# Foundational low-carbon hydrogen research

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Director of HydroGEN, NREL

20th International Conference on Carbon Dioxide Utilization
Bari, Italy
June 28, 2023

NREL
Transforming ENERGY

ENERGY earthshots U.S. DEPARTMENT OF ENERGY | Hydrogen

# Hydrogen Energy Earthshot

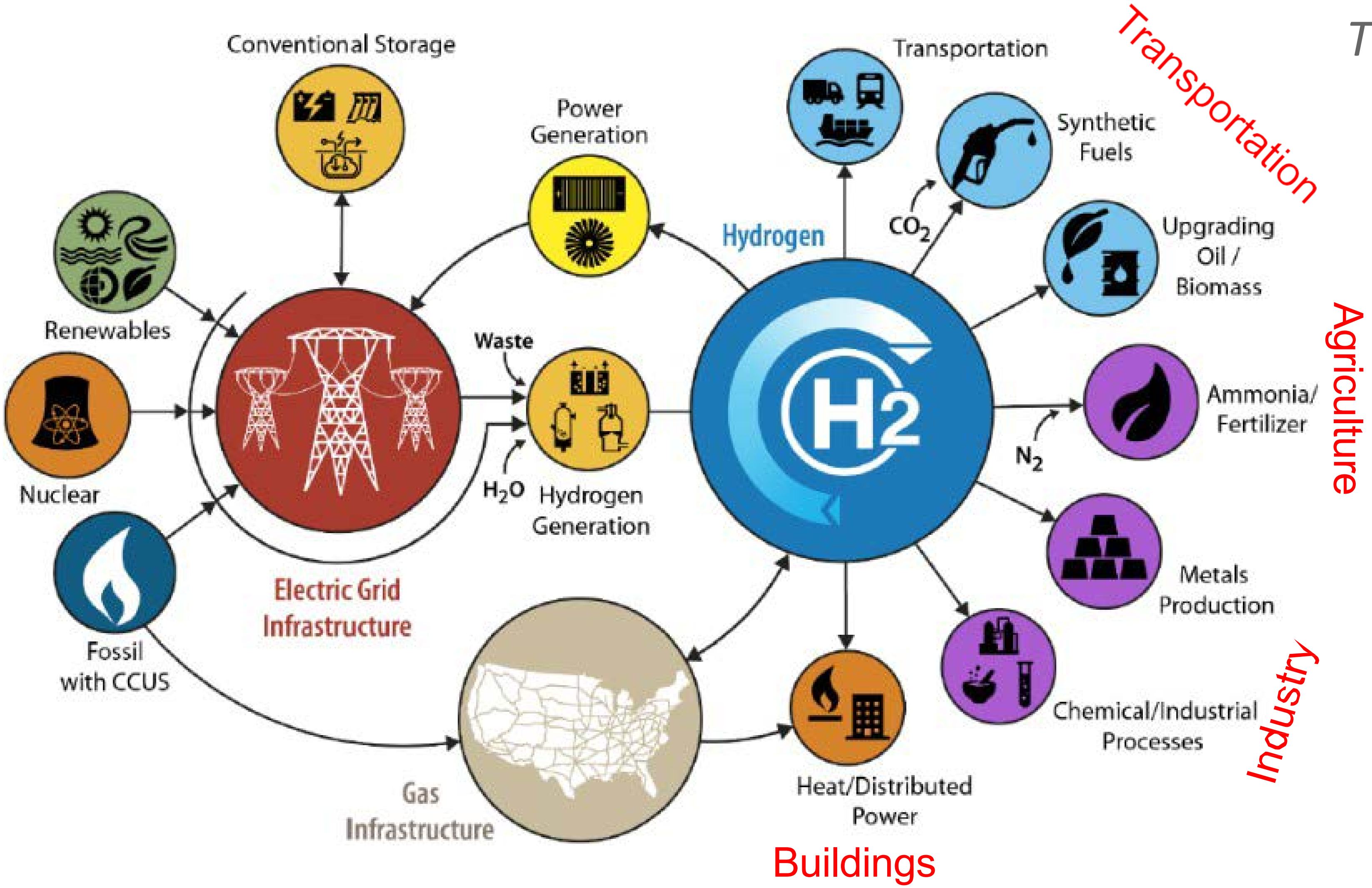
## “Hydrogen Shot”

## “1 1 1”
## $1 for 1 kg clean hydrogen in 1 decade

Launched June 7, 2021
Summit Aug 31-Sept 1, 2021

S. Satyapal, et al., “Overview of DOE RFI Supporting Hydrogen Bipartisan Infrastructure Law Provisions, Environmental Justice, and Workforce Priorities, Feb. 24, 2022

# H2@Scale: Enabling Affordable, Reliable, Clean and Secure energy



Illustrative example, not comprehensive
https://www.energy.gov/eere/fuelcells/h2-scale

## *Transportation and Beyond*

- Large-scale, low-cost hydrogen from diverse domestic resources enables an economically competitive and environmentally beneficial future energy system across sectors
- Hydrogen can address specific applications that are hard to decarbonize
- Today: 10 MMT $H_2$ in the US
- Economic potential: 2x to 4x more

Timeframe is short, competition intense, coordinated effort critical for domestic competitiveness.

# NREL Research Spans MAKE/MOVE/STORE/USE

**Make**

R&D on Advanced Production Technologies

**Move**

Infrastructure Research & Large Scale Demonstration and Deployment

**Store**

Hydrogen Storage Materials and Systems Research

**Use**

Hydrogen Penetration into Heavy-Duty Transportation Sector

Expanding Green Hydrogen Into New End-Use Cases

## NREL's HFCT Program Strategy is on Accelerating Progress & Impact

Energy justice and American jobs are considerations that underly all these efforts.

# National Laboratory Collaboration is Critical for Success

**H2NEW** Hydrogen from Next-generation Electrolyzers of Water
U.S. DEPARTMENT OF ENERGY

**Hydrogen Production**

NREL Transforming ENERGY
INL Idaho National Laboratory
Argonne NATIONAL LABORATORY
BERKELEY LAB Bringing Science Solutions to the World
Lawrence Livermore National Laboratory
Los Alamos NATIONAL LABORATORY EST. 1943
NETL NATIONAL ENERGY TECHNOLOGY LABORATORY
OAK RIDGE National Laboratory
Pacific Northwest NATIONAL LABORATORY

**HydroGEN** Advanced Water Splitting Materials

**Hydrogen Production**

NREL Transforming ENERGY
BERKELEY LAB Bringing Science Solutions to the World
Sandia National Laboratories
Lawrence Livermore National Laboratory
INL Idaho National Laboratory

**BioH2**

**Hydrogen Production**

NREL Transforming ENERGY
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Argonne NATIONAL LABORATORY
Pacific Northwest NATIONAL LABORATORY

**HyMARC** Hydrogen Materials Advanced Research Consortium

**Hydrogen Storage**

Sandia National Laboratories
NREL Transforming ENERGY
Pacific Northwest NATIONAL LABORATORY
Lawrence Livermore National Laboratory
BERKELEY LAB Bringing Science Solutions to the World

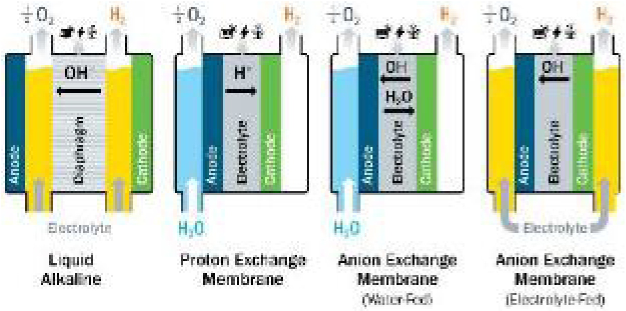
**M2FCT** MILLION MILE FUEL CELL TRUCK
U.S. DEPARTMENT OF ENERGY

**Fuel Cells**

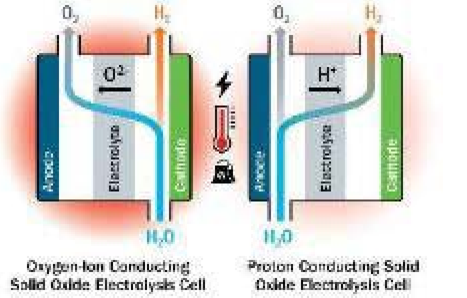
BERKELEY LAB Bringing Science Solutions to the World
Los Alamos NATIONAL LABORATORY EST. 1943
Argonne NATIONAL LABORATORY
NREL Transforming ENERGY
OAK RIDGE National Laboratory

# R&D on Advanced Production Technologies

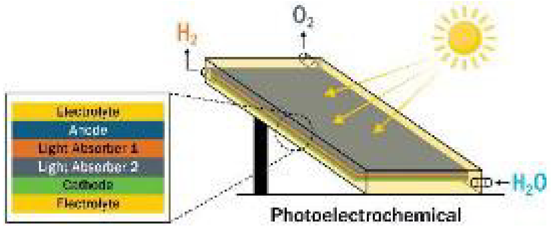
- **Near-term:** focus on electrolysis (water splitting with electricity and nuclear)
  - Accelerate **research on advanced water-splitting** technologies – take advantage of today’s renewable and nuclear power
  - Achieve $100/kW electrolyzer stack goal in just 5 years through **H2NEW** consortium
  - Include research on both low temperature electrolysis [**LTE] (PEM, liquid alkaline), and high temperature electrolysis [HTE] (solid oxide) electrolyzer** technologies
  - *$1B BIL activity now enables an* order of magnitude increase in effort on electrolysis to accelerate development
- **Longer-term:** Use solar energy or heat to more directly split water
  - Photoelectrochemical (PEC) and solar thermochemical (STCH) $H_2$ production
  - Incubate and support promising technology development through **HydroGEN** consortium



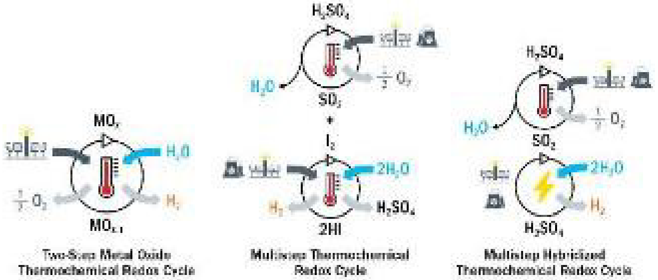
**LTE**



**HTE**



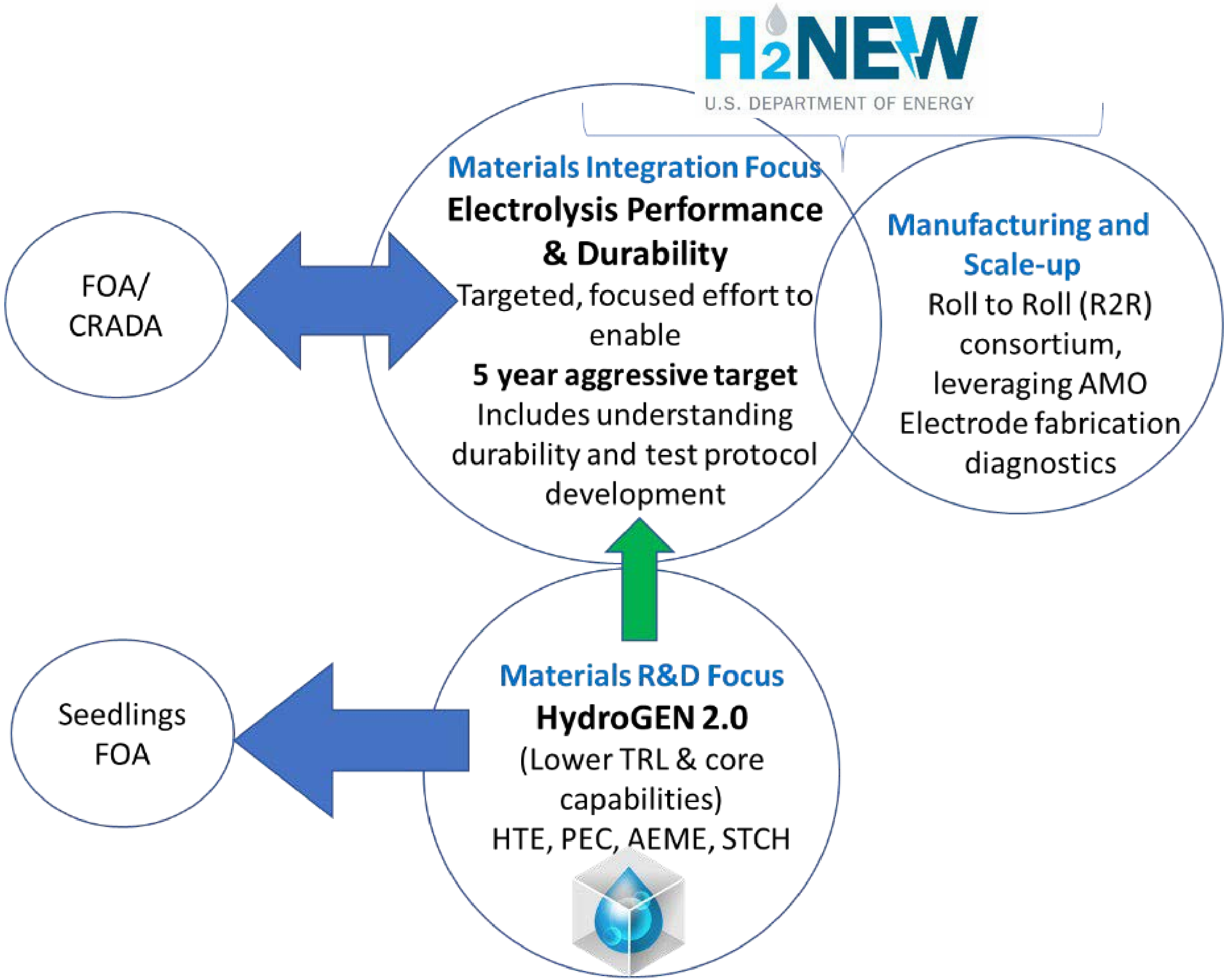
**PEC**



**STCH**

S. Alia, D. Ding, A. McDaniel, F. M. Toma, H.N. Dinh, “**How to Make Clean Hydrogen AWSM:** ***The Advanced Water Splitting Materials Consortium” ECS Interface, 30(4) Winter 2021.***

# HydroGEN Materials R&D Feeds to H2NEW Materials Integration



**Materials Integration Focus**

**Electrolysis Performance & Durability**

Targeted, focused effort to enable

**5 year aggressive target**

Includes understanding durability and test protocol development

**Manufacturing and Scale-up**

Roll to Roll (R2R) consortium, leveraging AMO

Electrode fabrication diagnostics

**Materials R&D Focus**

**HydroGEN 2.0**

(Lower TRL & core capabilities)

HTE, PEC, AEME, STCH

H2NEW | Hydrogen from Next-generation Electrolyzers of Water

U.S. DEPARTMENT OF ENERGY

- **Polymer electrolyte membrane (PEM) electrolysis**
- **Oxygen-conducting solid oxide electrolysis (SOEC)**
- **Liquid alkaline electrolysis**

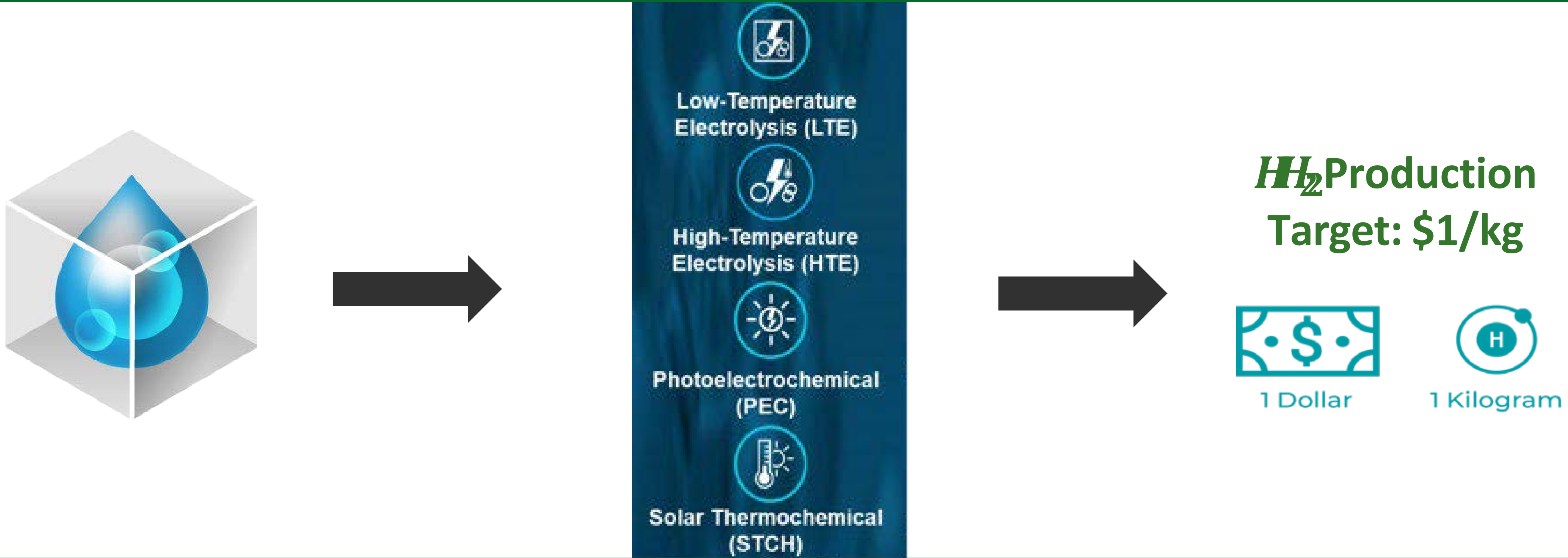
HydroGEN **2.0 (lower TRL AWS)**

- **Alkaline exchange membrane (AEM) electrolysis**
- **Metal-supported SOEC (MS-SOEC)**
- **Proton-conducting SOEC (p-SOEC)**
- **Photoelectrochemical (PEC)**
- **Solar thermochemical (STCH)**

# HydroGEN Consortium Goal

***Website: https://www.h2awsm.org/***

Goal: Accelerate foundational R&D of innovative materials for advanced water splitting (AWS) technologies to enable clean, sustainable, and low-cost (\$1/kg $H_2$) hydrogen production.



**$H_2$ Production Target: \$1/kg**

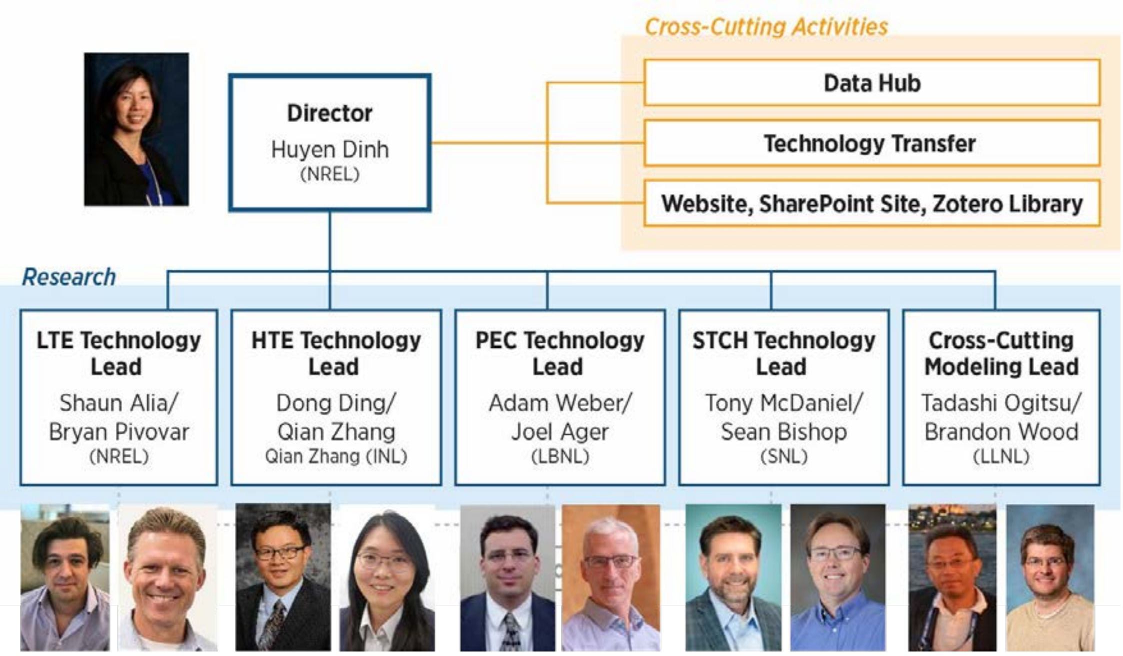
***HydroGEN is focused on early-stage R&D in $H_2$ production and fosters cross-cutting innovation using theory-guided applied materials R&D to advance all emerging water-splitting pathways for hydrogen production***

# HydroGEN Lab R&D + Lab Capability Support

## EMN Collaboration and Approaches

### HydroGEN 2.0: Lab R&D

Early-Stage Materials R&D Projects



*Cross-Cutting Activities*

- Data Hub
- Technology Transfer
- Website, SharePoint Site, Zotero Library

**Director**
Huyen Dinh
(NREL)

*Research*

| LTE Technology Lead | HTE Technology Lead | PEC Technology Lead | STCH Technology Lead | Cross-Cutting Modeling Lead |
|---|---|---|---|---|
| Shaun Alia/<br>Bryan Pivovar<br>(NREL) | Dong Ding/<br>Qian Zhang<br>Qian Zhang (INL) | Adam Weber/<br>Joel Ager<br>(LBNL) | Tony McDaniel/<br>Sean Bishop<br>(SNL) | Tadashi Ogitsu/<br>Brandon Wood<br>(LLNL) |

NREL Transforming ENERGY · INL Idaho National Laboratory · BERKELEY LAB · Sandia National Laboratories · Lawrence Livermore National Laboratory

### HydroGEN 1.0: Lab Support

Lab capabilities + experts support projects

**HydroGEN Materials Capability Network**

**31 Lab – FOA Projects**

**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 FOA Projects**

nel
Argonne National Laboratory
Northeastern University Center for Renewable Energy Technology
Los Alamos National Laboratory (2)
Georgia Institute of Technology
University of Oregon
Chemours

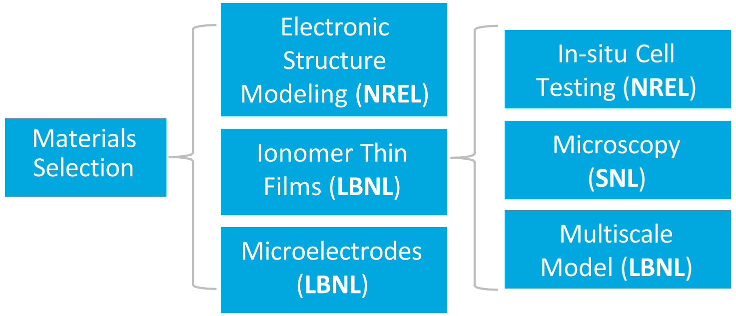
# Enabling High Efficiency, Durable AEM Electrolysis Performance

## LTE Lab R&D Goals and Approach

5 Nodes

**Goals: Determine the role of the supporting electrolyte and the limiting factors behind water operation in AEM electrolysis**

- Evaluate AEM's ability to approach PEM performance/durability
- Elucidate interactions at the ionomer/catalyst interface to assess ionomer stability and catalyst poisoning



Materials Selection

Electronic Structure Modeling (**NREL**)

Ionomer Thin Films (**LBNL**)

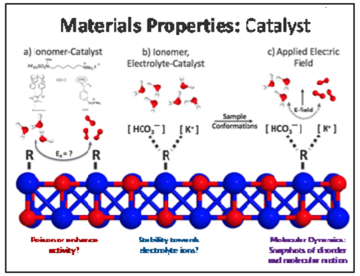
Microelectrodes (**LBNL**)

In-situ Cell Testing (**NREL**)

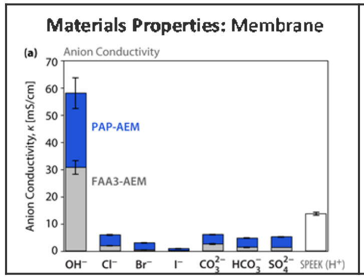
Microscopy (**SNL**)

Multiscale Model (**LBNL**)

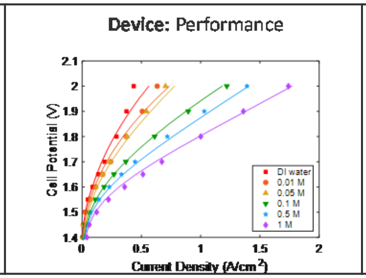
**Materials** → **Devices**



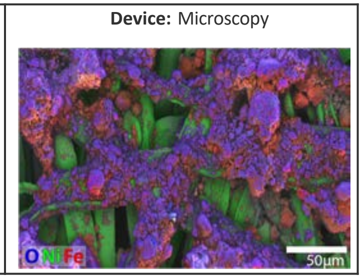
**Materials Properties:** Catalyst



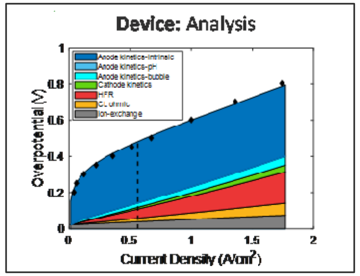
**Materials Properties:** Membrane



**Device:** Performance



**Device:** Microscopy



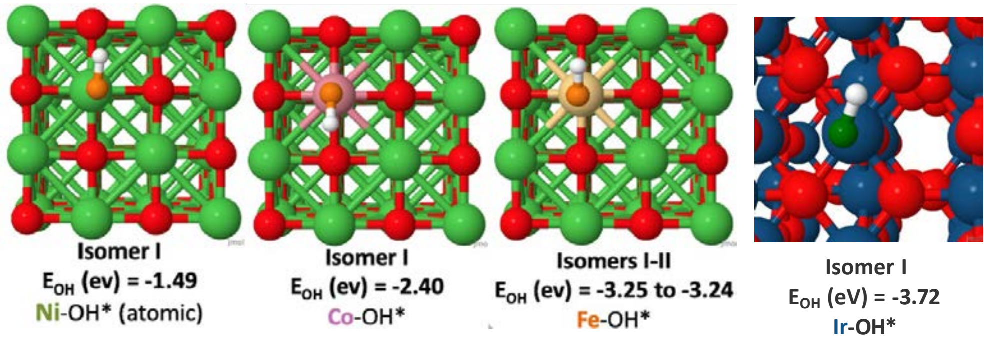
**Device:** Analysis

# Effect of Dopants on Adsorption and Ionomer-Catalyst Interactions

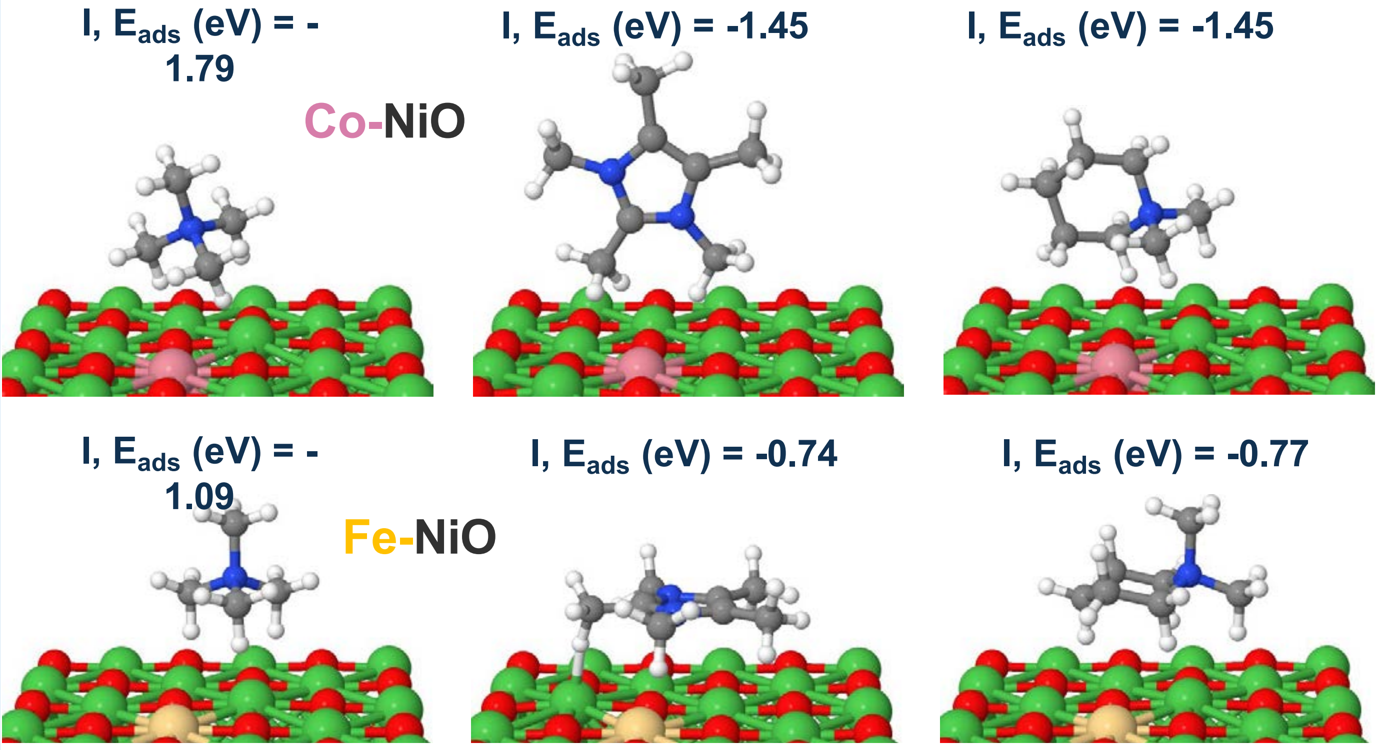
## Doping NiO with Fe or Co *stabilizes* ionomer fragments, incl. ETFE/GEN 2's tetramethylammonium

- Previous calculations showed that on NiO, *ETFE, GEN2 ionomers* are *unstable to demethylation* and *poison active sites*
- New calculations show that **adding Fe and Co *stabilizes tetramethylammonium fragment***

- OH* is *bound more strongly* on Fe- and Co-NiO



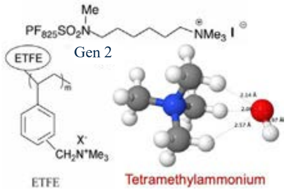
- ***OH* adsorption closer to $IrO_2$'s may increase activity***

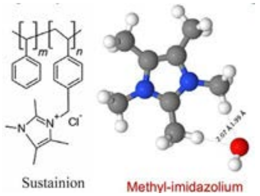


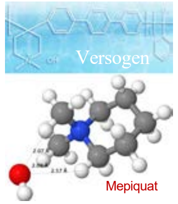
**ETFE/Gen 2 → Stable, Active Sites Available for OH**

**Sustainion → Stable, Active Sites Available for OH**

**Versogen → Stable, Active Sites Available for OH**



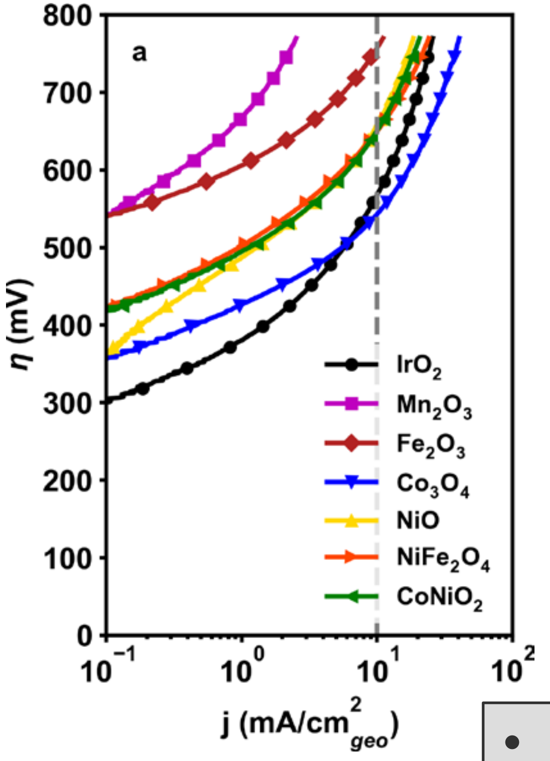




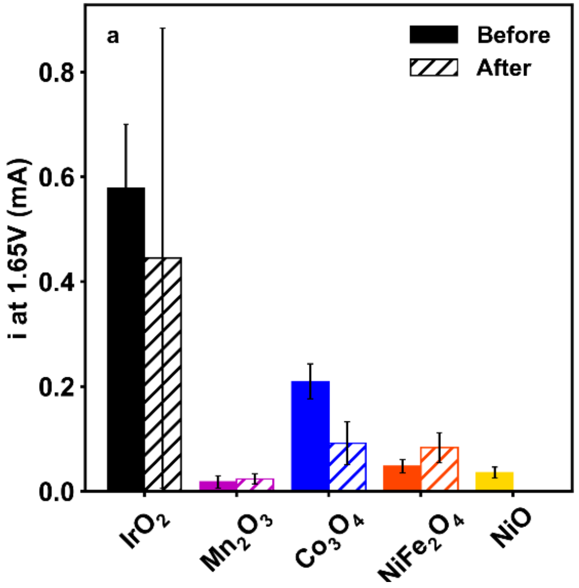
# Catalyst Screening for Oxygen Evolution Reaction (OER)

## Ex-situ Materials Characterization

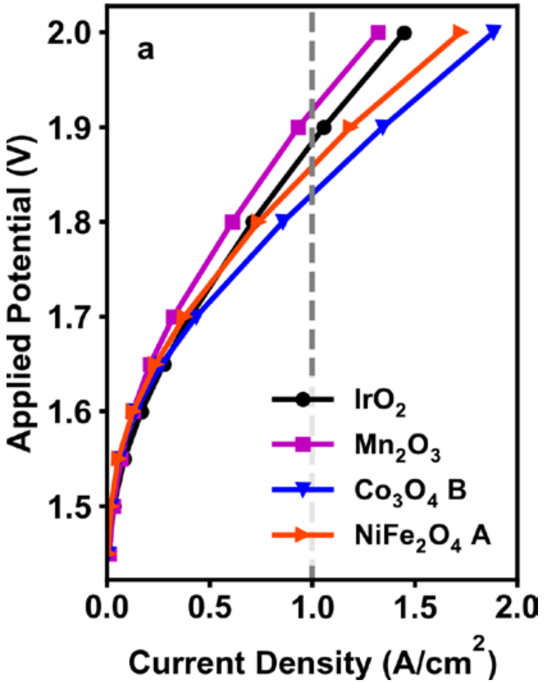
### Performance



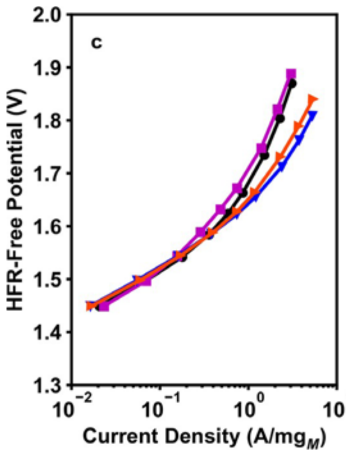
### Durability



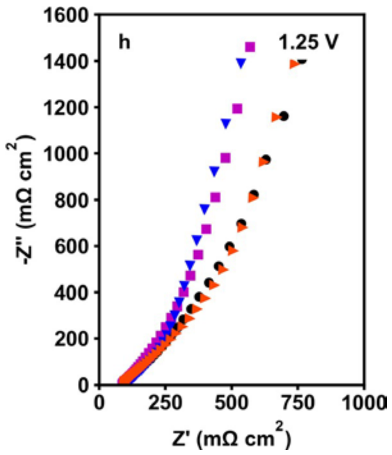
## Membrane Electrode Assembly (MEA) Testing



### HFR-free performance



### Catalyst Layer Resistance



5 cm² MEA in 1 M KOH,
Versogen (80 µm) membrane,
Versogen ionomer (30 wt%)

PGM: platinum group metal
RDE: rotating disk electrode

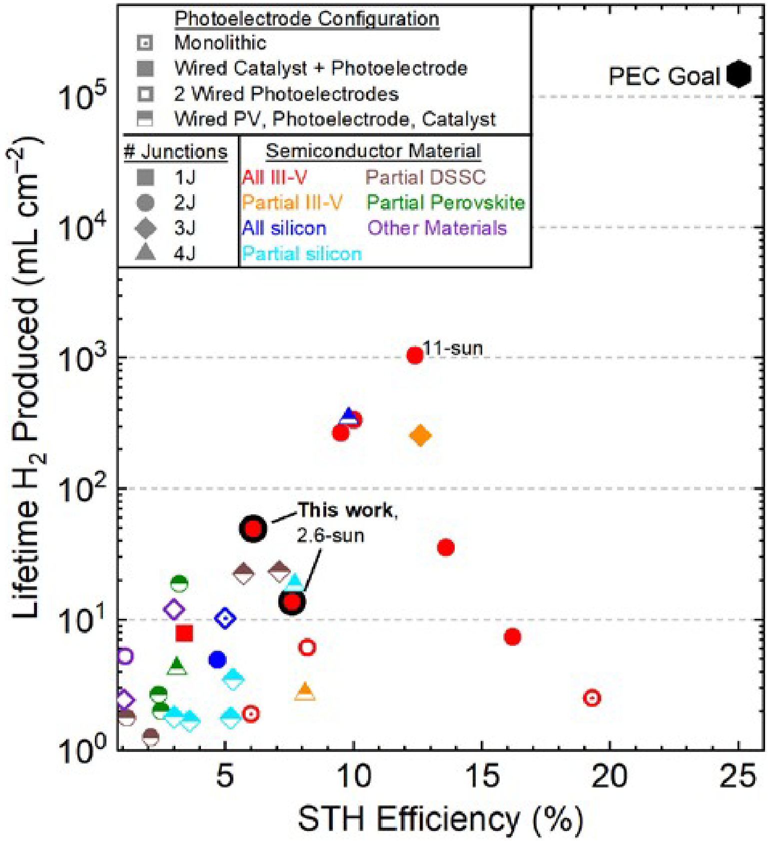
- Screened commercial catalyst materials for improved OER kinetics (RDE & MEA)
- PGM-free catalysts, nickel-iron ($NiFe_2O_4$) and cobalt ($Co_3O_4$) oxides, show promising OER activity: comparable to $IrO_2$
- $NiFe_2O_4$ OER activity improved after stress testing (13.5 h hold at 1.8 V), perhaps due dissolution of Fe and decrease in Fe content in spinel phase.

*Volk et al., Journal of the Electrochemical Society (2023) [Under Review]*

# HydroGEN PEC Lab R&D

## Solar to hydrogen (STH) efficiency has improved but durability has not and is limiting PEC advancement

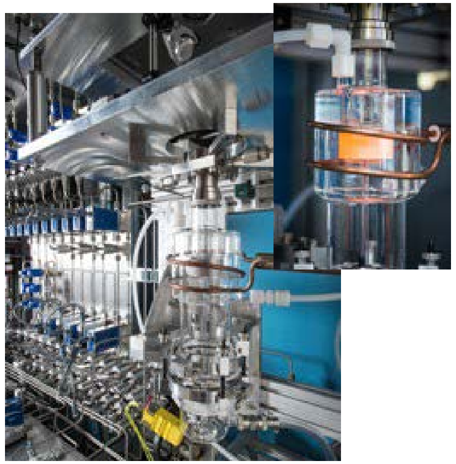
**Goal:** Elucidate the degradation mechanism(s) and improve the durability of PEC materials and devices.



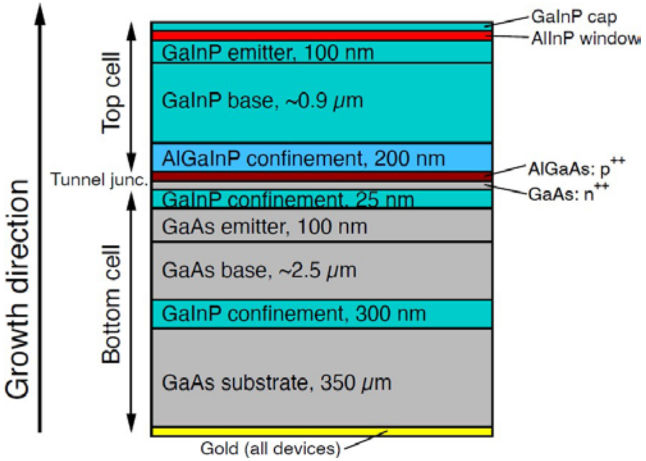
*Comparison of the solar to hydrogen efficiency (STH) and lifetime $H_2$ produced for unassisted water splitting devices. The "PEC Goal" point in the upper right was calculated assuming a 20% capacity factor and 10 year lifetime* (*ACS Energy Lett.* **2020**, *5*, 2631–2640)

# HydroGEN PEC Lab R&D Technical Progress

## Photoelectrode growth by metal organic vapor phase epitaxy (MOVPE)

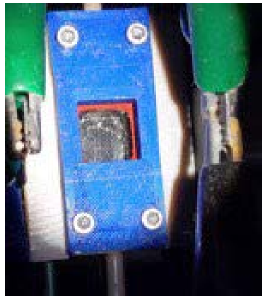


*MOVPE at 620℃ growth temperature*



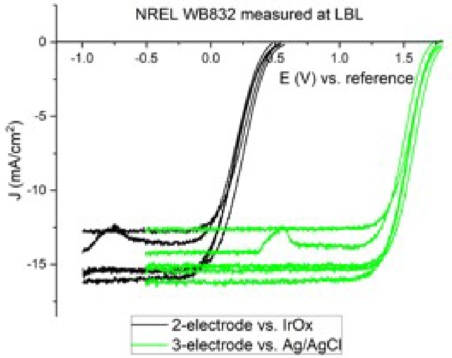
*Schematic of the III-V high efficiency photoelectrode*

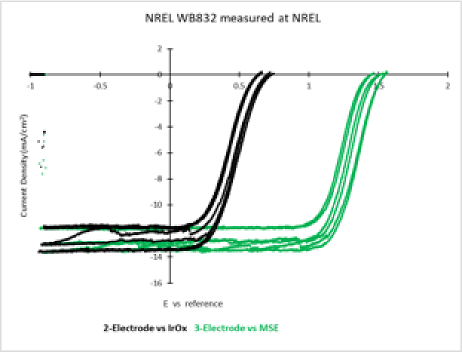
## Photoelectrode Fabrication and Testing at NREL and LBNL

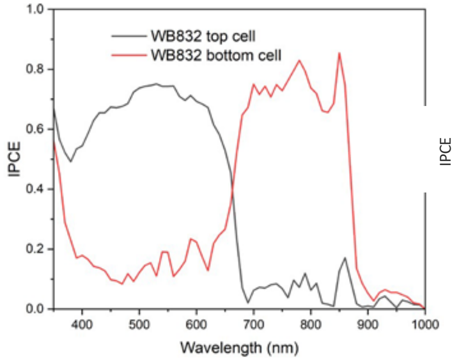


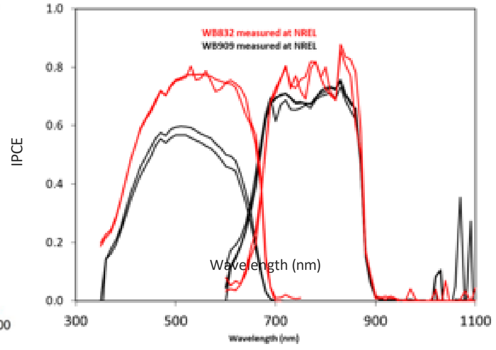
*Dual anode cell with high modularity and ease of fabrication*

## *Reproducibility achieved at both Labs*

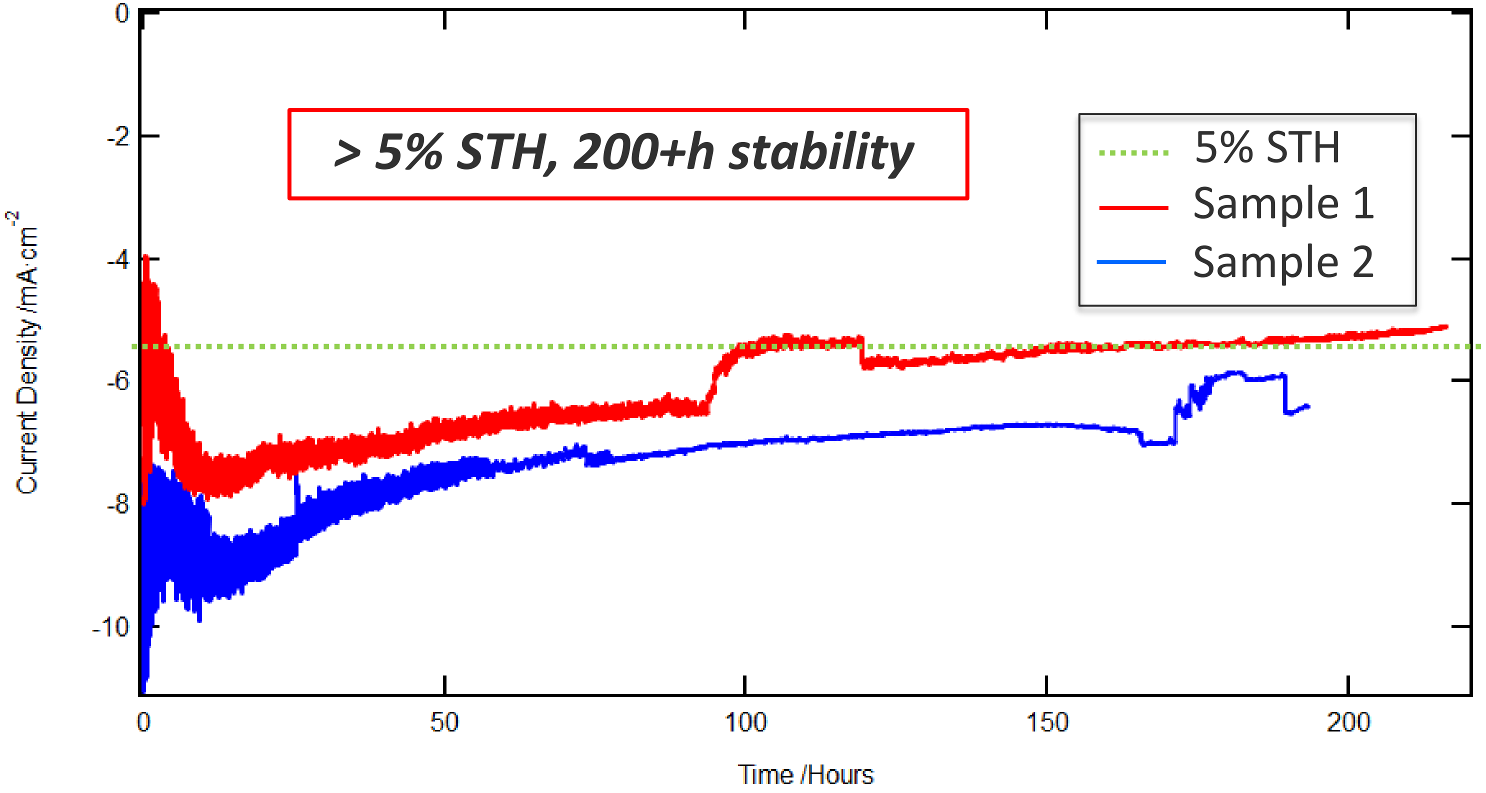








# PEC bias-free water splitting at neutral pH



***Cathode:*** *two electrodes from growth # WC106 of GaInP/GaAs III-V tandem, with PtRu catalyst*
***Cathode active area:*** *0.2 cm$^2$*
***Anode****: IrOx, separated from the photocathode via Ti mesh*
***Electrolyte****: pH 7.2 potassium phosphate remains at neutral pH in bulk throughout 200 hours*
***Measurement vessel****: cuvette cell*

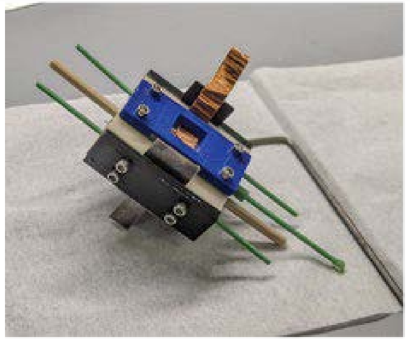
# Impactful standard protocol and benchmarking publication

## *Best Practices in PEC Water Splitting: How to Reliably Measure Solar-to-Hydrogen (STH) Efficiency of Photoelectrodes*[1]

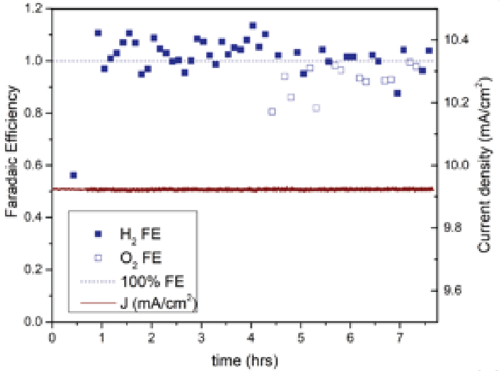
- Publication shares with PEC community best practices when measuring and reporting STH efficiency of new photoelectrodes and will improve the reproducibility of results across the field.

> *“This is a great paper for the community, thank you for dedicating the time to put this together, especially during this challenging historical time (pandemic)”*
> *–2023 attendee, Solar Fuels Gordon Conference*

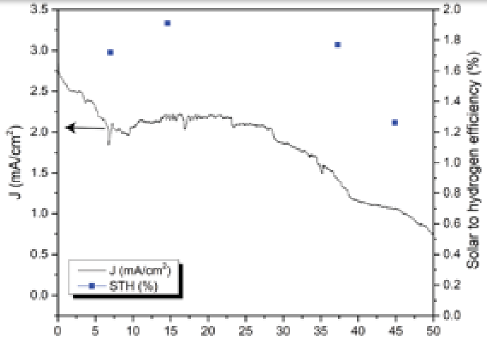
- Publication benchmarks a flow reactor for $H_2/O_2$ measurement, that any lab can produce from readily available materials using a CNC miller and 3D printer.
- 4098 views, 491 downloads, 10 mentions in news articles (4/10/2023)



**Reactor**



**Validation: dark Faradaic Efficiency**



**STH of III-V tandem at pH 0.4**

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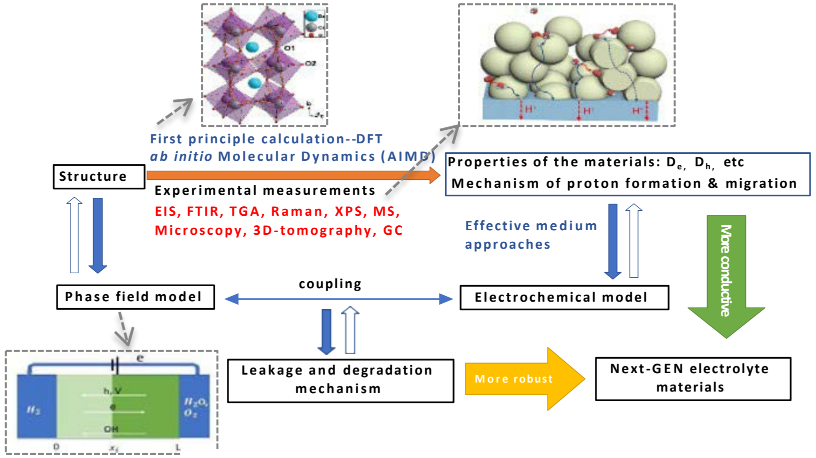
[1] *Front. Energy Res., 27 October 2022 Volume 10 - 2022 | https://doi.org/10.3389/fenrg.2022.884364*

# Combine Multi-Scale Computation and Experiment to Improve Faradaic Efficiency

## HTE Lab R&D p-SOEC Approach

- Develop effective approaches to suppress electronic leakage by understanding the proton conduction and electronic leakage mechanisms.
- Develop a robust, energy-efficient, and reliable electrolyte, for p-SOEC at 500-600°C, achieving high Faradaic efficiency (FE) and long durability.



Structure

First principle calculation--DFT

*ab initio* Molecular Dynamics (AIMD)

Experimental measurements

EIS, FTIR, TGA, Raman, XPS, MS, Microscopy, 3D-tomography, GC

Properties of the materials: $D_{e}$, $D_{h}$, etc

Mechanism of proton formation & migration

Effective medium approaches

Phase field model

coupling

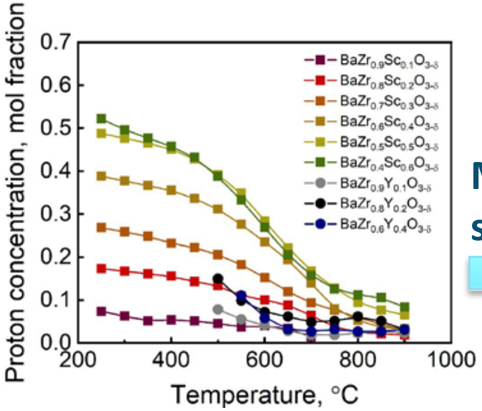
Electrochemical model

More conductive

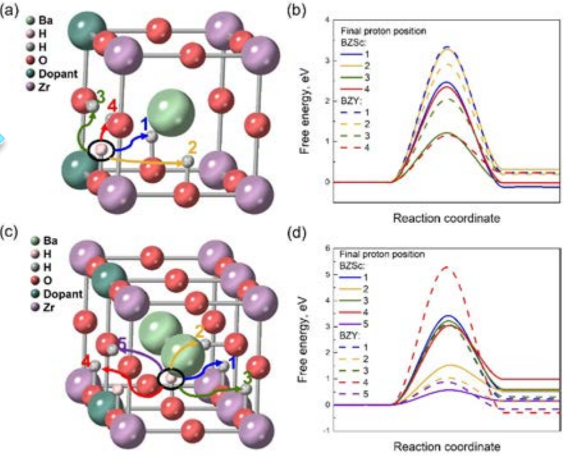
Leakage and degradation mechanism

More robust

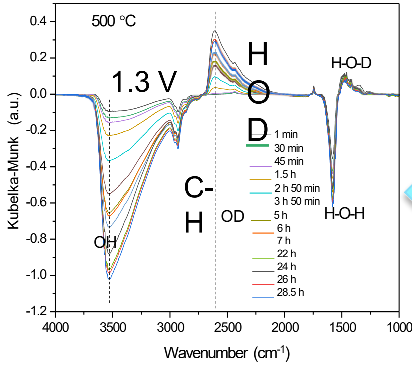
Next-GEN electrolyte materials

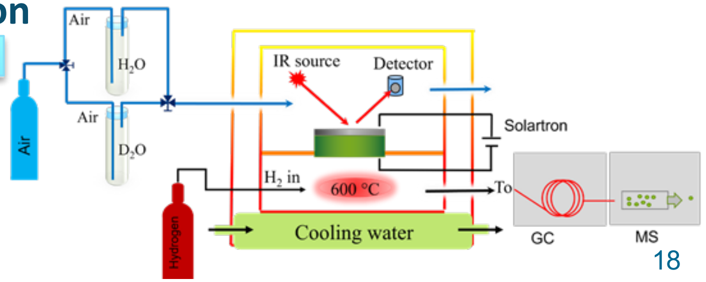


**Mechanism study**



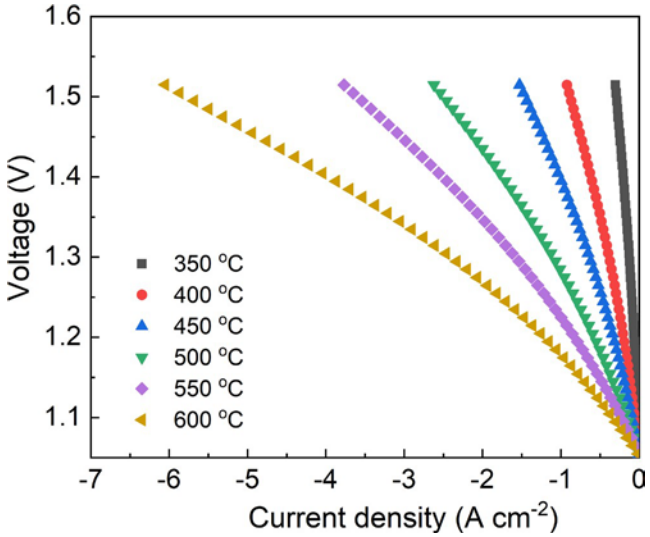
**Operando proton conducting investigation**

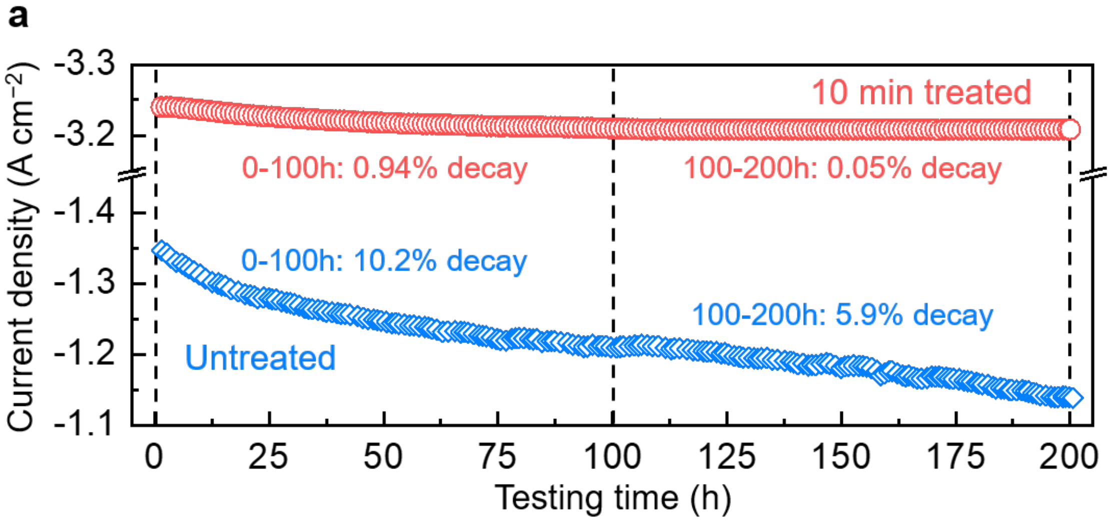


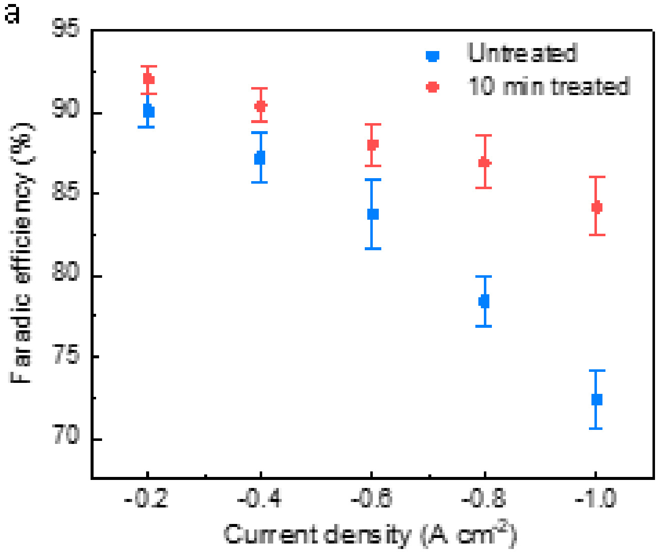


# Record performance of p-SOEC with improved Faradaic efficiency, smaller overpotential and lower operating temperatures

- Simple but scalable acid etching can significantly reduce both Ohmic and interfacial polarization resistance, thus improving the performance of p-SOEC (>2.8 A cm$^{-2}$ at 1.3 V @600$^{o}$C).
- Durability is also enhanced compared with the pristine cells.
- p-SOEC can maintain a reasonable performance @350$^{o}$C.
- Interface engineering represents a new direction for p-SOEC to bolster the performance and durability.







**W Bian, W. Wu, D Ding, et al. Nature, 2022**

# Assess Technology Viability, Enable DFT-ML Material Discovery

## STCH Lab R&D Goals and Approach

Goals: Comprehensively validate known STCH material properties and demonstrate theory-guided design of materials approach that optimizes the capacity/yield tradeoff.

- Develop a materials search strategy for optimizing the capacity/yield tradeoff using DFT + Machine Learning (ML).
- Find new materials using the ML model and characterize by detailed calculations, synthesis, and experimental validation.

DFT = density functional theory
$T_{RED}$ = reduction temperature

# High Throughput Screening of Materials Project Using DFT-ML

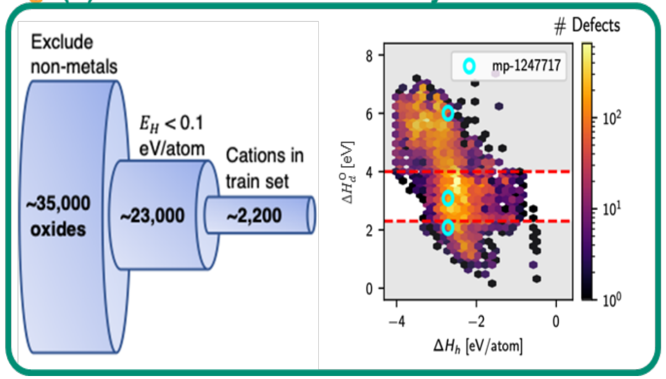
- Our high-throughput material discovery workflow has successfully trained the model to predict oxygen vacancy formation energy.
- It took one year to populate the DFT database needed to train the model and only minutes to search through thousands of compound structure models warehoused in the Materials Project (MP) and NRELmatdb
- Model rediscovers known water-splitting oxides and identifies new ones.

**ML screens 10,000's of MP structures in minutes that would take 1,000's of DFT months**

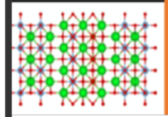
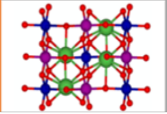
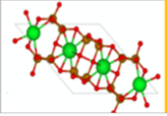
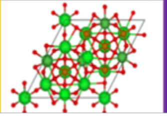
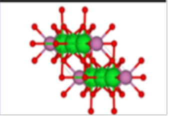
**(1) Co-design of defects and stability for water-splitting**

| Metric | Requirement |
|---|---|
| Frac. of defects w/$\Delta H_d^O$ > 2.3 eV | $x_{\min} = 1$ |
| Frac. of defects w/$\Delta H_d^O$ ∈ [2.3, 4.0] eV | $x_{\mathrm{rng}} > 0$ |
| STCH operating range conditions $(P_{O_2})$ | $\Delta\mu'_{O_2}$ |
| Compound stability range | $\Delta\mu_{O_2}^{\phi_H < \{0, 0.1, \ldots\}}$ |
| Stable in the target range | $\Delta\mu_{O_2}^{\phi_H < X} \cap \Delta\mu'_{O_2}$ |

**(2) Screen the Materials Project for all defects**



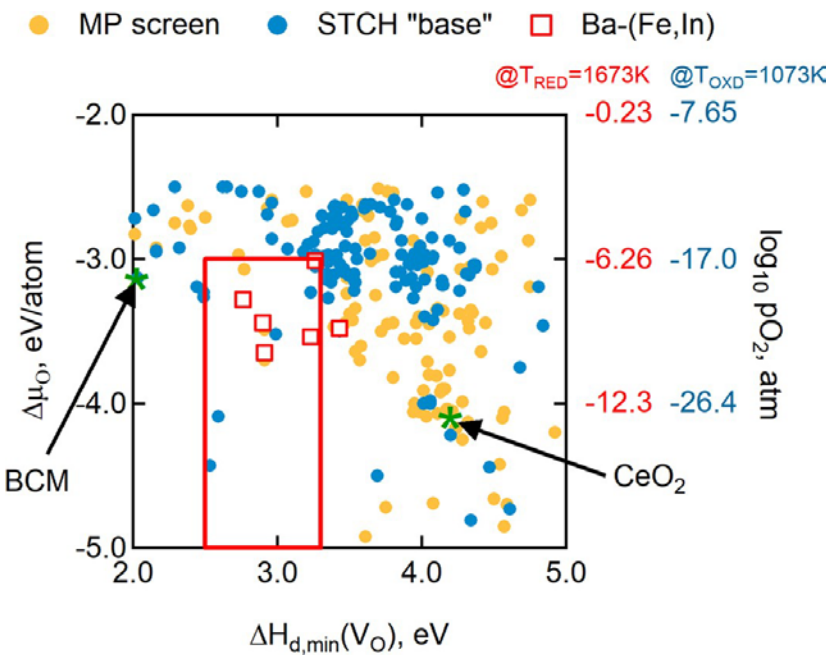
**(3) Identify targets w/increasingly stringent metrics**

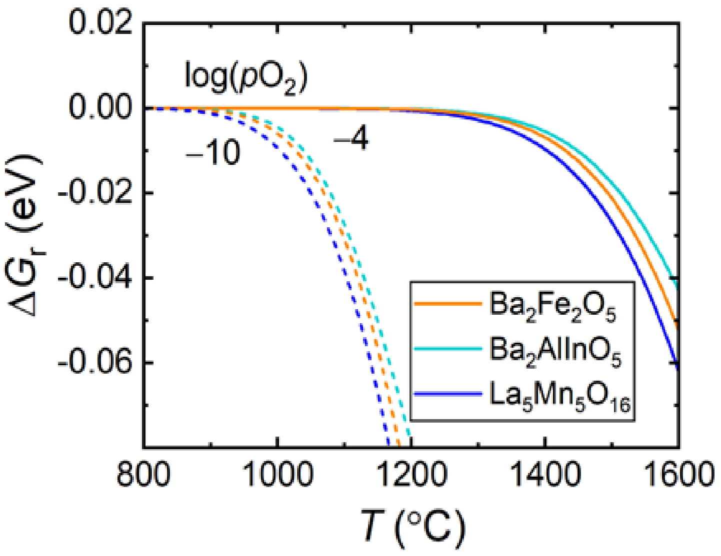
| 197 formulas (48 training) | 114 formulas (33 training) | 34 formulas (17 training) | 16 formulas (11 training) | 9 formulas (9 training) |
|---|---|---|---|---|
| ➢ $x_{\min,1} = 1$<br>➢ $x_{\mathrm{rng},1} > 0$<br>➢ $\Delta\mu_{O_2}^{\phi_H<0.1}$ | ➢ $x_{\min,2} = 1$<br>➢ $x_{\mathrm{rng},2} > 0$<br>➢ $\Delta\mu_{O_2}^{\phi_H<0.1}$ | ➢ $x_{\min,3} = 1$<br>➢ $x_{\mathrm{rng},3} > 0$<br>➢ $\Delta\mu_{O_2}^{\phi_H<0.05}$ | ➢ $x_{\min,3} = 1$<br>➢ $x_{\mathrm{rng},3} > 0$<br>➢ $\Delta\mu_{O_2}^{\phi_H=0}$ | ➢ $x_{\min,3} = 1$<br>➢ $x_{\mathrm{rng},3} = 1$<br>➢ $\Delta\mu_{O_2}^{\phi_H=0}$ |
| $Sr_6Ti_3FeO_{14}$ (mp-1645141) | $La_2MnCoO_6$ (mp-19208) | $BaSr(FeO_2)_4$ (mp-1228024) | $Ba_5SrLa_2Fe_4O_{15}$ (mp-698793) | $Ba_3In_2O_6$ (mp-20352) |
|  |  |  |  |  |

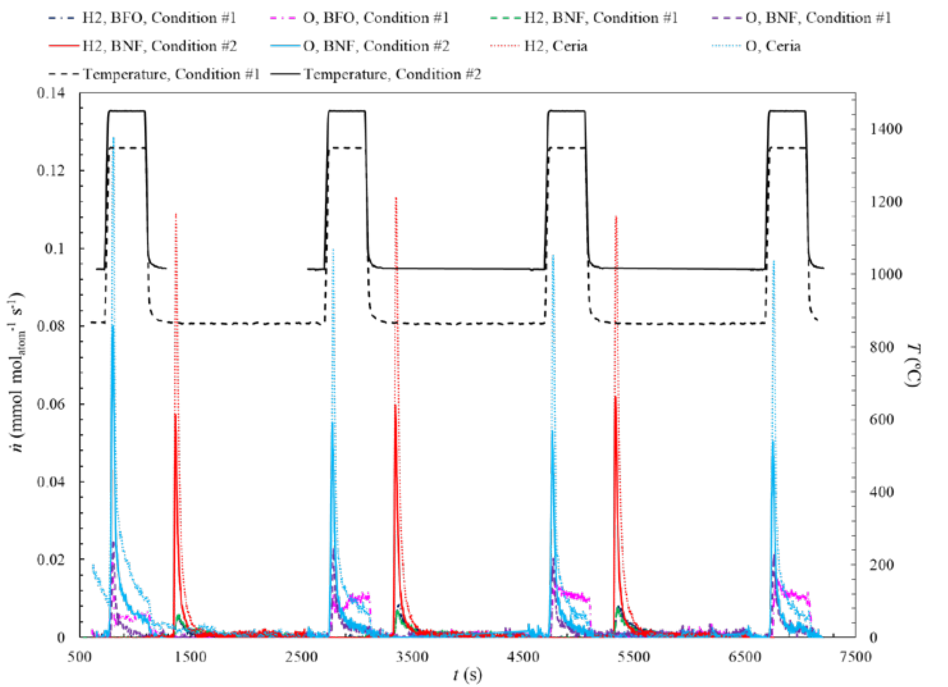
- ➢ Identify all candidates satisfying minimum requirements
- ➢ Identify candidates with increasingly certain performance
- ➢ Mainly IDs known, synthesizable compounds

MAE = mean absolute error
MP = Materials Project (https://materialsproject.org/)

# High Throughput Screening of MP Identified New STCH Materials







- Created thermodynamic analysis tool that interfaces with the DFT-ML data.
  - Predict crystal structures from MP that satisfy our search criteria for STCH active compounds
  - Bypass time-consuming supercell defect calculations
- Synthesized >10 identified compounds of interest; resulting in ≥ 2 new validated water splitting materials with screening ongoing on others.

# Community Approach to Benchmarking and Protocol Development for AWS Technologies

## Accomplishments

P170

***Goal:* Develop best practices in materials characterization and benchmarking: Critical to accelerate materials discovery and development**

## Best Practices in Materials Characterization

Kathy Ayers, Nel Hydrogen (LTE)
Ellen B. Stechel, ASU (STCH)
Olga Marina, PNNL (HTE)
CX Xiang, Caltech (PEC)
Consultant: Karl Gross, George Roberts

- Strong community engagement and participation, nationally and internationally
  - Participation from both HydroGEN and H2NEW consortia
- Disseminated information to AWS community via HydroGEN Data Hub, website, SharePoint site, email, quarterly newsletters, workshops

## Accomplishments:

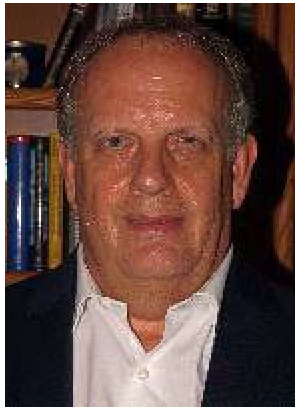
- **19 standardized measurement protocols and benchmarks published in open-access journal Frontiers in Energy Research special issue: free to download: https://www.frontiersin.org/research-topics/16823/advanced-water-splitting-technologies-development-best-practices-and-protocols#articles**
  - **7 LTE, 4 HTE, 5 PEC, 3 STCH**
  - **4,912 total downloads and 36,000 views**
- **4 Annual AWS community-wide benchmarking workshop**
- **Developed high-level roadmaps by AWS technology**

# LTE Standard Protocols Published in Frontiers in Energy Research

1. Rotating disk electrode standardization and best practices in acidic oxygen evolution for LTE
2. Protocol for screening water oxidation or reduction electrocatalysts activity in a three-electrode cell for AEME
3. Assessing the oxidative stability of AEMs in oxygen saturated aqueous alkaline solutions
4. Standard operating protocol for ion-exchange capacity of AEMs
5. Gas permeability test protocol for ion-exchange membranes
6. Measurement of resistance, porosity, and water contact angle of porous transport layers for LTE technologies
7. Standard operating procedure for post-operation component disassembly and observation of benchtop electrolyzer testing

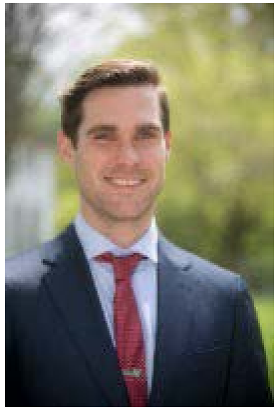
# Acknowledgements

**This work was supported by the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy (EERE), Hydrogen and Fuel Cell Technologies Office (HFTO).**


**Ned Stetson**


**Katie Randolph**


**David Peterson**


**James Vickers**


**William Gibbons**


**Eric Miller**

# Thank You

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NREL/PR-5900-87215

This work was authored 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 Renewable Energy Hydrogen 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.

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