Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

HydroGEN: Photoelectrochemical (PEC) Hydrogen Production

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April 30, 2019

Annual Merit Review

PD148C

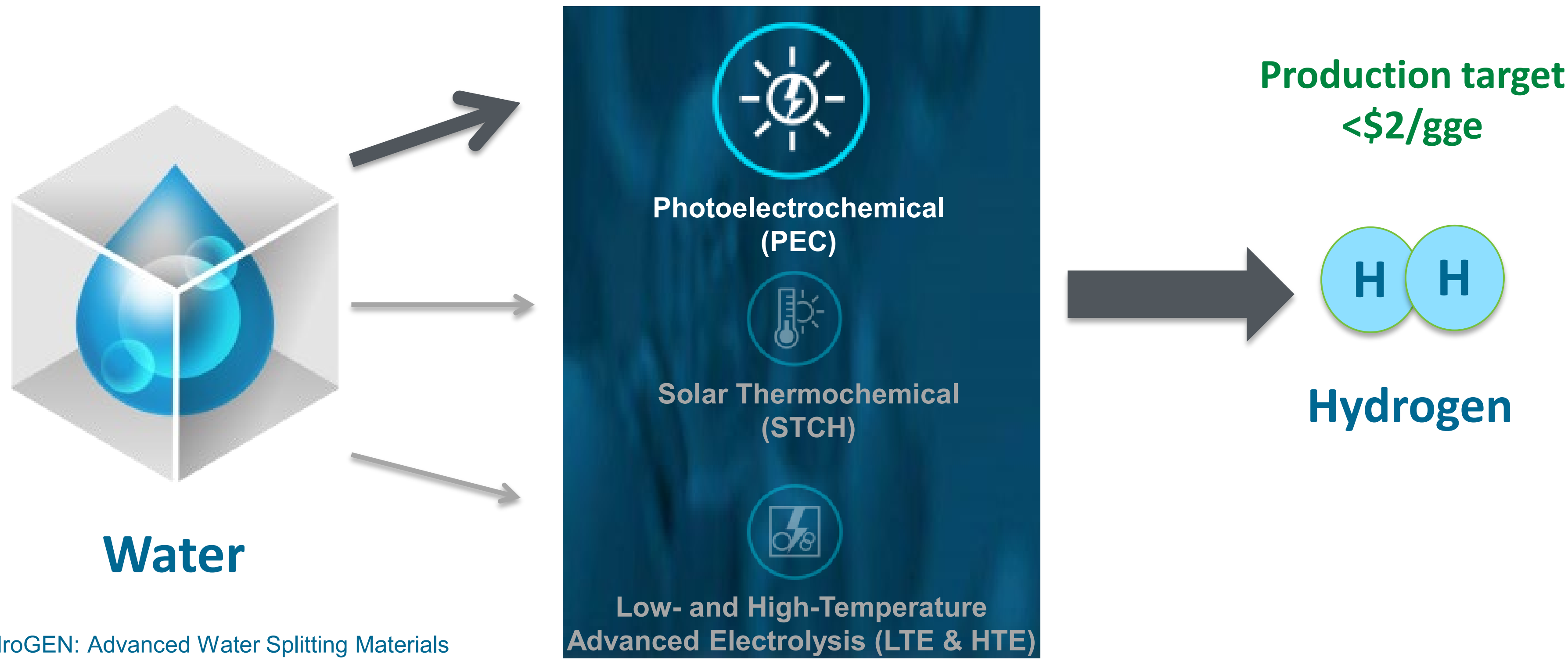
NREL · Berkeley Lab · Sandia National Laboratories · Idaho National Laboratory · Lawrence Livermore National Laboratory · SRNL

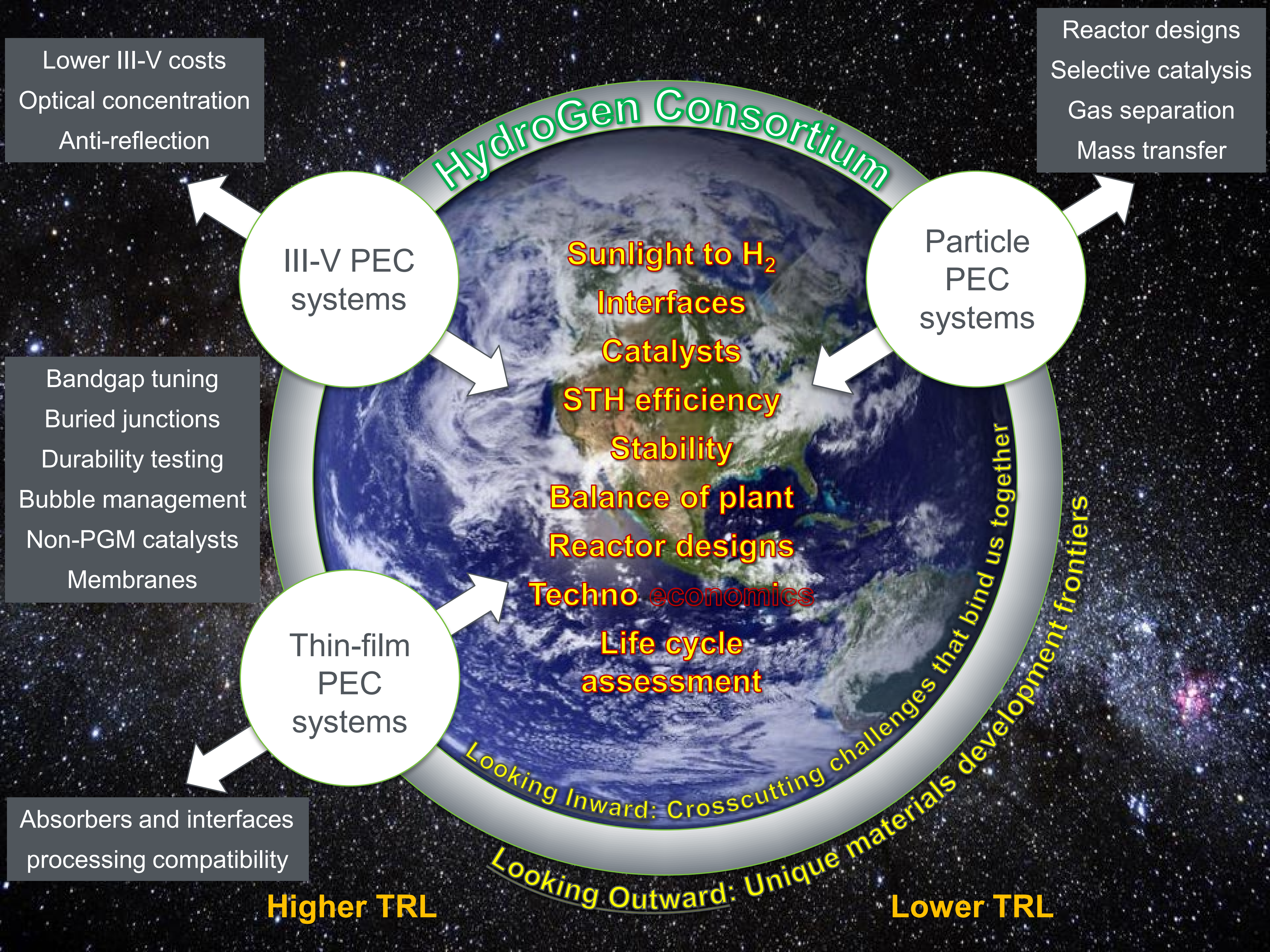
Advanced Water-Splitting Materials (AWSM)
Relevance, Overall Objective, and Impact

AWSM Consortium 6 Core Labs:

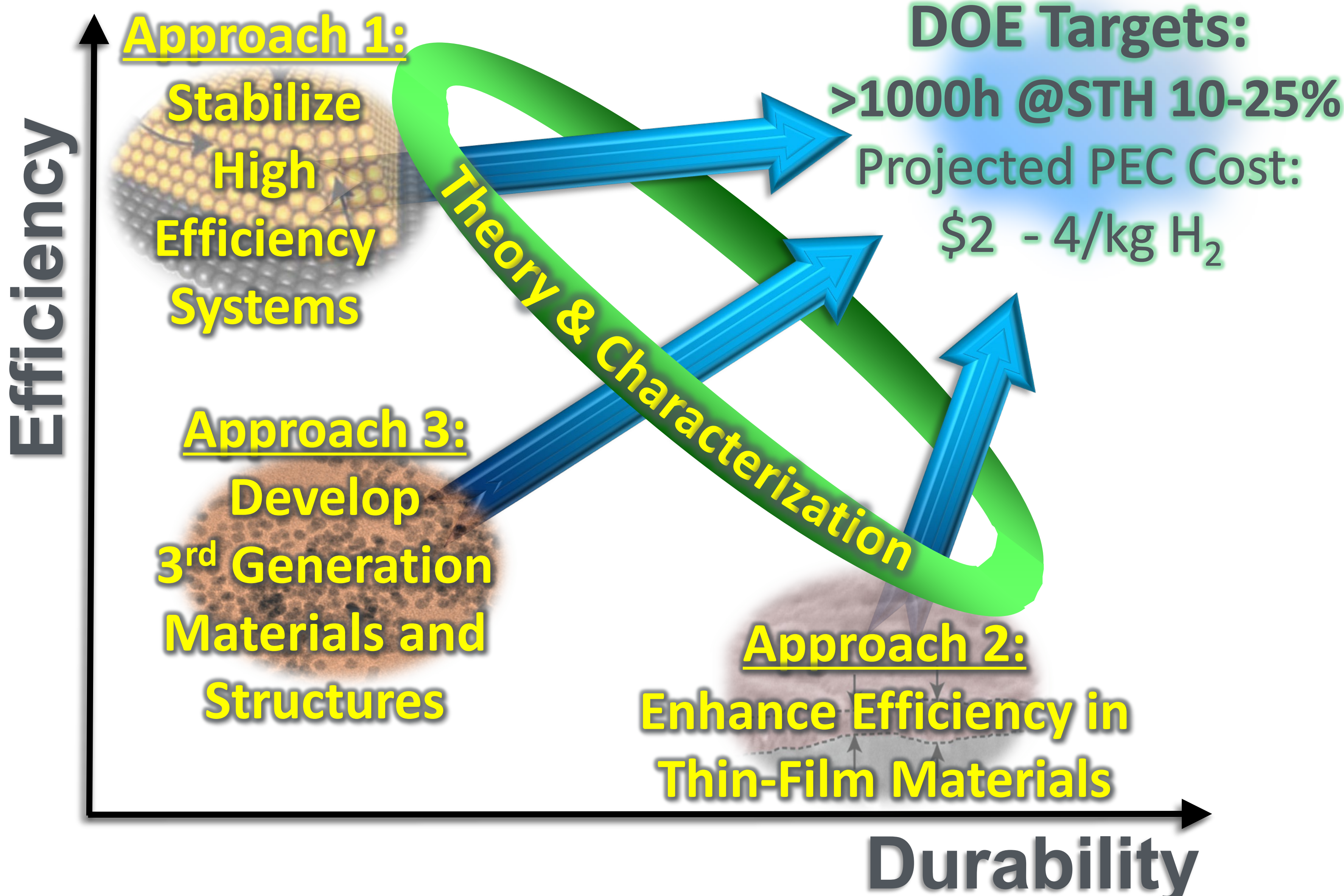
- NREL – National Renewable Energy Laboratory
- Berkeley Lab
- Sandia National Laboratories
- INL – Idaho National Laboratory
- Lawrence Livermore National Laboratory
- SRNL

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

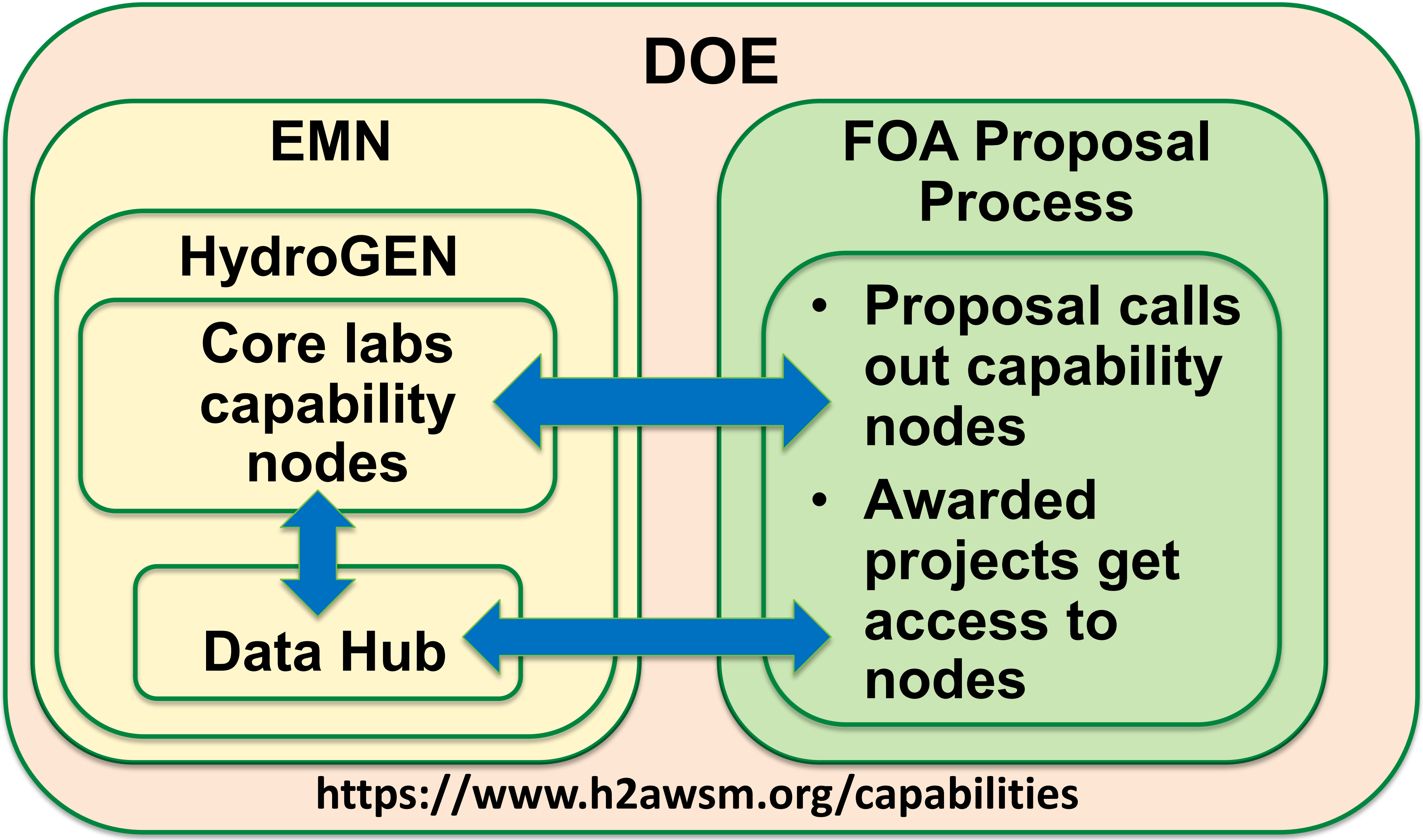



HydroGen Consortium
Lower III-V costs
Optical concentration
Anti-reflection
Reactor designs
Selective catalysis
Gas separation
Mass transfer
III-V PEC systems
Particle PEC systems
Thin-film PEC systems
Sunlight to H_2
Interfaces
Catalysts
STH efficiency
Stability
Balance of plant
Reactor designs
Techno economics
Life cycle assessment
Bandgap tuning
Buried junctions
Durability testing
Bubble management
Non-PGM catalysts
Membranes
Absorbers and interfaces
processing compatibility
Looking Inward: Crosscutting challenges that bind us together
Looking Outward: Unique materials development frontiers
Higher TRL
Lower TRL

Synopsis of Photoelectrode-based Approaches



Approach – HydroGEN EMN



Approach – EMN HydroGEN

PEC: Photoelectrochemical Electrolysis

Barriers
- Cost
- Efficiency
- Durability

PEC Node Labs

NREL – National Renewable Energy Laboratory
Berkeley Lab
Sandia National Laboratories
Lawrence Livermore National Laboratory

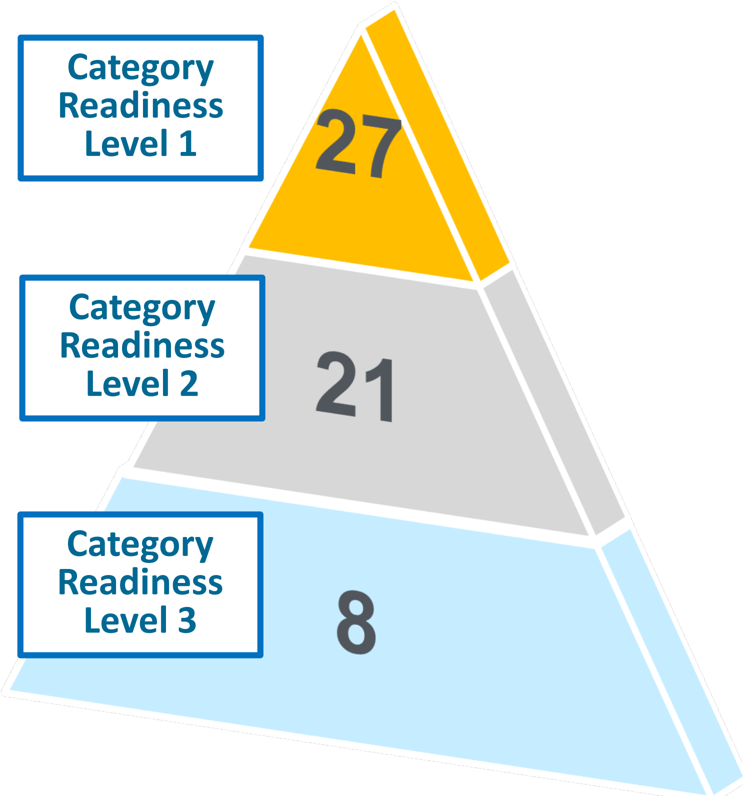
Support through:

Personnel
Equipment
Expertise
Capability
Materials
Data

PEC Projects

University of Hawai'i
Rutgers, The State University of New Jersey
Stanford University
University of Michigan

Collaboration: 56 PEC Nodes, 2 Supernodes



Category Readiness Level 1 (27):
Analysis: 2
Computation: 8
Characterization: 15
Synthesis: 5

Category Readiness Level 2 (21):
Analysis: 2
Computation: 6
Characterization: 13
Synthesis: 5

Category Readiness Level 3 (8):
Analysis: 3
Computation: 3
Characterization: 3
Synthesis: 2

- Nodes comprise equipment and expertise including uniqueness
- Category refers to availability and readiness
- Many nodes span classification areas

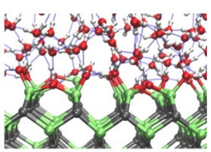
16 (13 by FOA) Nodes utilized
18 Lab PIs engaged
100s of files on Data Hub

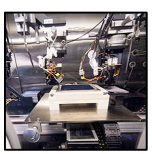
Collaboration: HydroGEN PEC Node Utilization

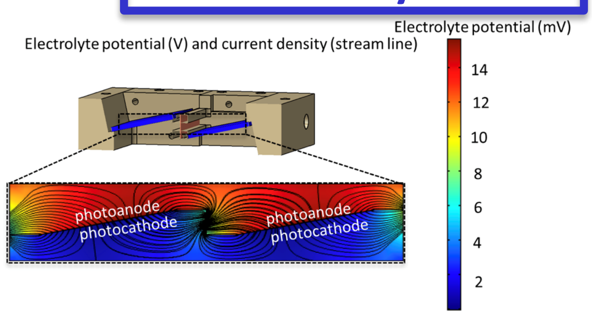
Lab	Node	Hawaii	Stanford	Rutgers	Michigan	Super
LLNL	Material Design and Diagnostics	✓			✓	
LLNL	Interface Modeling	✓			✓	✓
LBNL	Multiscale Modeling					✓
NREL	Structure Modeling					✓
NREL	MOVPE		✓	✓		✓
NREL	CIGS	✓				
NREL	Combi/High Throughput	✓		✓		
NREL	Surface Modifications				✓	

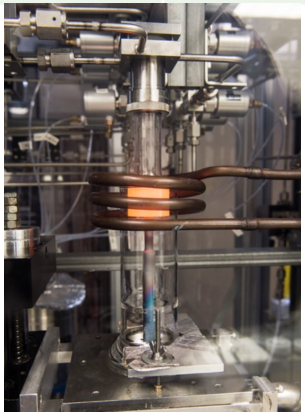
Computation

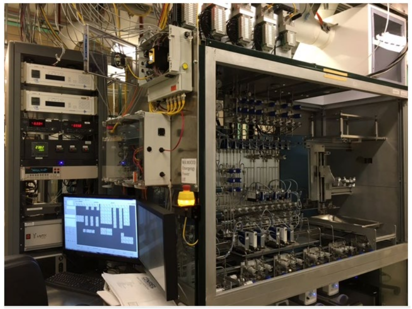
Material Synthesis







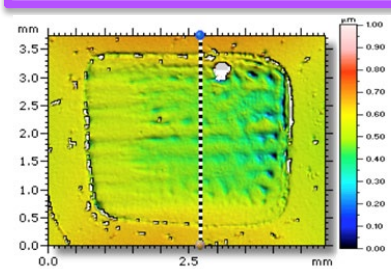


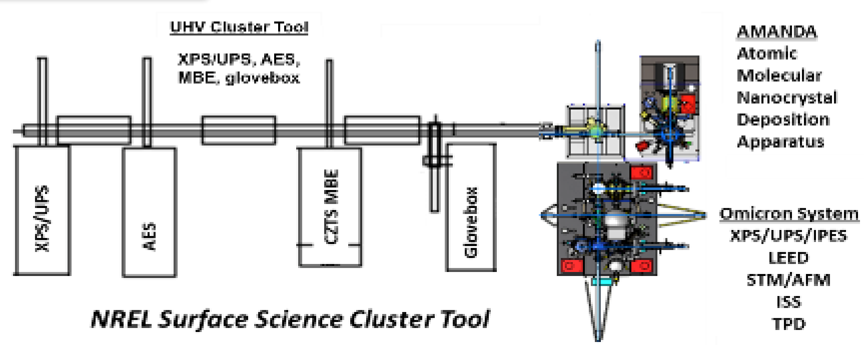


Collaboration: HydroGEN PEC Node Utilization

Lab	Node	Hawaii	Stanford	Rutgers	Michigan	Super	DMREF
LBNL	Corrosion				✓	✓	
LBNL/ NREL	RDE/Cell Testing					✓	
LBNL	Prototyping					✓	
LBNL	Photophysical Characterization	✓	✓				
NREL	Surface Analysis Cluster Tool				✓		
NREL	PEC Characterizations		✓	✓		✓	✓
LBNL	On-Sun Testing					✓	
NREL	On-Sun Efficiency Benchmarking	✓	✓			✓	
NREL	Corrosion Analysis of Materials	✓	✓			✓	
LBNL	In situ APXPS and XAS					✓	✓

Characterization





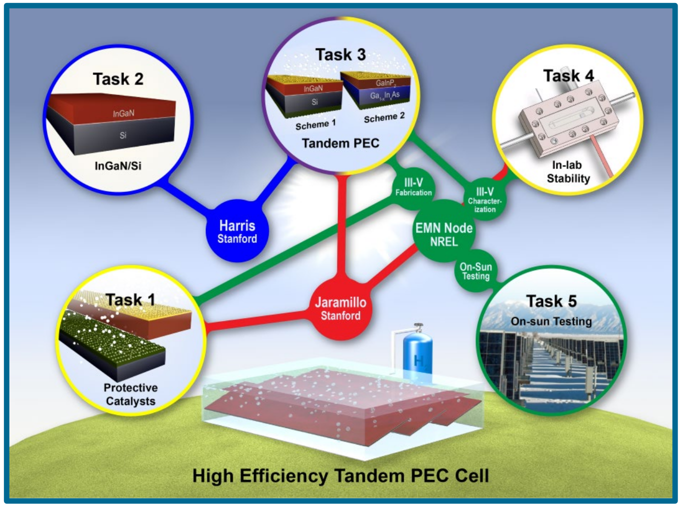
Protective Catalyst Systems on III-V and Si-based Semiconductors for Efficient, Durable Photoelectrochemical Water Splitting Devices

Stanford University

#P161

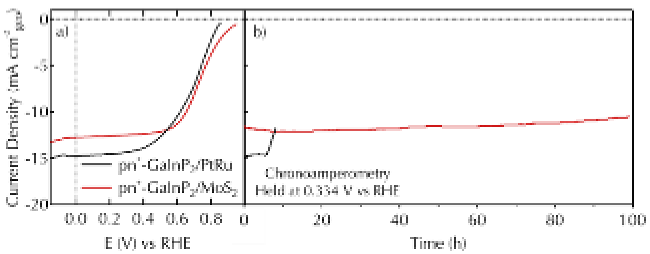
Goals:

- To develop unassisted water splitting devices that can achieve > 20% solar-to-hydrogen (STH) efficiency.
- Devices that can operate on-sun for at least 2 weeks.
- Devices tat can provide a path toward electrodes that cost $200/m^2 by incorporating earth-abundant protective catalysts and novel epitaxial growth schemes.

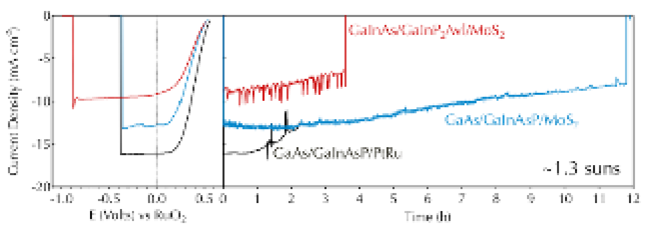


Accomplishments in BP1

Go/No-Go #1: Photoelectrode that achieves >10mA/cm^2 under 1 sun for >100h



Go/No-Go #2: Unassisted PEC water-splitting with non-precious metal HER catalyst that achieves STH >5% under 1 sun

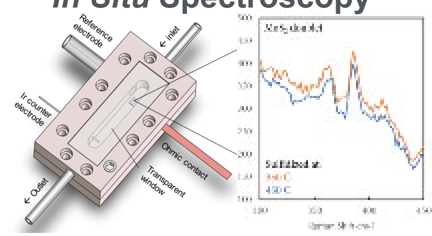


Focus of BP2

Fabrication Approach towards DOE Targets

Scheme 1 III/V-III/V		Scheme 2 III/V-Si
a. Upright Tandem	b. IMM/High Efficiency Tandem	
GaInP	GaInP	InGaN
GaAs	GaInAs	Si

In Situ Spectroscopy



On-sun Testing

https://h2awsm.org/capabilities/sun-photoelectrochemical-solar-hydrogen-benchmarking

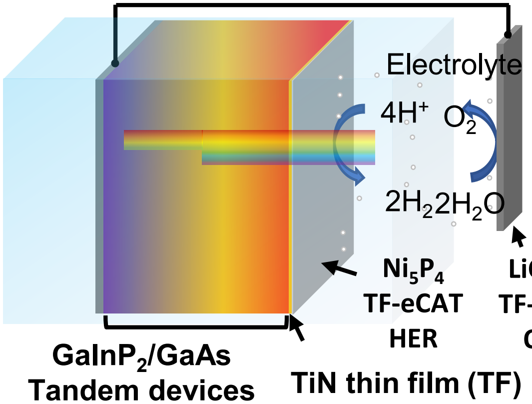
Best-in-class Platinum Group Metal-free Catalyst Integrated Tandem Junction PEC Water Splitting Devices

Rutgers University #P160

Goals:

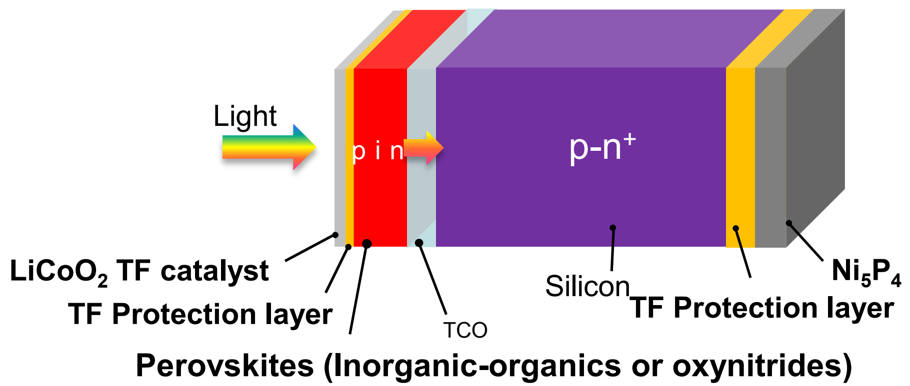
High-Performance (HP) devices

Goal: >10% STH, > 100h durability



High-Value (HV) devices

Goal: ~10% STH, > 100h durability

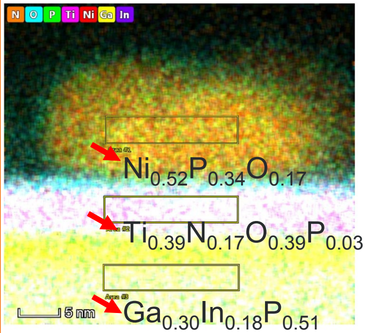


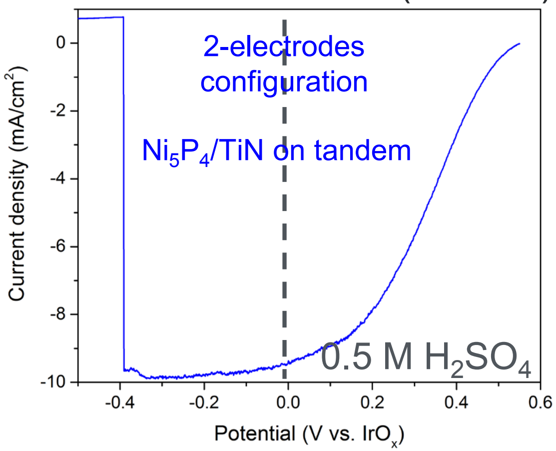
Accomplishments in BP1

Successful TF integration of Ni_5P_4/TiN on GaInP

STH = 11.5%

> 120 h duration (half-cell)





Focus of BP2

HP devices

- STH >12% by 2nd GEN upright tandem + window layer
- Extend the tandem device stability > 2days

HV devices

- Demonstrate half-cell performance with perovskites absorbers & eCATS.

Novel Chalcopyrites for Advanced Photoelectrochemical Water-Splitting

University of Hawaii

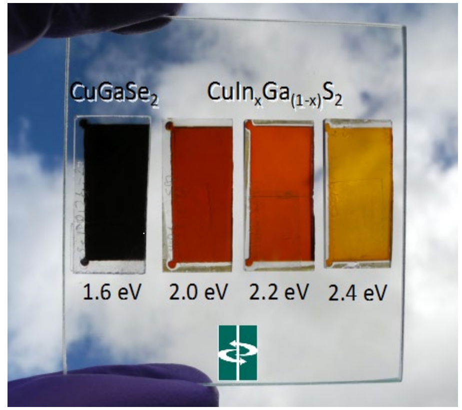
#P162

Project Vision

Strengthen **theory, synthesis and advanced characterization "feedback loop"** to accelerate the development of efficient materials for H_2 production.

Project Goal

Develop innovative technologies to synthesize and integrate chalcopyrites into efficient and low-cost PEC devices.



Addressing materials **efficiency**, **durability** & **integration** barriers through multi-disciplinary research.

N. Gaillard (Device integration)

C. Heske (Spectroscopy)

T. Jaramillo (Catalysis/Corrosion)

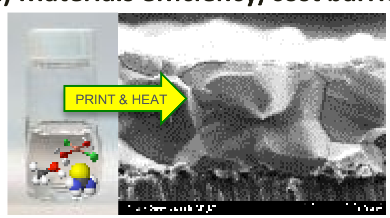
T. Ogitsu (Theory)

J. Cooper (Carrier dynamics)

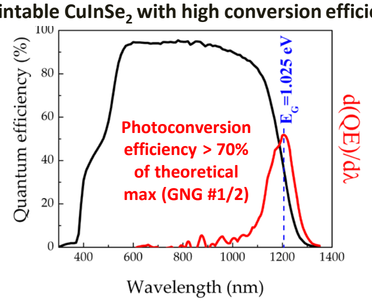
K. Zu (absorbers)
A. Zakutayev (junctions)
T. Deutsch (benchmarking)

Accomplishments in BP1

1) Materials efficiency/cost barriers

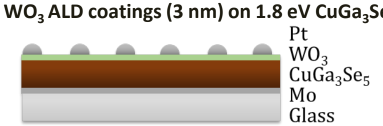


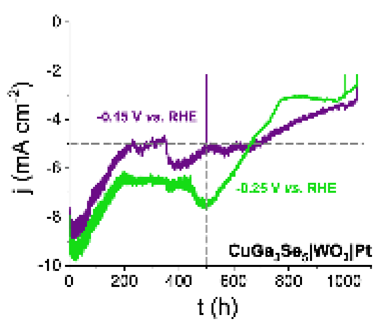
Printable $CuInSe_2$ with high conversion efficiency



2) Materials durability barrier

WO_3 ALD coatings (3 nm) on 1.8 eV $CuGa_3Se_5$



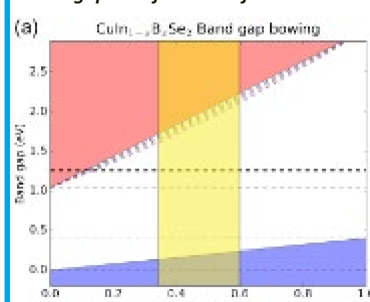


Focus of BP2

1) Materials efficiency/cost barriers

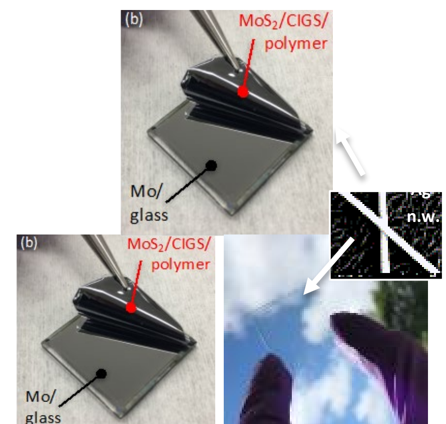
Expend printable $CuInSe_2$ baseline process to novel wide bandgap chalcopyrites
e.g. $Cu(In,B)Se_2$ with 40-60% B content
$Cu(In,Al)Se_2$ with 20-40% Al content

Theoretical prediction of $Cu(In,B)Se_2$ bandgap as a function of boron content



2) Materials integration barrier

Demonstrate chalcopyrite-based tandem device integration with exfoliation/transfer techniques



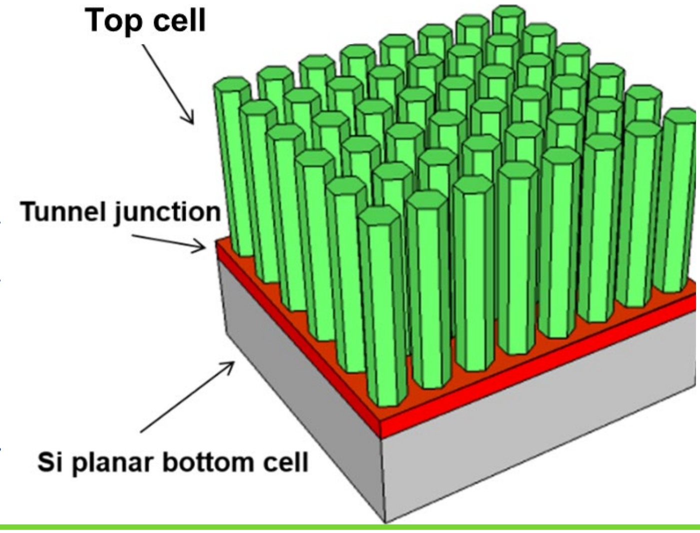
Monolithically Integrated Thin-Film/Si Tandem Photoelectrodes

University of Michigan

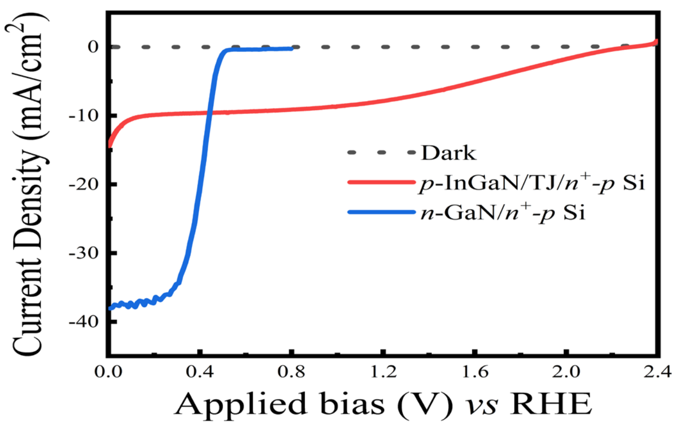
#P163

Goal: Develop Si-based low cost tandem photoelectrodes to achieve high efficiency (>15%) and stable (>1,000 hrs) water splitting systems

Approach: (i) The use of Si and GaN, the two most produced semiconductors, for scalable, low cost manufacturing; (ii) The incorporation of nanowire tunnel junction for high efficiency operation; (iii) The discovery of N-rich GaN surfaces to protect against photocorrosion and oxidation



Accomplishments in BP1



First demonstration of functional Si/InGaN tandem photoelectrode

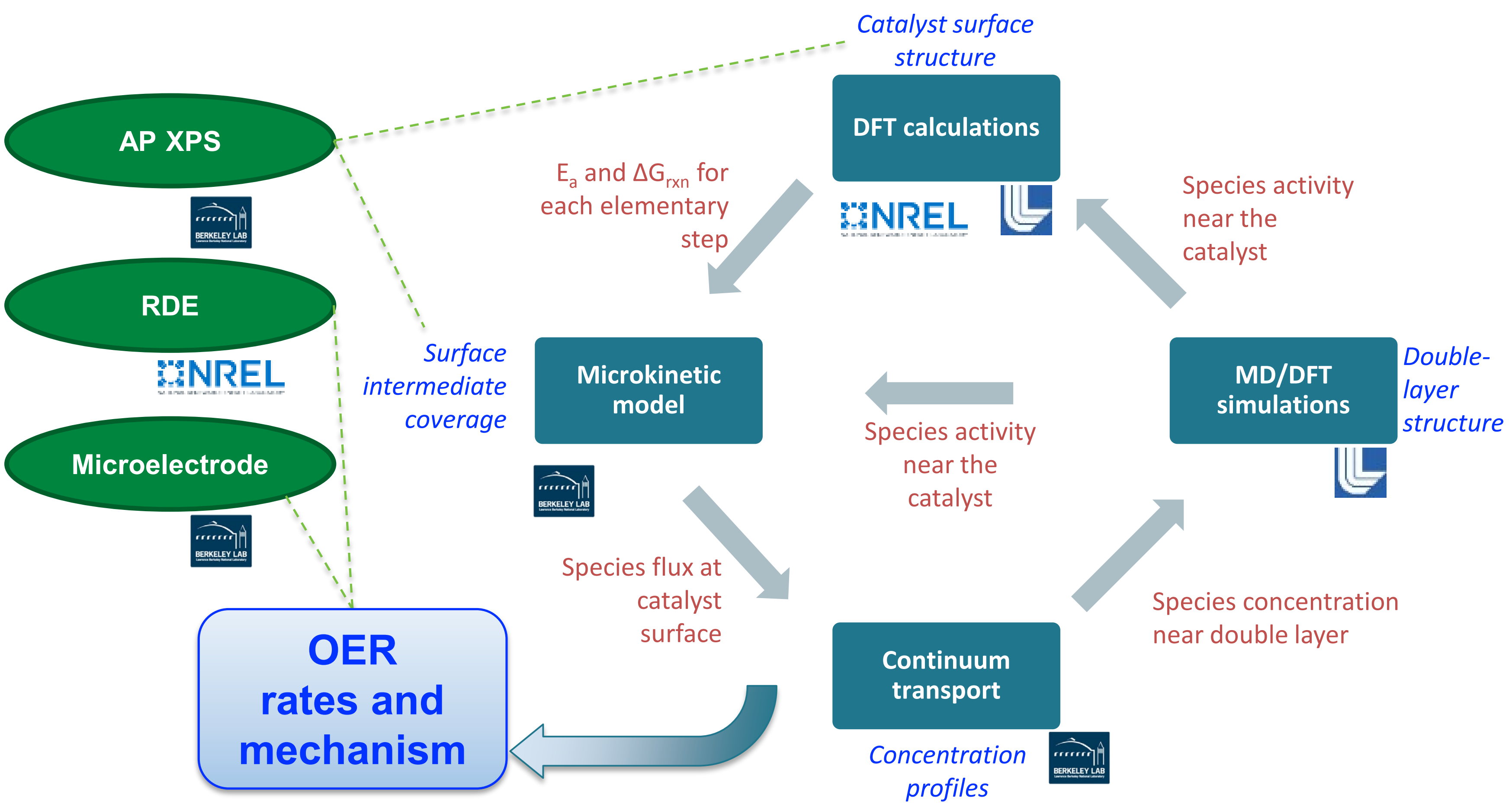
Focus of BP2

Design, modeling, epitaxy/ synthesis, testing, and spectroscopic and kinetic studies of InGaN/Si double-junction photoelectrodes:

- **Achieve Si-based low cost PEC water splitting device with STH >10%**
- **Achieve stable operation >500 hrs by using N-rich GaN self-protection**

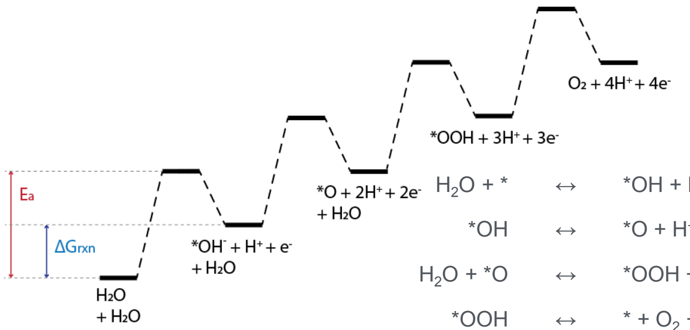
OER Supernode: Approach (utilize 6 nodes)

***Goal**: Validated multiscale modeling to understand OER across pH scale using a modeling framework on IrO_2 informed and validated by experiments*



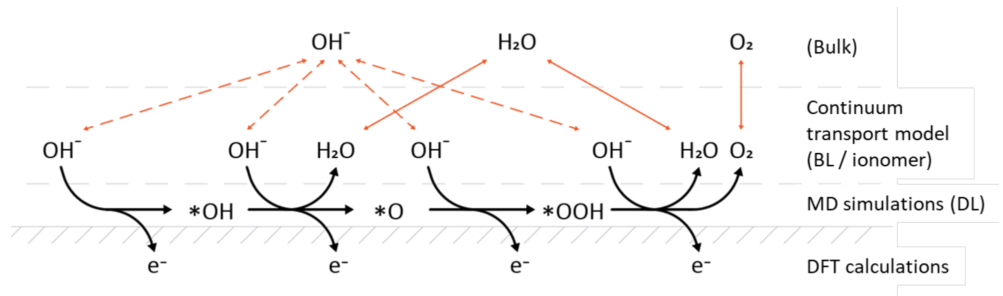
OER Supernode: Results

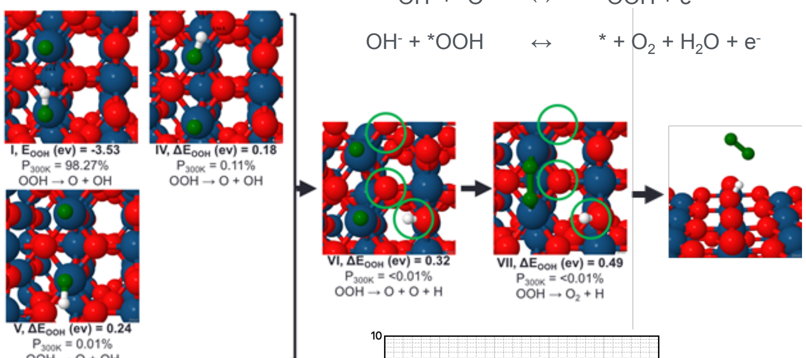
Acid mechanism



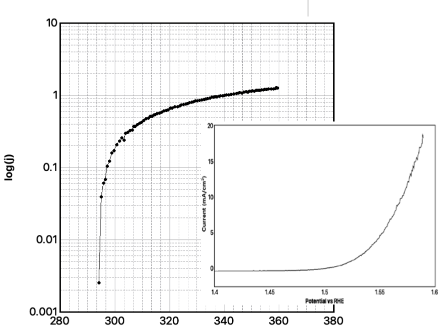
H_2O + *	↔	*OH + H^+ + e^-
*OH	↔	*O + H^+ + e^-
H_2O + *O	↔	*OOH + H^+ + e^-
*OOH	↔	* + O_2 + H^+ + e^-
OH^- + *	↔	*OH + e^-
OH^- + *OH	↔	*O + H_2O + e^-
OH^- + *O	↔	*OOH + e^-
OH^- + *OOH	↔	* + O_2 + H_2O + e^-

Alkaline mechanism





Co-adsorption Pathway (calculating):
O* + OH* → O* + O* + H* → O_2* + H* → O_2 + H*



***Accomplishments*:**

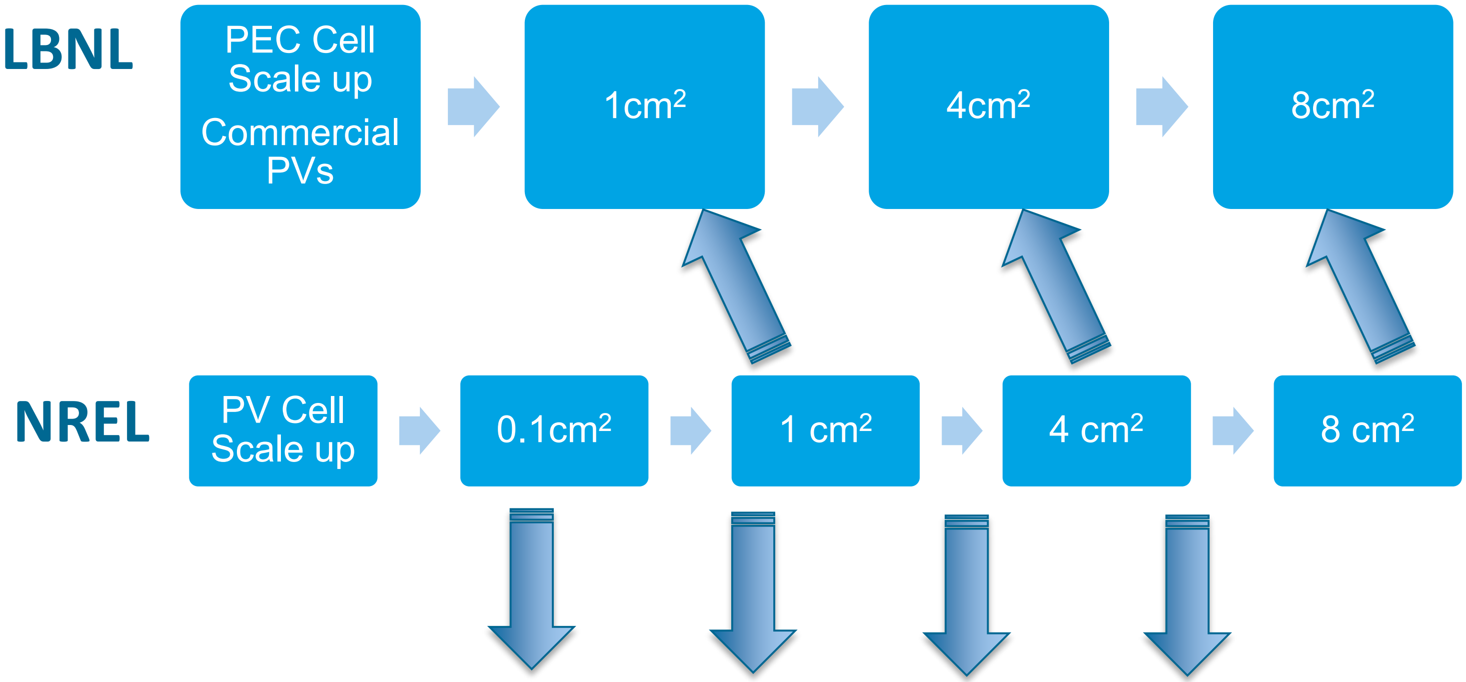
- *Developed methodology and intersections between the mathematical models*
  - *Transfer of surface states and topology in vacuum to solvent simulation*
  - *Transfer of energy barriers to microkinetics*
  - *Microkinetics incorporated into continuum transport simulations*
- *Established ab-initio computational spectroscopy methods and experiments to validate theoretical structural models*
- *Initial measurements of kinetic rates and surface species on IrO_2*

OER Supernode: Future Work

- Experiments on IrO_2
  - Measure OER kinetics in alkaline, acid, and neutral (buffer) solutions using RDE
  - Measure OER kinetics with alkaline and acid ionomers in microelectrode setup
  - Measure and quantify surface species using ambient-pressure XPS and concomitant modeling
- Calculations
  - Calculate free-energy barriers and reaction mechanisms as a function of
    - Applied potential
    - Electrolyte composition
    - Species concentration
    - Surface coverage
  - Estimate the effect of pH variation and/or bias potential on the OER reaction pathways
  - Examine possibility of site-exchange for OER on IrO_2
- Incorporate the knowledge gained in the multiscale modeling framework and compare to experimental data

PEC Supernode Approach

***Goal**: Understand integration issues and emergent degradation mechanisms of PEC devices at relevant scale, and demonstrate an integrated and durable 50 cm^2 PEC panel.*



Benchmarking

In situ degradation and characterization

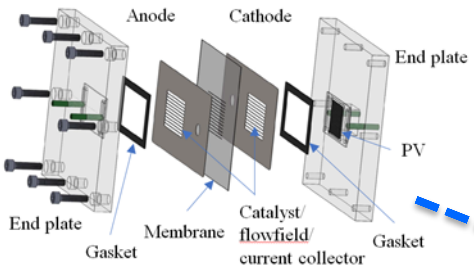
Emerging Degradation Pathways

Modeling

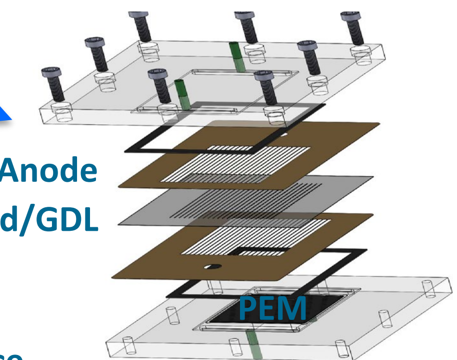
PEC Supernode: Results

Scale up of LBNL PEC Devices

1 cm² PEC



4 cm² PEC

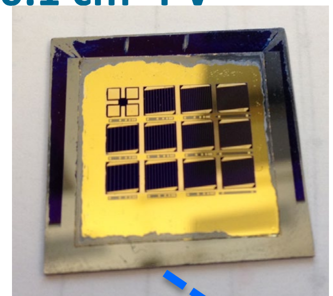


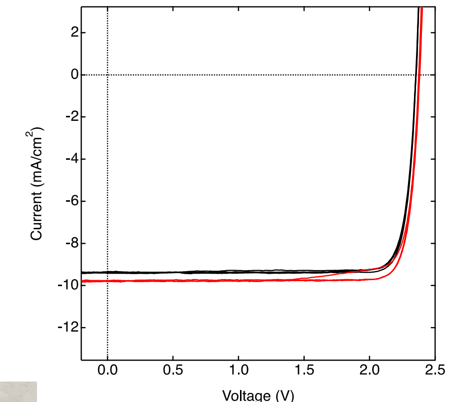
Anode Flowfield/GDL

Cathode Flowfield/GDL

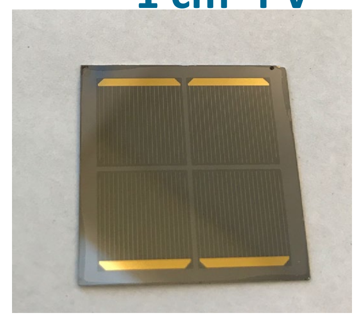
Scale up of NREL PV/PEC Cells

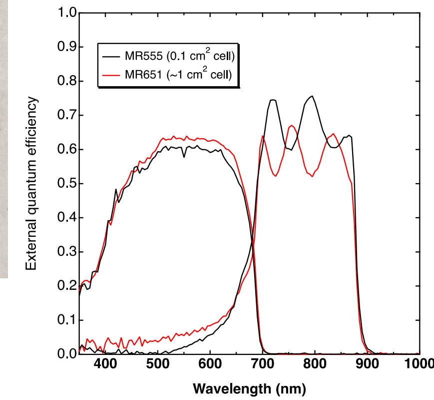
0.1 cm² PV





1 cm² PV



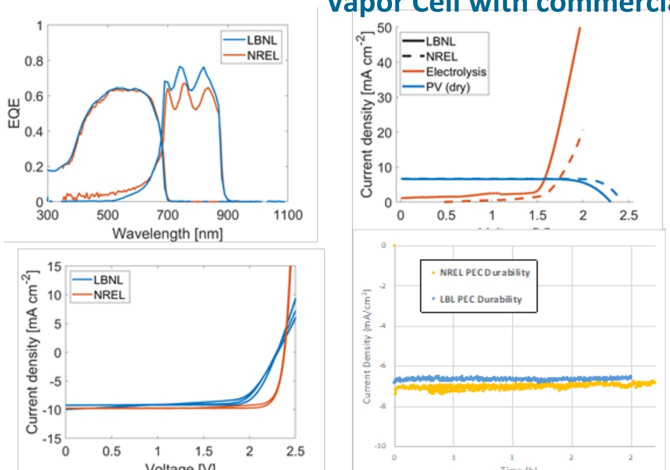


Benchmarking PV/PEC Performance

NREL 1cm² PV

LBNL 1cm² PEC

Vapor Cell with commercial PV



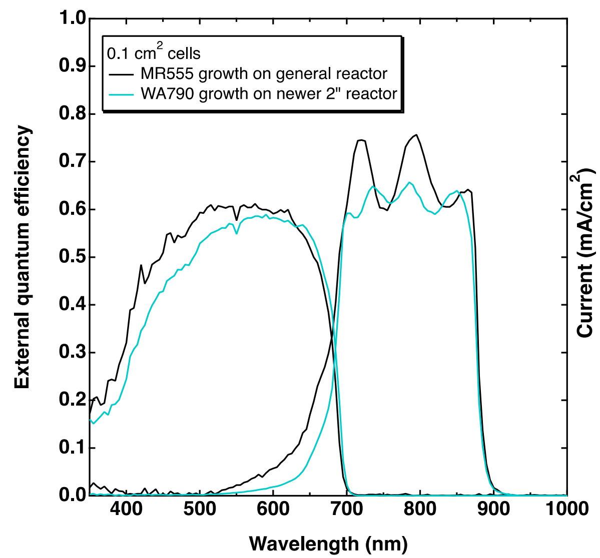
Accomplishments:

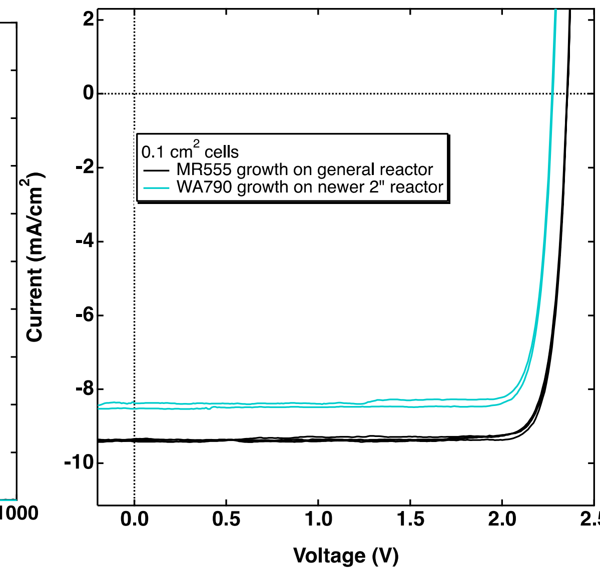
- *Benchmarking PV and PEC cell performance between Labs*
- *PV fabrication scale up from 0.1 to 1cm²*
- *PEC vapor cell scale up from 1 to 4 cm²*

PEC Supernode: Future Work

PV scale up

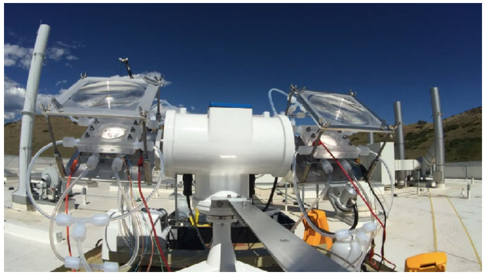
- Developing GaInP/GaAs growths on a newer 2” reactor
    - GaInP quality not quite as good yet, but we are making progress
- In the process of testing the uniformity of the IV curves for tandems over a 2” wafer
- Upcoming plans to make processing masks for 4 cm^2 and 8 cm^2 devices
- Characterize freshly prepared PVs and after PEC testing

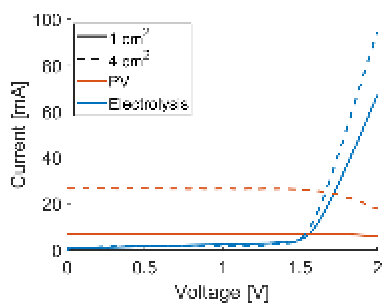




PEC scale up

- Continue scale up and evaluation of 4 cm^2 vapor and liquid PEC cells
- Translate to 8 cm^2 PEC cells
- Benchmark performance and durability with NREL
- On sun and diurnal testing





Degradation and Modeling

- Integrate in situ durability testing via ICPMS
- Visualization of gas and liquid water bubble formation in vapor/liquid cells and feed modeling effort
- Model emergent degradation mechanisms and define cell geometries

Engagement with 2B Team

- Collaboration with 2B Team Benchmarking Project
- All HydroGEN PEC node capabilities were assessed for AWS technology relevance and readiness level
- PEC data metadata definitions exchanged
- PEC questionnaire responses collated and disseminated
  - Defining: baseline materials sets, test cells, testing conditions
  - Published on the DataHub
- 2B working groups and annual meeting

Future Work

- Leverage HydroGEN Nodes at the labs to enable successful budget period 2 activities
  - Increased durability and lifetime
  - Decrease cost
- Conduct case studies and integrated research in 2 supernodes
  - PEC scaleup and integration
  - OER multiscale modeling
- Enable and work with possible new seedling projects
- Work with the 2B team and PEC working group to further establish testing protocols and benchmarks
- Utilize data hub for increased communication, collaboration, generalized learnings, and making digital data public
- Leverage community resources

Summary

- Supporting 4 FOA projects with 13 nodes and 11 PIs
  - Synthesis, benchmarking, modeling, characterization
  - 100s of files on the data hub and numerous exchanged samples
  - Personnel exchange of postdocs, students, and PIs to the labs
- Working closely with the project participants to advance knowledge and utilize capabilities and the data hub
- Projects demonstrate improvements in durable, less expensive materials with high performance and improved durability
- Future work will include continuing to enable the projects technical progress and develop & utilize lab core capabilities
- Supernode research underway to integrate nodes and systematic exploration of critical PEC-related questions

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HydroGEN
Advanced Water Splitting Materials

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