories | NREL NATIONAL RENEWABLE ENERGY LABORATORY | BERKELEY LAB | 4

High-Performance Ultralow-Cost Non-Precious Metal Catalyst System for AEM Electrolyzer

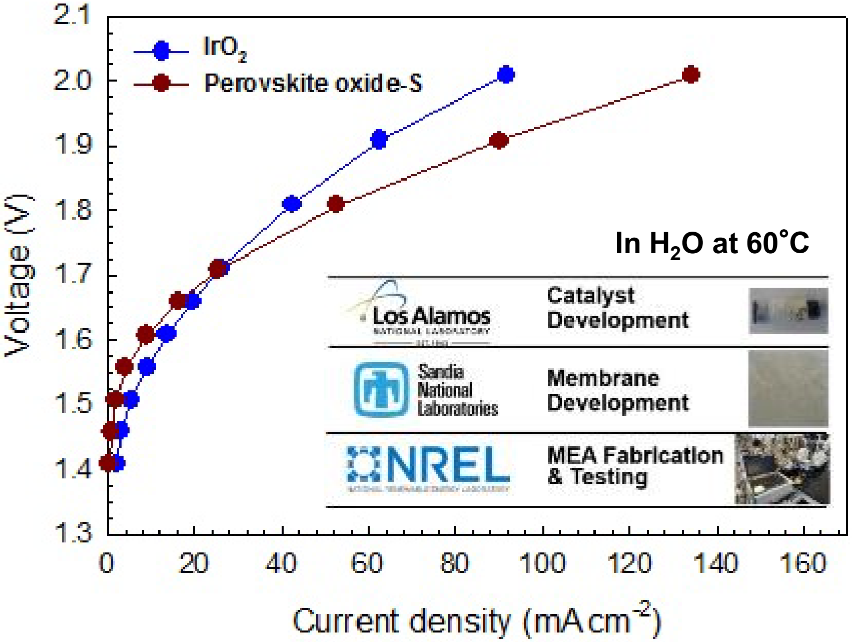


OER Catalyst Go/No-Go:

(1) 5.1 mA/cm² at 1.65 V vs RHE

(2) the same degradation rate compared with IrO_2 catalyst

Catalyst	Current density (mA/cm²) in 0.1 M KOH		Current density (mA/cm²) in 0.1 M BTMAOH	
	initial	after 1000 cycles	initial	after 1000 cycles
IrO_2	5.5	1.9	1.0	0.2
Perovskite oxide-S	3.1	2.0	4.1	1.8
Perovskite oxide-A	2.5	0.9	-	-
Perovskite oxide-B	4.4	2.5	5.5	3.9
Perovskite oxide-C	3.8	2.7	6.8	5.3
Perovskite oxide-D	3.9	2.7	6.2	4.8
Perovskite oxide-E	4.1	3.4	5.2	2.7



- **Targeting high AEM performance without feeding alkaline solution**
- **Ex-situ characterization of 6 LANL PGM- and carbon-free OER catalysts**
- **Promising first results with baseline perovskite oxide-S (ex-situ & in-situ)**

H. Chung, PD158, 6/13/18 Wed.

Scalable Elastomeric Membranes for Alkaline Water Electrolysis

Styrene-Ethylene-Butylene-Styrene Block Copolymer

- **Robust polymer backbone**

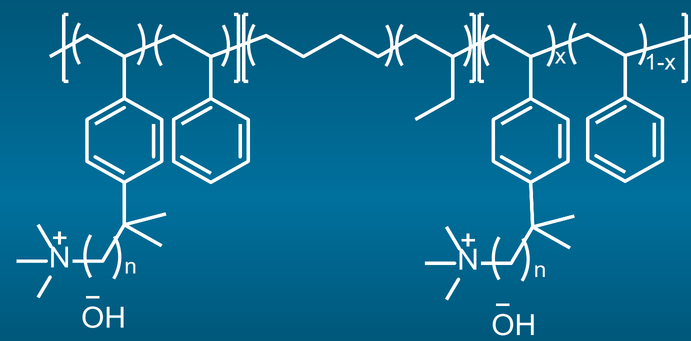
→ No aryl-ether polymer backbone provides chemical stability.

- **Block copolymer architecture**

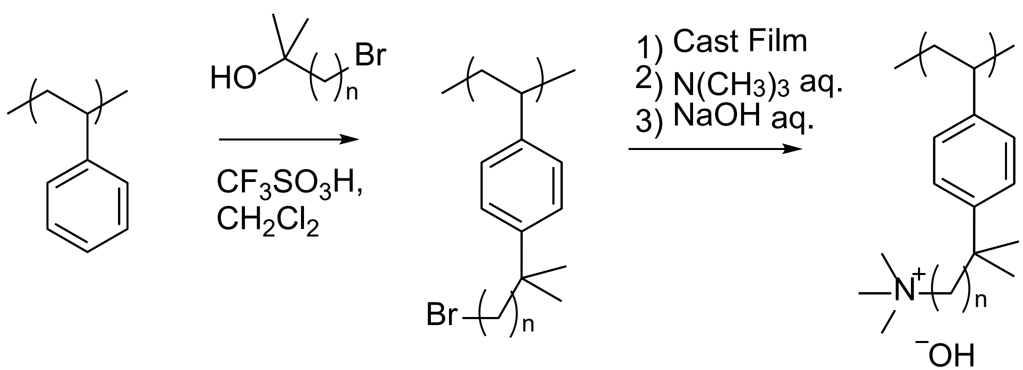
→ Soft block provides toughness under dry & wet conditions.

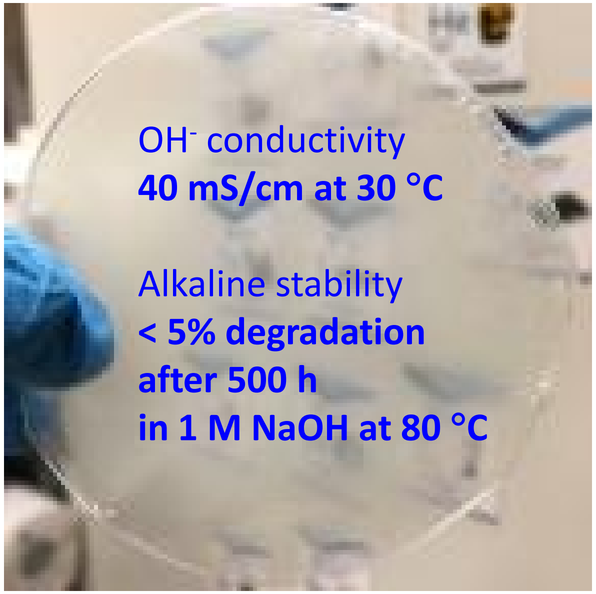
- **Cheap base polymer**

→ Various SEBS are commercially available on the market.



Friedel-Crafts Alkylation

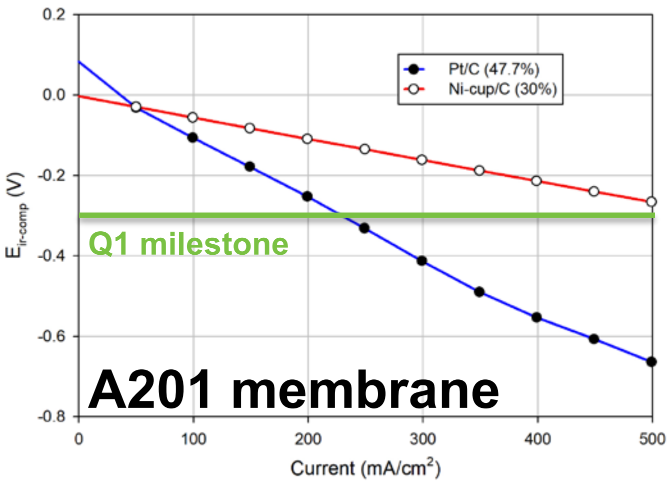




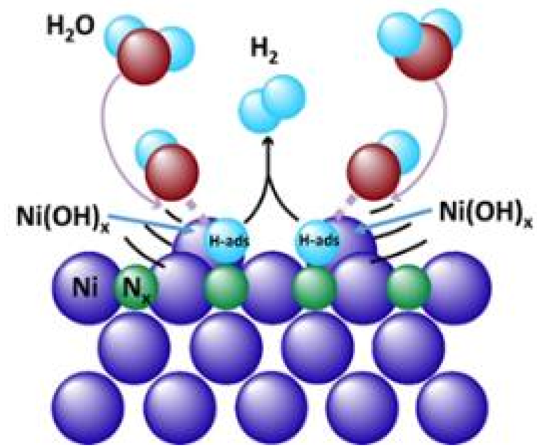
Y.S. Kim, PD159, 6/13/18 Wed.

Developing Novel PGM-Free Catalysts for Alkaline HER and OER Evolution

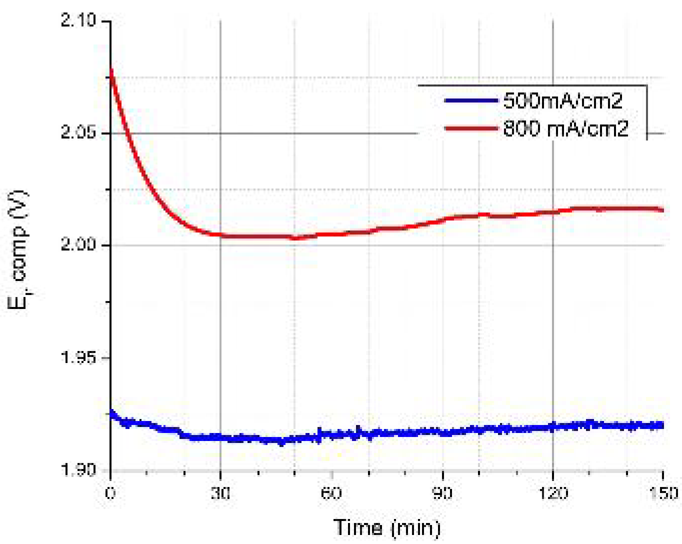
H_2 Pump - Performance



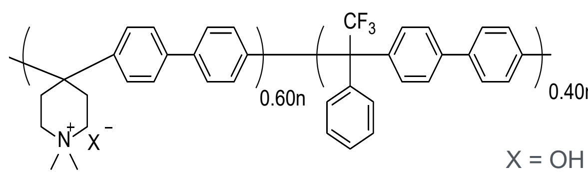
Catalyst



Electrolysis Mode - Steady State



Membrane / Ionomer



Temp. (°C)	Conductivity (mS/cm)	Water uptake (wt%)	Swelling ratio (%)
50	90	27	9
60	104.1	28	10
70	116.5	29	11
80	130.9	30	12
90	142.4	33	13
95	150.5	35	14

- **Develop AEM electrolysis**
  - **PGM-free HER and OER catalysts**
  - **AEM membranes and ionomers**
  - **Electrodes**
- **Targeting < \$2/kg$_{H2}$ with efficiency of 43 kWh/kg H_2**

S. Mukerjee, PD156, 6/13/18 Wed.

Accomplishments and Progress – Benchmarking

- Collaboration with Proton 2B Benchmarking Project
- Node feedback on questionnaire & draft test framework on material, component, and device level properties:
  - Ex-situ material testing
  - In-Situ testing at simulated conditions
  - In-Situ testing at operating conditions
- All HydroGEN LTE node capabilities were assessed for AWS technology relevance and readiness level

Summary - HydroGEN LTE Projects

- **HydroGEN structure promoting research and development of advanced materials for water splitting devices**
- **EMN structure supports interaction and collaboration between core capabilities of national labs and funded project partners**
- **5 LTE projects funded across PEM and AEM technologies**
- **Ongoing data, information, and personnel exchange for improved collaboration**

Future Work

- **Leverage HydroGEN Nodes at the labs to enable successful achievement of Phase 1 project Go/No-Go's**
  - Increased durability and lifetime
  - Rational design of catalysts, electrode structures and cells
  - Understanding the role of ionomers and electrified interfaces
- **Enable research in Phase 2 work for some projects and enable new seedling projects**
- **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**

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

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HydroGEN
Advanced Water Splitting Materials

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Technical Backup Slides

Summary – Case Study

- **Case study highlights HydroGEN consortia approach**
  - **FOA projects bring technical challenges and advanced materials**
  - **Nodes collaborate to help resolve challenges, enhance scientific effort**
- **Proton project statistics: 3 partners, 7 nodes**

  $\Rightarrow$ 22 personnel + 30 samples
- **Q2 milestone achieved: 3 OER catalysts meet performance target <1.85V @ 1.8 A/cm^2 over 800 hrs**
  - **OER catalyst prescreened at NREL node for activity and stability**
- **EMN approach allows for longer path length deep dives into understanding fundamental properties of AWS materials**
  - **Multiscale modeling integrated with in situ tomography (MGI approach) to understand water consumption at interfaces**
  - **Membrane and MEA fabrication after understanding ionomer, ink and dispersion fundamentals translate to in-situ cell testing of advanced materials**

LTE Presentations & Papers

Presentations

1. "Low Temperature Electrolysis for Hydrogen and Oxygen Generation - a Tutorial on Catalyst and Electrode Development for Proton and Anion Exchange Membrane-Based Systems", K.E. Ayers, (Invited), 233rd Electrochemical Society Meeting, Seattle, WA, May 2018.
2. "Carbon-Free Perovskite Oxide Oxygen Evolution Reaction Catalysts for AEM Electrolyze", H. T. Chung, A. S. Lee, Y. S. Kim, C. Fujimoto, L. W. Wang, G. Teeter, G. Bender, and P. Zelenay, 233rd Electrochemical Society Meeting, Seattle, WA, May 2018.
3. "HydroGEN LTE/HTE Benchmarking Discussion", organized by K. E. Ayers, H. Dinh, and N. Danilovic, 233rd ECS, Seattle, WA, May 2018.
4. "Current understanding of the slow kinetics of the hydrogen evolution reaction in alkaline media", S. Mukerjee, J. Li and Q. Jia, (Invited), 233rd Electrochemical Society meeting, Seattle, WA, May 2018
5. "Understanding the improved kinetics of the hydrigen evolution/oxidation reactions of the Pt-oxophilic metal systems in alkaline medium", Q. Jia, J. Li and S.Mukerjee, 233rd Electrochemical Society Meeting, Seattle, WA, May, 2018

Papers

1. "Hydrogen oxidartion reaction in alkaline media: Relationship between electrocatalysis and electrochemical double layer", N. Ramaswamy, S. Ghoshal, M. K. Bates, Q. Jia, J. Li and S. Mukerjee*, Nano Energy, 41 (2017) 765-771
2. "Experimental Proof of the Bifunctional Mechanism for Hydrogen Oxidation", J. Li, S. Ghoshal, M. K. Bates, T. E. Miller, V. Davies, E. Stavitski, K. Attenkofer, S. Mukerjee, Zi-Feng Ma and Q. Jia*, Angewandte Chemie Comm., 56 (2017) 15594