Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

HydroGEN: Photoelectrochemical (PEC) Hydrogen Production

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June 13, 2018

Annual Merit Review

PD148C

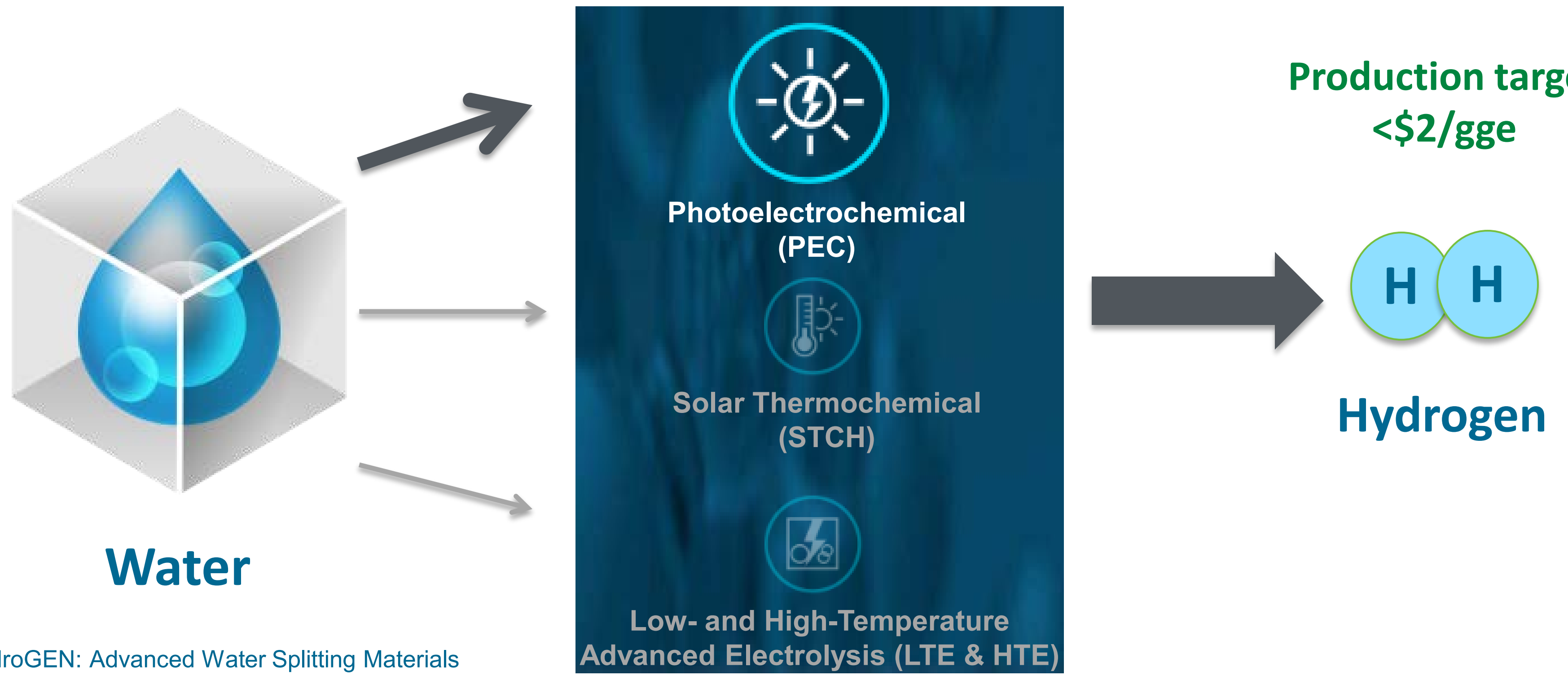
NREL National Renewable Energy Laboratory | Berkeley Lab | Sandia National Laboratories | INL Idaho National Laboratory | Lawrence Livermore National Laboratory | SRNL

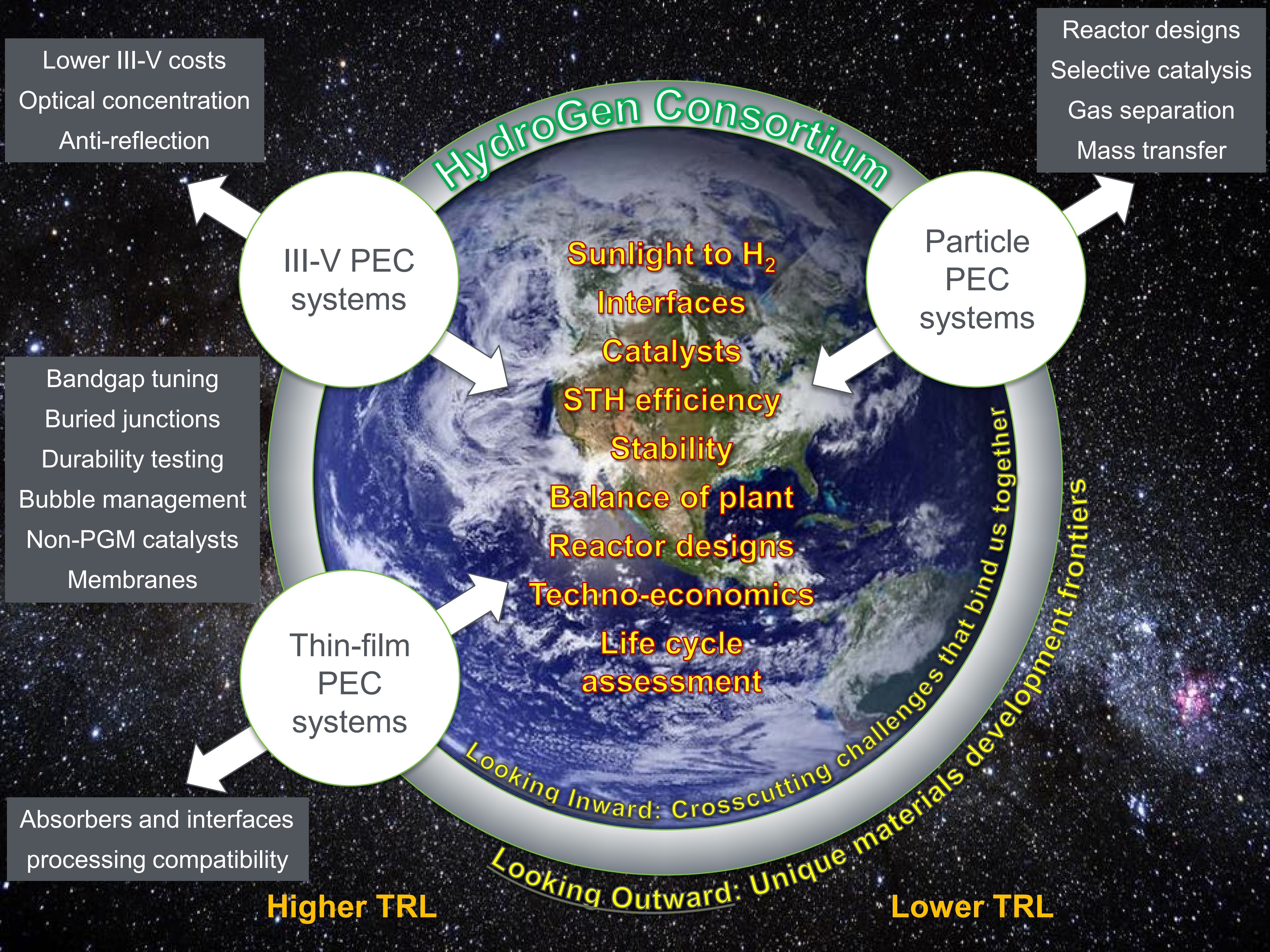
Advanced Water-Splitting Materials (AWSM)
Relevance, Overall Objective, and Impact

AWSM Consortium 6 Core Labs:

NREL (National Renewable Energy Laboratory), Berkeley Lab, Sandia National Laboratories, INL (Idaho National Laboratory), Lawrence Livermore National Laboratory, SRNL

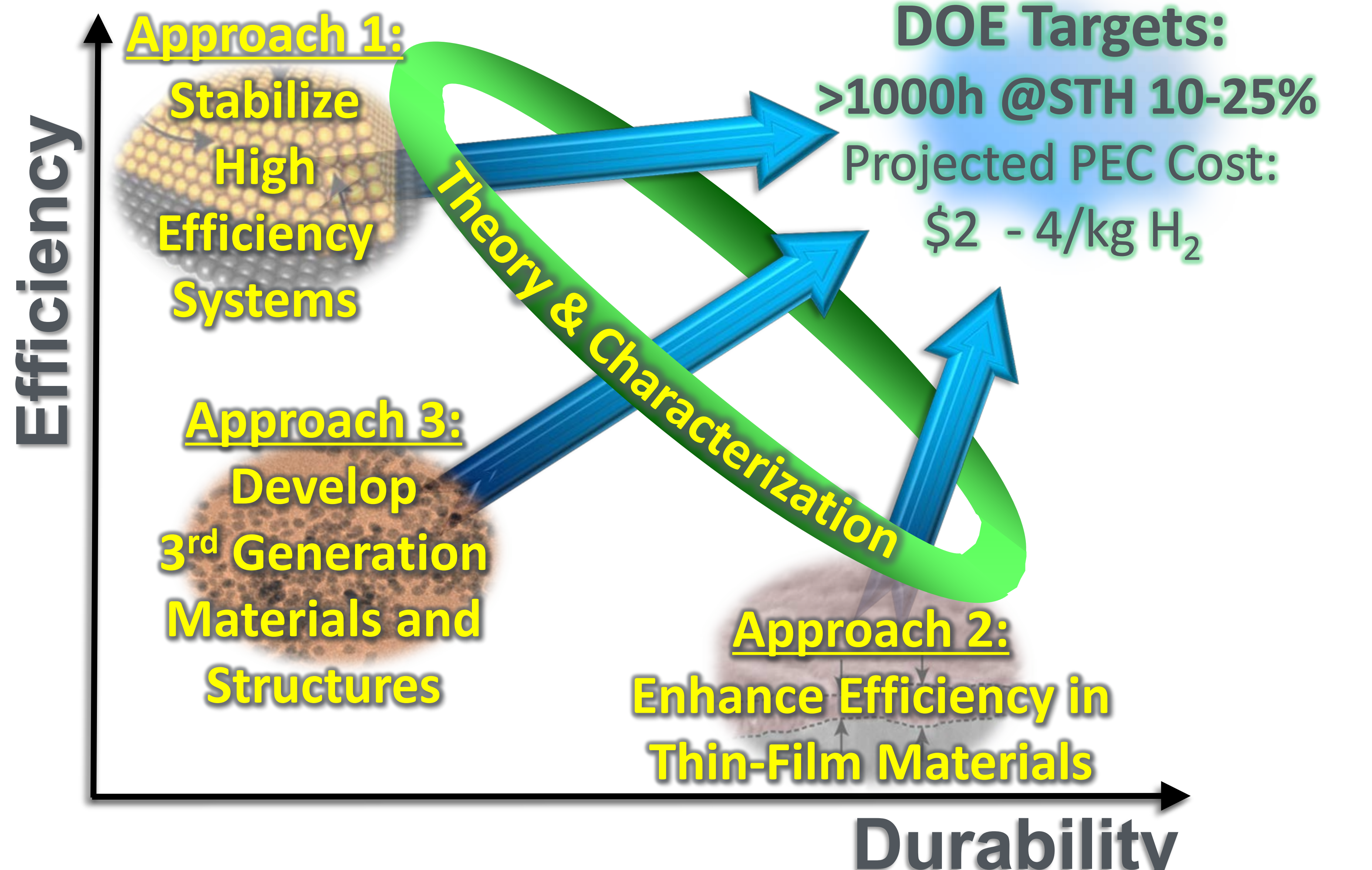
Accelerating R&D of innovative materials critical to advanced water splitting technologies for clean, sustainable & low cost H_2 production, including:



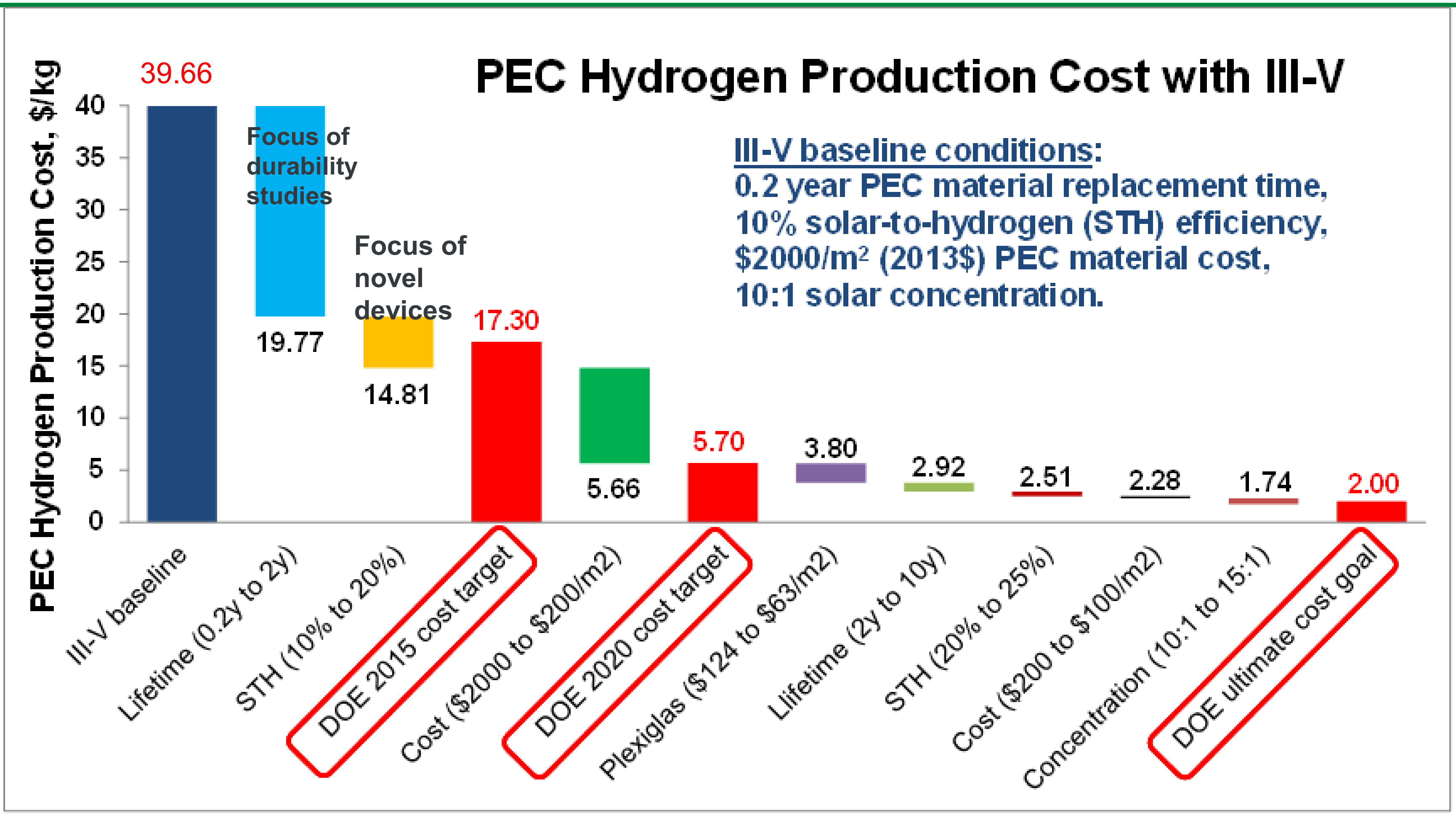


Lower III-V costs
Optical concentration
Anti-reflection
HydroGen Consortium
Reactor designs
Selective catalysis
Gas separation
Mass transfer
III-V PEC systems
Particle PEC systems
Sunlight to H_2
Interfaces
Catalysts
STH efficiency
Stability
Balance of plant
Reactor designs
Techno-economics
Life cycle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

Synopsis of Photoelectrode-based Approaches

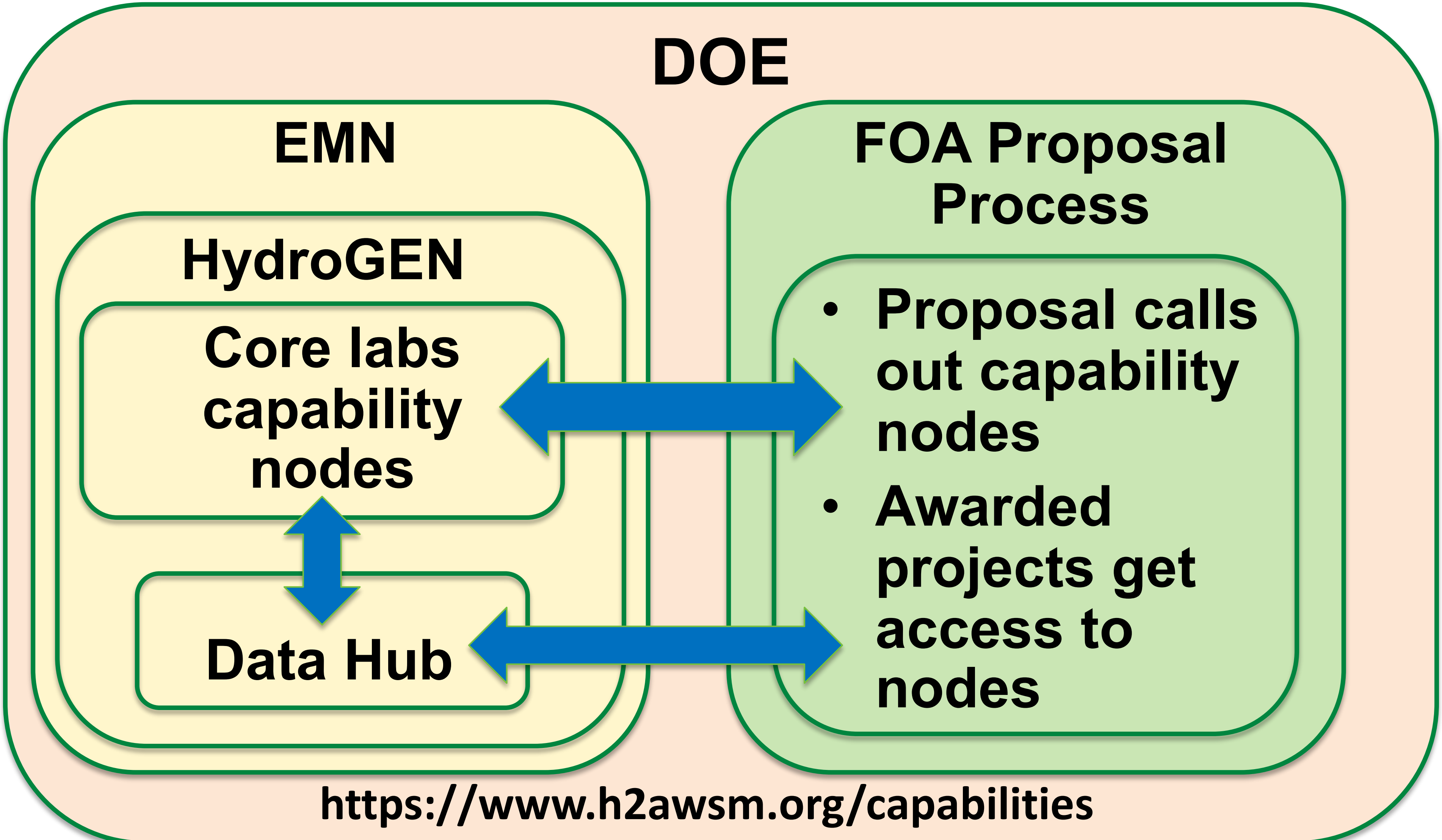


Waterfall Chart: One Pathway to Meet H_2 Cost Target



Waterfall chart projecting cost reductions in PEC hydrogen production by making serial iterations with the H2A Future Central Hydrogen Production from Photoelectrochemical Type 4 version 3.0 case study (scaled to 2000 kg/day, 98% plant capacity factor) with our anticipated progress towards technical targets.

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:

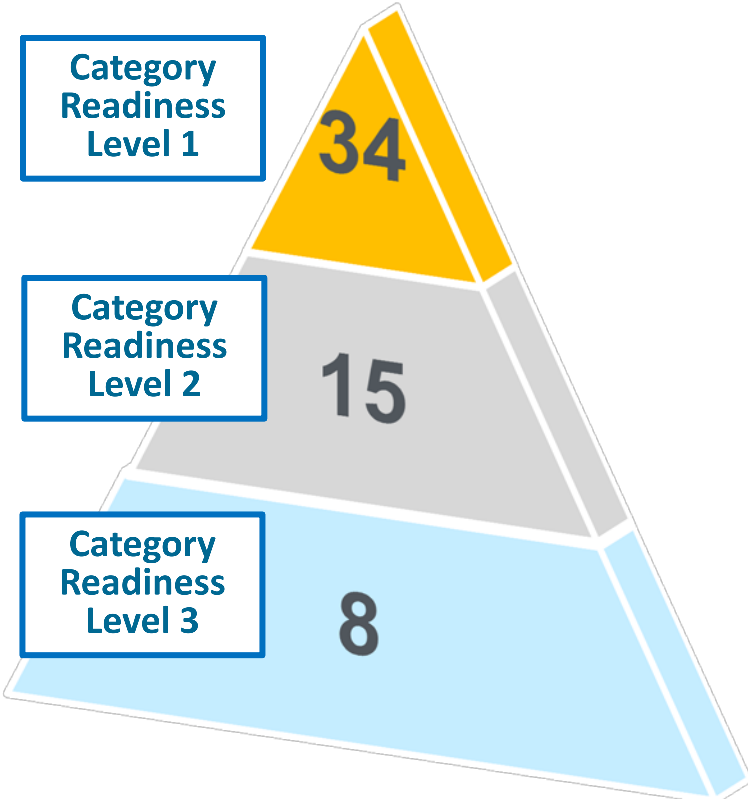
↔

- Personnel
- Equipment
- Expertise
- Capability
- Materials
- Data

PEC Projects

University of Hawai'i
Rutgers, The State University of New Jersey
University of Michigan
Stanford University
Los Alamos National Laboratory

Collaboration: 57 PEC Nodes



Category Readiness Level 1
- Analysis: 2
- Computation: 11
- Characterization: 13
- Synthesis: 8

Category Readiness Level 2
- Analysis: 0
- Computation: 3
- Characterization: 7
- Synthesis: 5

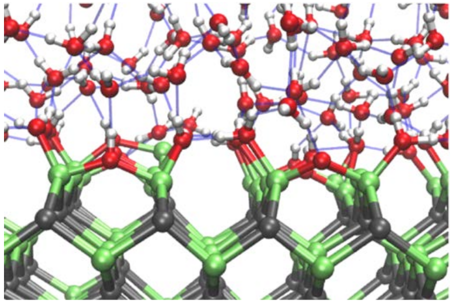
Category Readiness Level 3
- Analysis: 1
- Computation: 3
- Characterization: 2
- Synthesis: 2

- Nodes comprise equipment and expertise including uniqueness
- Category refers to availability and readiness and not necessarily the expense and time commitment
- Note that many nodes span classification areas

Example node: LLNL - LTE 2, PEC 1
Ab initio modeling of electrochemical interfaces

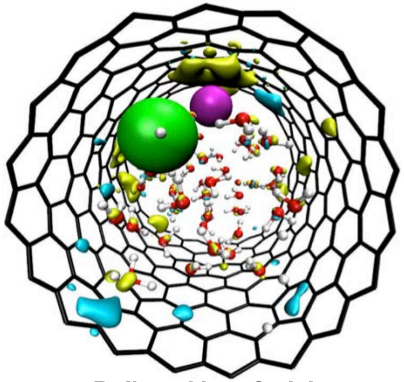
Solid-liquid interfacial chemistry

JACS 135, 15774 (2013); Nat. Mater. (In press)



Ab initio molecular dynamics of semiconductor-water and metal-water interfaces

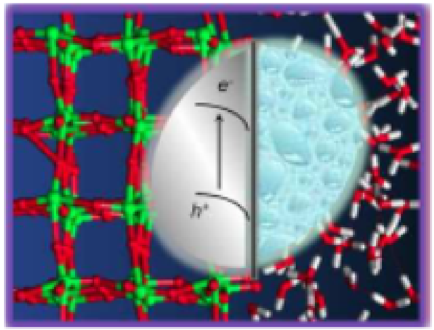
JPCC 120, 7332 (2016)



Bulk and interfacial properties of aqueous electrolytes

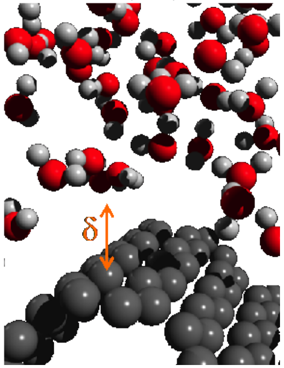
Electronic properties of interfaces

JACS 136, 17071 (2014); PRB 89, 060202 (2014)



Electronic properties of electrode-electrolyte interfaces (from GW)

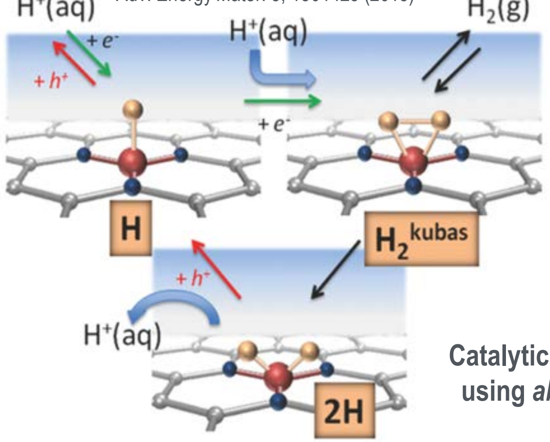
PRB 91, 125415 (2015); JPCC 118, 4 (2014)



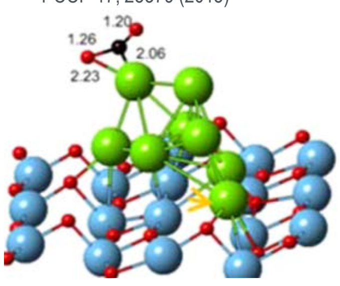
Simulations under applied bias or photobias

Electrocatalysis and photocatalysis

Adv. Energy Mater. 5, 1501423 (2015)

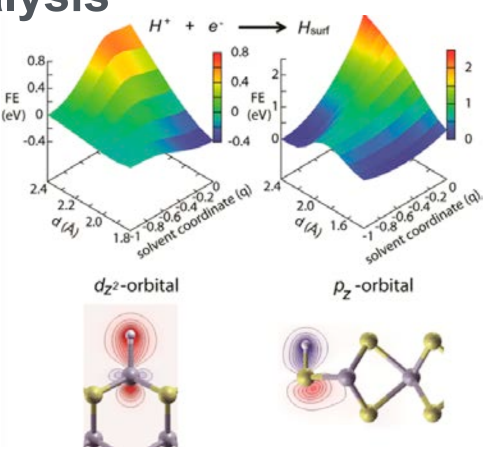


JPCC 118, 26236 (2014); PCCP 17, 25379 (2015)



Catalytic activity predictions using *ab initio* descriptors

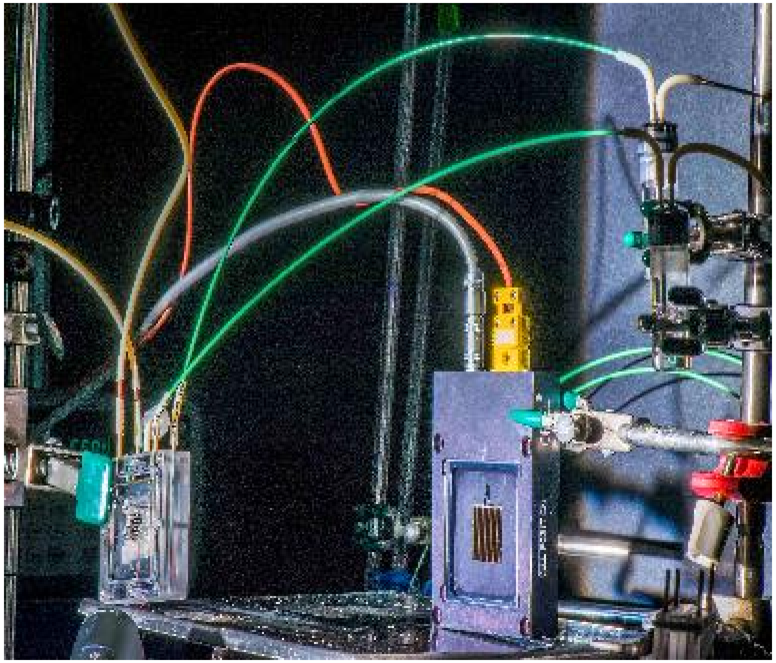
Charge-transfer barriers for H_2 evolution



JPCC 117, 21772 (2013)

Example node: LBNL - LTE 1, PEC 1
Water-splitting device testing

- Electro- and photoelectro- chemical, testing and characterization stations
  - 30 x 30 cm Oriel Sol3A solar simulator (model: SP94123A-5354, vendor: Newport) with dose exposure control, and calibrated Si reference cell
  - 2x channel gas chromatography
    - 50 ppm sensitivity for hydrogen and oxygen
  - Inverted-burette with digital manometer for production rate
  - Biologic potentiostats with impedance, computer system, and video camera
  - High current power supplies and various testing hardware
  - Multiple Scribner and Fuel Cell Technologies test stations outfitted for electrolysis and Maccor Battery Cycler (up to 120A)
  - Various cell assemblies and architectures



Overview: FOA Seedling Projects

17 Nodes utilized
14 Lab PIs engaged
1 User facility proposal submitted
26 samples exchanged
100's of files on Data Hub

1. **Rutgers**: PGM Free electrocatalysts on GaInP or Si PV cells
2. **Stanford**: Protective Catalyst Systems on III-V and Si-based Semiconductors for Efficient, Durable PEC Water Splitting Devices
3. **U. Hawaii**: Novel Chalcopyrites for Advanced Photoelectrochemical Water-Splitting
4. **U. Michigan**: Monolithically Integrated Thin-Film/Silicon Tandem Photoelectrodes for High Efficiency and Stable PEC Water Splitting
5. **LANL**: Efficient Solar Water Splitting with 5,000 Hours Stability Using Earth-Abundant Catalysts and Durable Layered 2D Perovskite

- Interact with the PEC Working Group and 2B

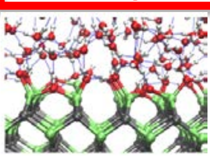
Collaboration: HydroGEN PEC Node Utilization

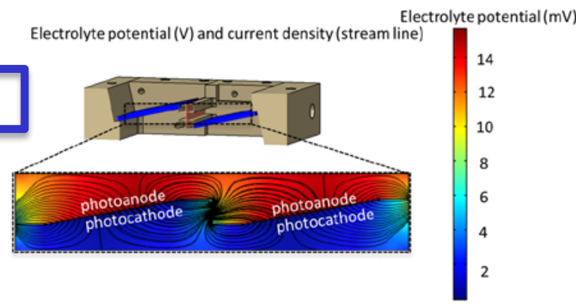
Lab	Node	Hawaii	Stanford	Rutgers	Michigan	LANL
LLNL	Material Design and Diagnostics	✓			✓	
LLNL	Interface Modeling	✓			✓	
NREL	Techno-Economic Analysis					✓
LBNL	Multiscale Modeling					✓
NREL	MOVPE		✓	✓		
NREL	CIGS	✓				
NREL	HTE	✓		✓		
NREL	Surface Modifications				✓	
NREL	High Throughput Processing			✓		

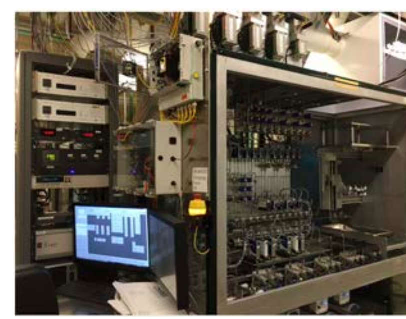
Processing & Scale Up

Computation

Material Synthesis



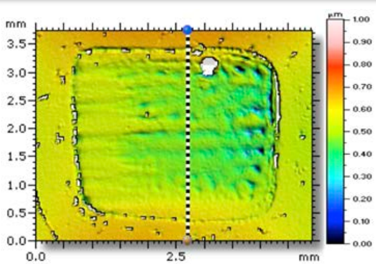



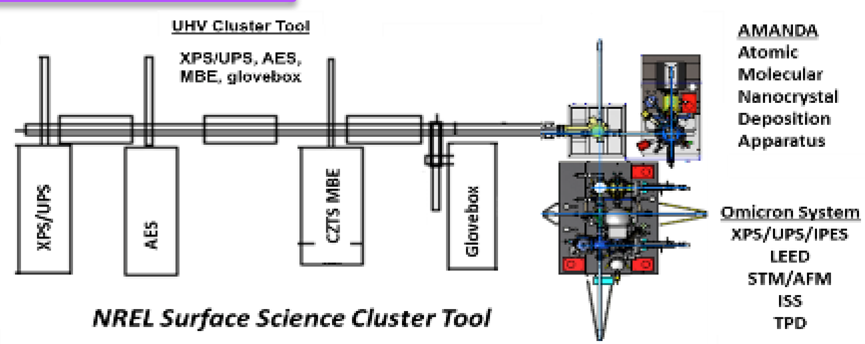


Collaboration: HydroGEN PEC Node Utilization

Lab	Node	Hawaii	Stanford	Rutgers	Michigan	LANL
LBNL	Corrosion				✓	✓
LBNL	AFM					✓
LBNL	Cell Testing					✓
LBNL	Prototyping					✓
NREL	Surface Analysis Cluster Tool				✓	
NREL	PEC Characterizations		✓	✓		
NREL	On-Sun Efficiency Benchmarking	✓	✓			
NREL	Corrosion Analysis of Materials	✓	✓			

Characterization





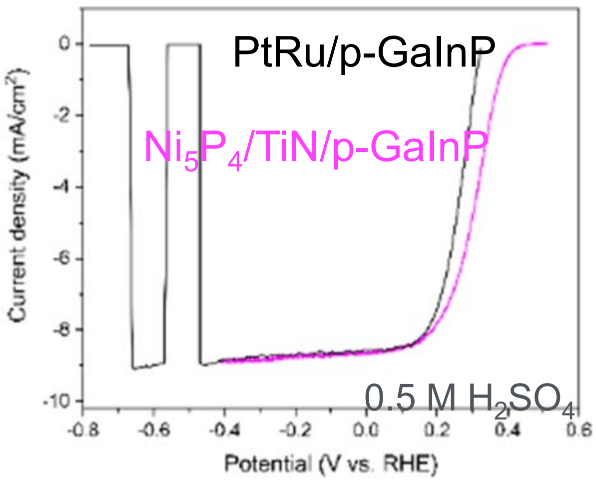
Rutgers Project Accomplishments

See Poster PD160

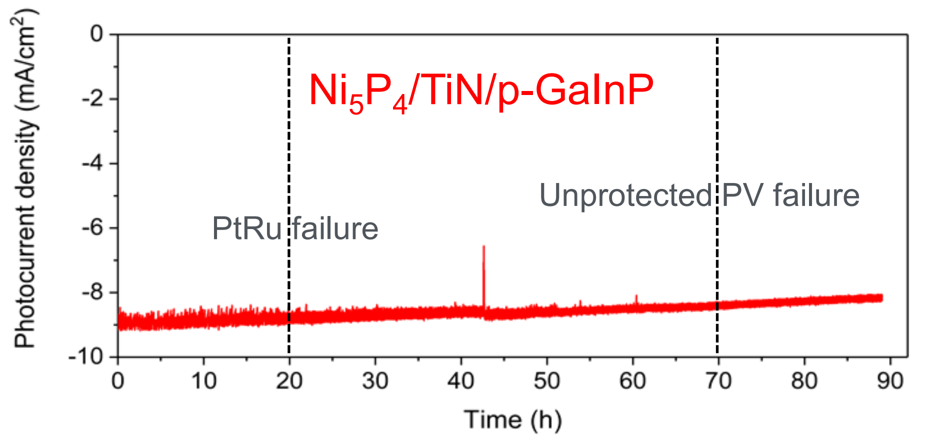
PI: Eric Garfunkel &
G.C. Dismukes

Photocathode: thin films Ni_5P_4/TiN on p-GaInP/GaAs

J-V performance similar to PtRu benchmark

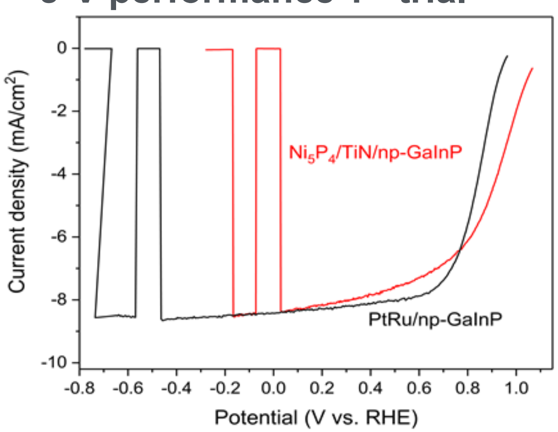


XPS & helium ion microscopy verify conformal catalyst coating
Durability test exceeds two benchmarks

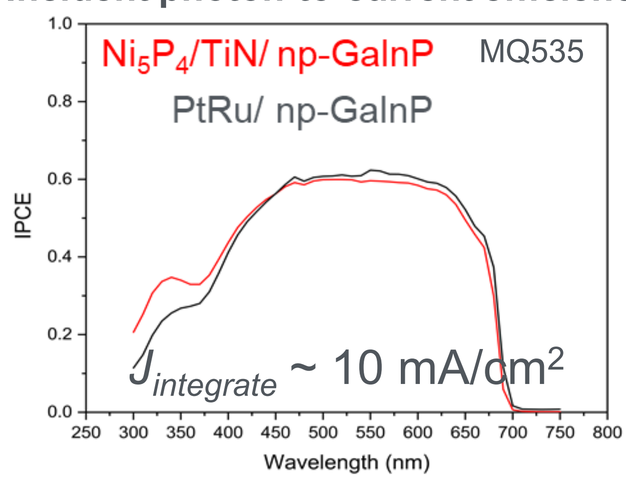


Proof of concept: buried junction fabrication Ni_5P_4/TiN on np-GaInP/GaAs

J-V performance 1st trial



Incident photon-to-current efficiency



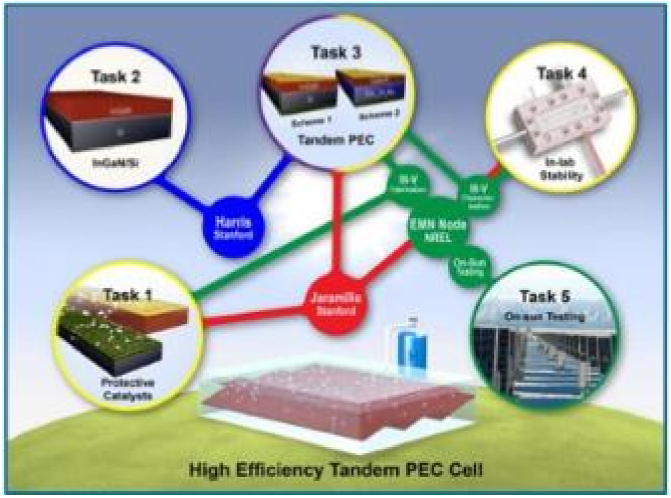
CONCLUSION:
TiN protection layer & Ni_5P_4 hydrogen electrocatalyst on GaInP are more stable, efficient and spectrally as good as PtRu.

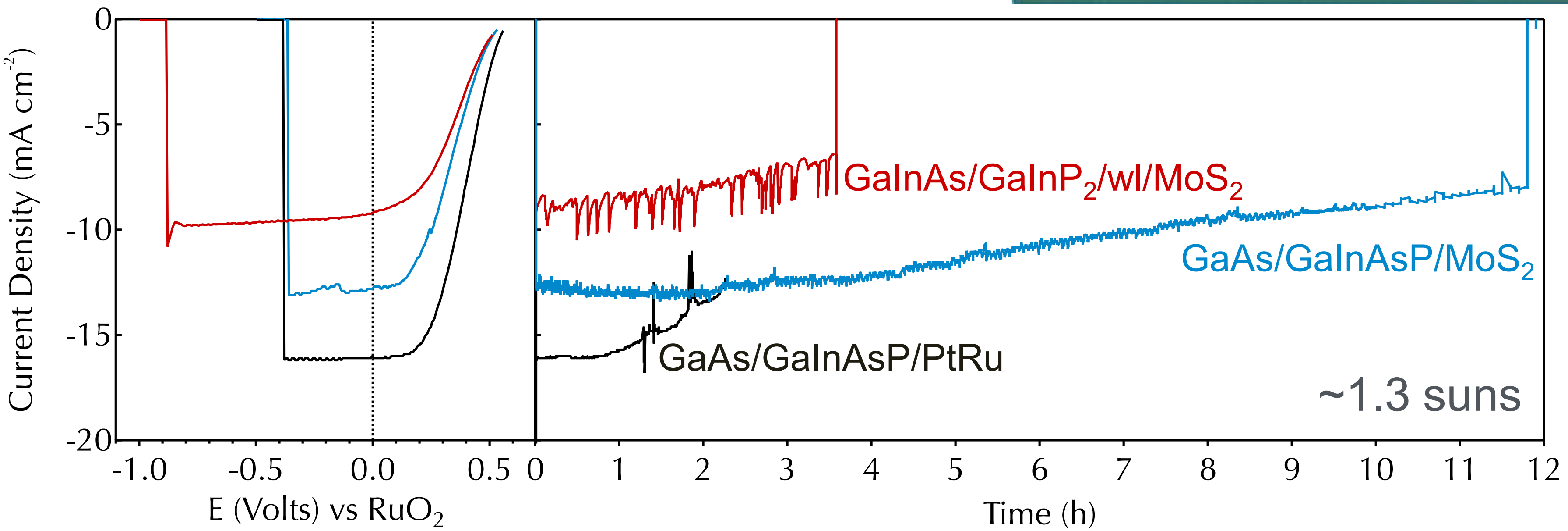
Stanford Project Accomplishments

See Poster PD161

PI: Tom Jaramillo

Unassisted water splitting for ~12 hours and solar to hydrogen (STH) efficiency > 5% with a III-V/III-V inverted metamorphic multijunction (IMM) PEC device using MoS_2 as a protective catalyst coating.



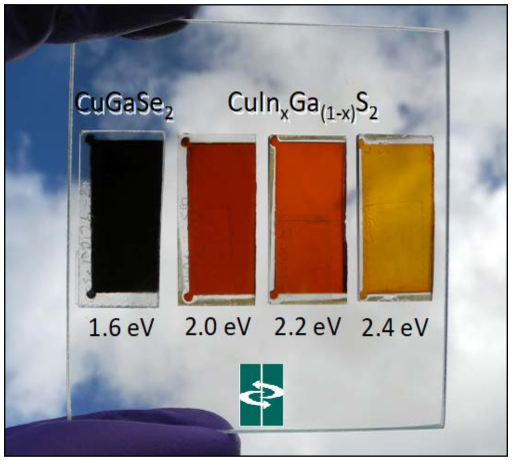


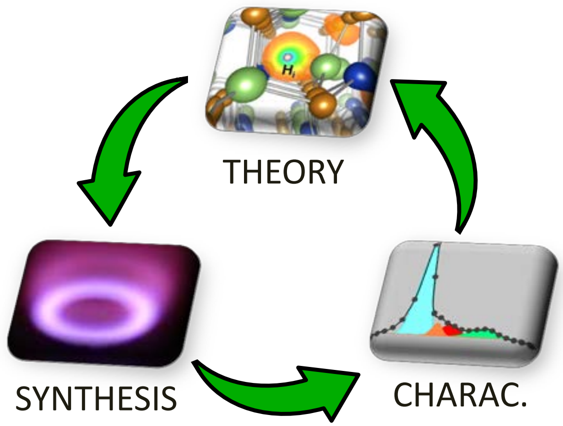
U. Hawaii Project Accomplishments

See Poster PD162

PI: Nicolas Gaillard

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





Scope of work addressing technical barriers

Material barrier: synthesize novel chalcopyrites with alloying techniques

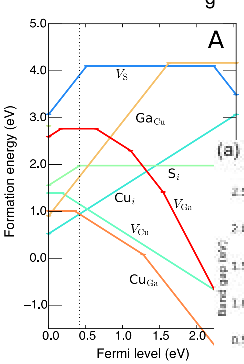
Efficiency barrier: increase efficiency with tunable solid/solid interfaces

Device integration barrier: "transferable" PEC layers for efficient tandem devices

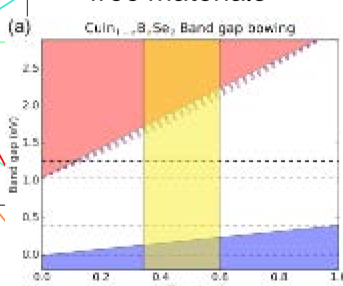
Durability barrier: protect devices with ultra-thin corrosion-resistant layers

Theoretical Modeling

Defect identification in known gallium-based wide E_g chalcopyrites (LLNL)



Identifying new Ga free materials

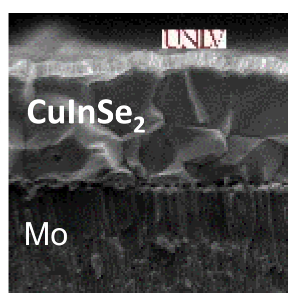


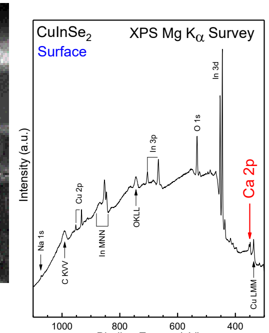
Thin film chalcopyrite "printed" with molecular inks

High quality polycrystalline chalcopyrites via printing

Q1 milestone achieved

Crystallization in Se atmosphere



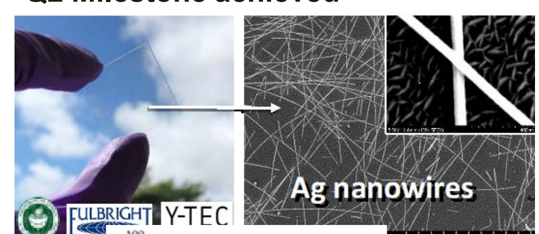


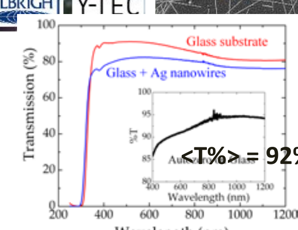
Spectroscopic analysis of printed CuInSe$_2$ (UNLV)

Device Integration

Transparent conductive (TC) binder for semi-monolithic tandem PEC integration

Q2 Milestone achieved



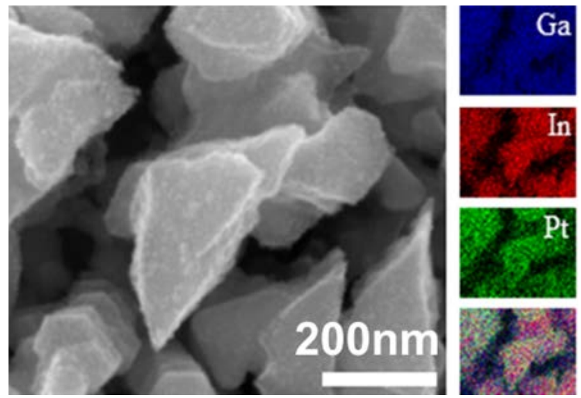


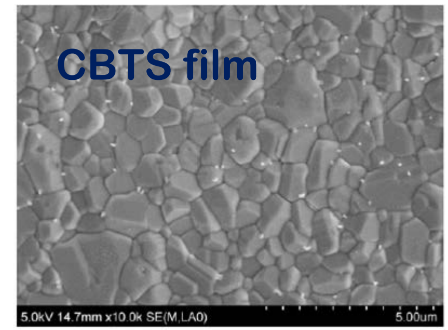
U. Michigan Project Accomplishments

See Poster PD163

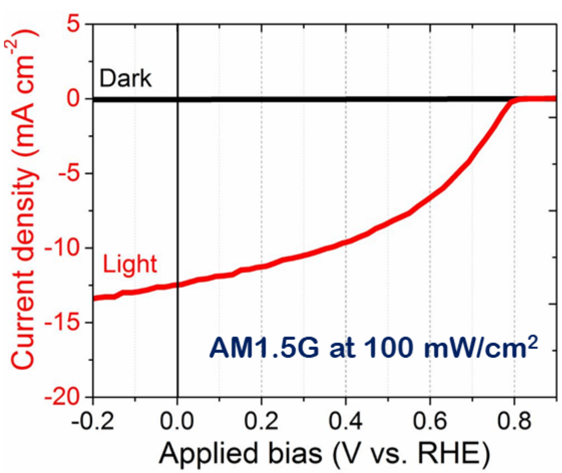
PI: Zetian Mi

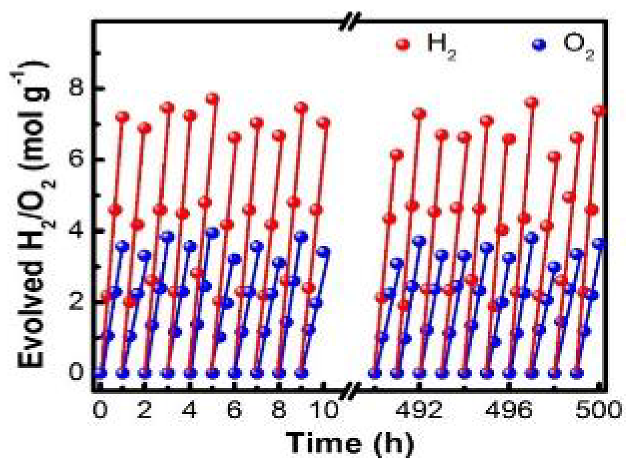
Controlled synthesis of BCTSSe, InGaN and T_3N_5 photoelectrodes (~1.7-2.0 eV bandgaps)

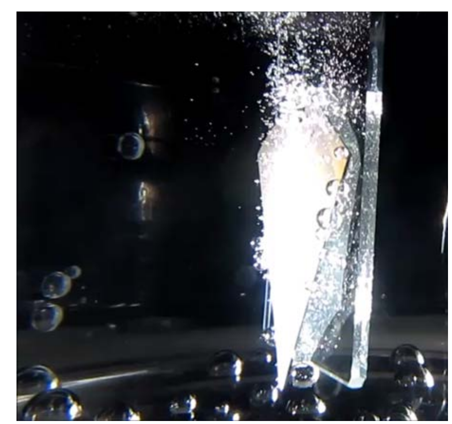




Unassisted overall pure water splitting on InGaN nanowires on Si



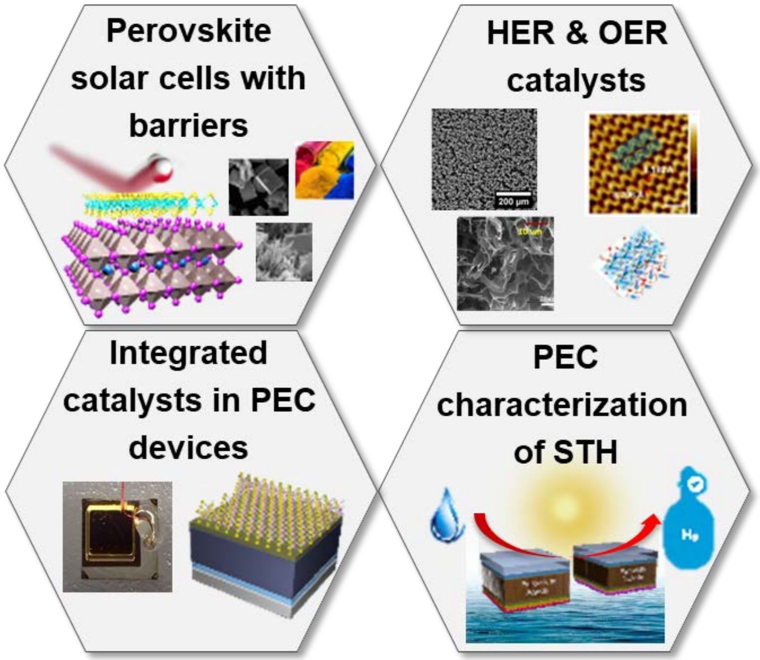


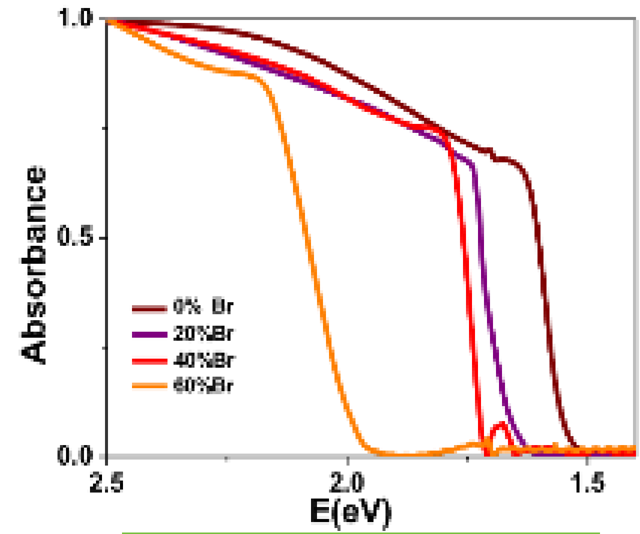


LANL Project Accomplishments

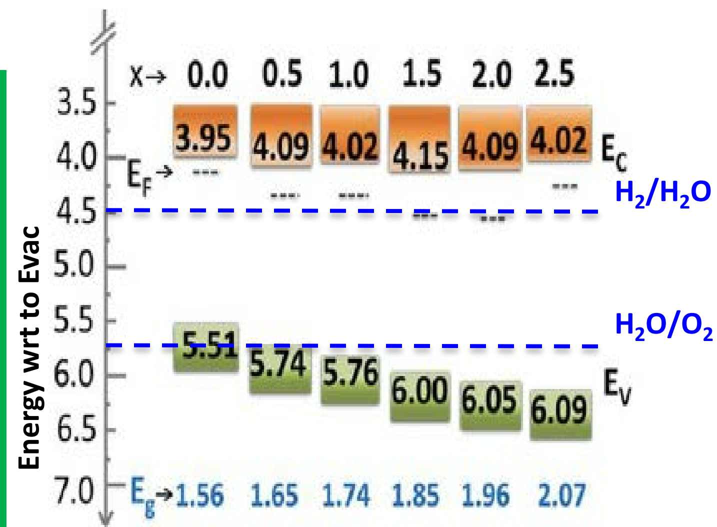
See Poster PD164

PI: Aditya Mohite





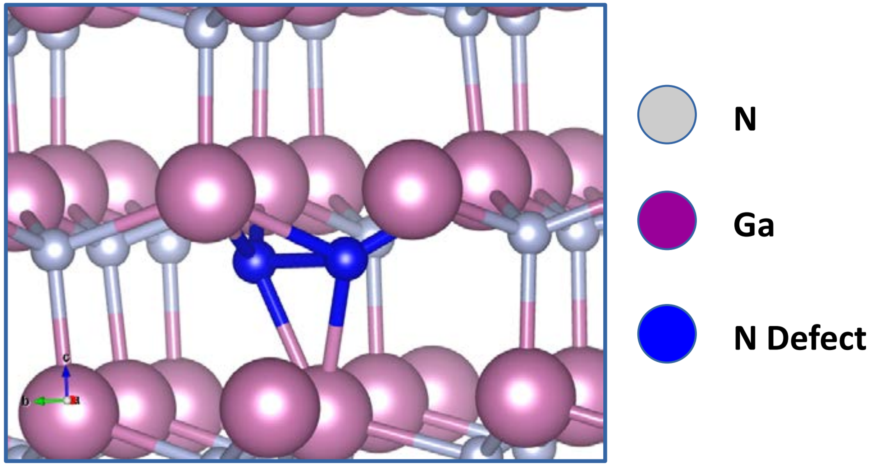
Work func. vs. Br conc.



Tunable band-gap

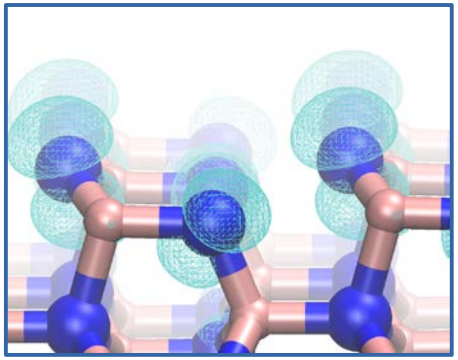
- Discovery of a new mechanism to stabilize perovskite thin films
  - Perovskite with tunable bandgap (1.5 – 2 eV) and optimized band alignment
- Nb HER catalyst with overpotential <150 mV and >>20 mA/cm^2 with stability 100 h
- Ni-Fe@MW-rGO OER catalyst with overpotential < 200mV and 1 mA/cm^2

Accomplishments and Collaboration: Modeling Node utilized by U Hawaii and U Michigan Projects

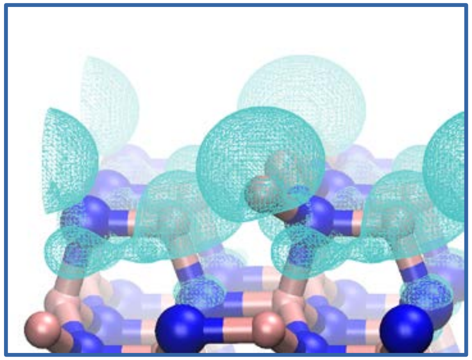


Materials Diagnostic (Varley/Ogitsu)

- Developed defects structure models to identify the origin of the OCP saturation
- Construction of defect phase diagrams is underway to identify detrimental defects, and to understand how working conditions (temperature, chemical potentials) affect the defect density, and hence identifying the optimal synthesis condition



N-rich surface: Dangling bond character of the VBM



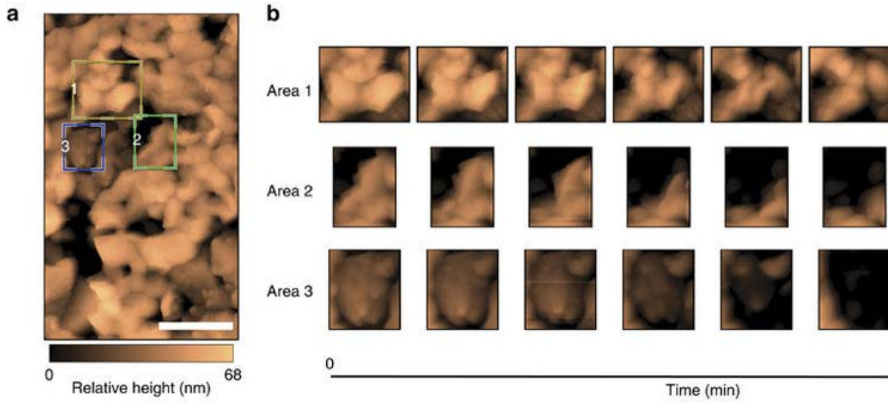
Ga-rich surface: Bonding character of the VBM

Interface Modeling (Pham/Ogitsu)

- Developed N/Ga-rich GaN surfaces to investigate the atomistic origin of chemical stability and performance
- Developed structure models of GaN/water interface to investigate chemical activities at the photoelectrochemical interface, and elucidate their influence on water-splitting reactions and materials stability

Theoretical models and interpretations will be validated by experimental characterization

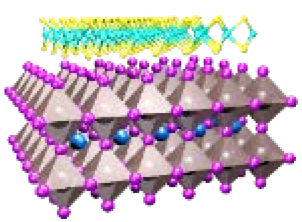
Accomplishments and Collaboration: Characterization Node utilized by LANL and U Michigan projects



a) EC-AFM scan of $BiVO_4$. b) The three regions indicated in a) were used to monitor corrosion-induced changes to $BiVO_4$ morphology.

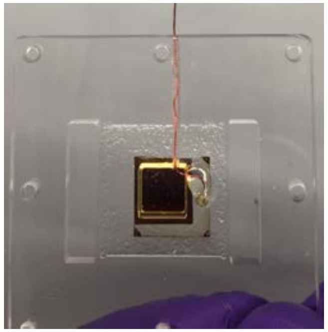
Materials Diagnostic (Toma)

- Assessment of the chemical and photochemical stabilities of (photo)electrochemical assemblies
- Utilized to explore the U Michigan catalysts and their connectivity, InGaN and TaN based
- Utilized to explore LANL halide perovskite based photoanode and photocathode, protective barriers and HER/OER catalysts
- AFM, EC-AFM, and PEC-AFM techniques



Louisville and Rutgers HER/OER catalysts

LBNL ALD or Molecular Foundry



Halide perovskite

Barrier/catalyst addition

PV integration and barrier/catalyst addition

Materials Integration and Optimization (Toma)

- A combination of different approaches to optimize photoelectrochemical assemblies
- Integrating protective barriers and catalysts to halide perovskite
  - Molecular Foundry and ALD coatings
  - Project partner HER/OER catalysts
- Integration of PV/PEC into test bed for PEC testing to meet G./N.G.

Accomplishments & Collaboration: PEC Project Node Usage Case Study: Rutgers

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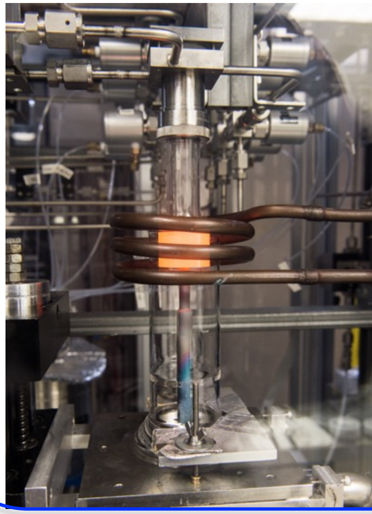
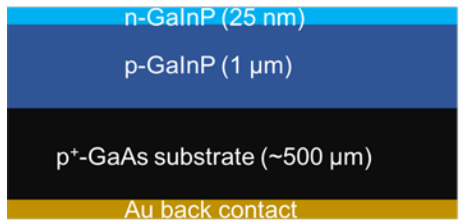
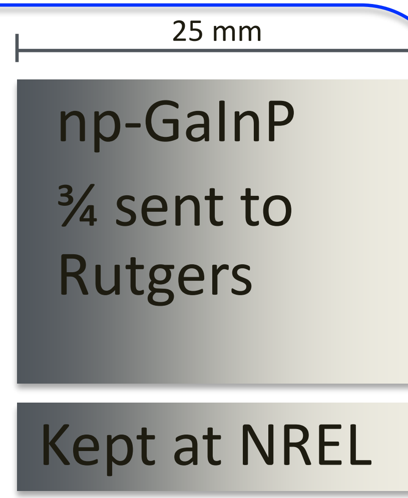


NREL: MOVPE

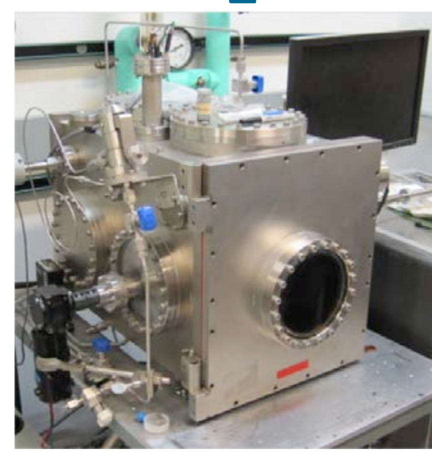
NREL synthesizes III-V sample





PtRu sputtering

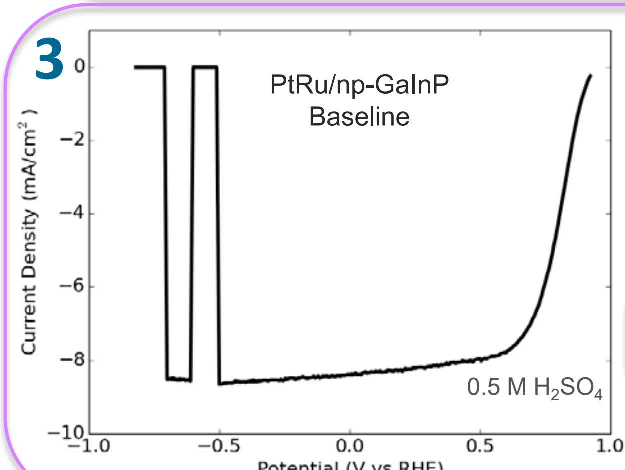
2

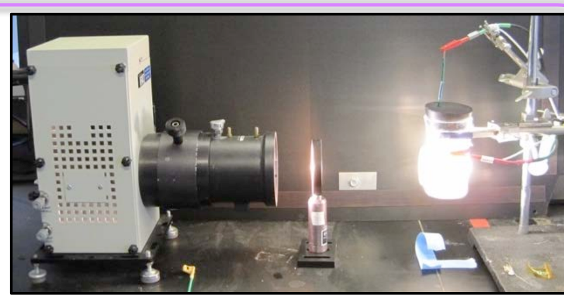


NREL: Surface Mods

Electrode fabrication and baseline testing

3



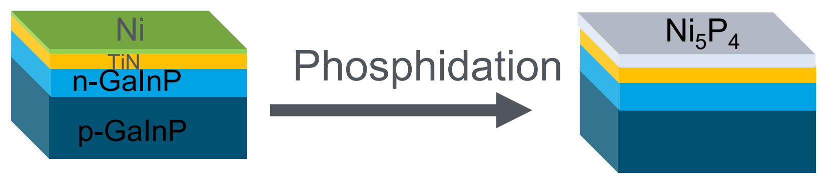


NREL: PEC Characterization

Material Synthesis | **Characterization**

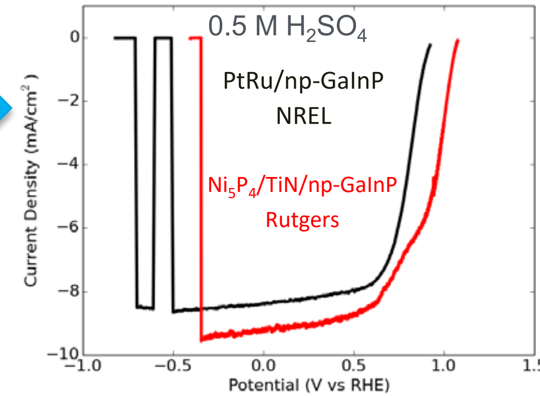
Accomplishments & Collaboration: PEC Project Node Usage Case Study : Rutgers

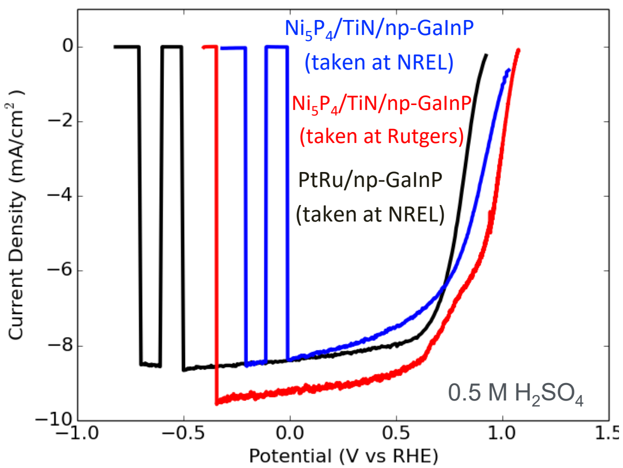
Rutgers modifies III-V sample surface



PEC Characterizations

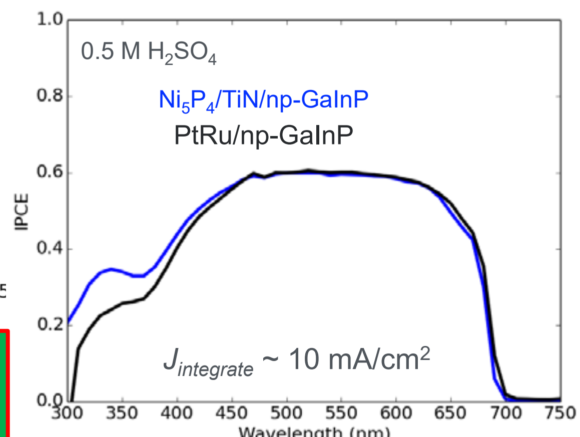
PEC data taken at Rutgers compared with NREL baseline





J-V measurements of modified surface validated at NREL and compared with baseline

- **Concurrence on voltage**
- **Current density difference could be due to light source**
  - **NREL sending wide band gap reference cells to Rutgers to calibrate light source**



Incident photon-to-current efficiency (IPCE)

Modified samples sent back to NREL

NREL performs additional measurements on the modified samples

NREL: PEC Characterization

Characterization

Engagement with 2B Team

- Collaboration with 2B Team Benchmarking Project
- Node feedback on questionnaire & draft test framework on material, component, and device level properties
  - Defining: baseline materials sets, test cells, testing conditions
- All HydroGEN PEC node capabilities were assessed for AWS technology relevance and readiness level
- PEC data metadata definitions exchanged
- PEC working group meeting at ECS in Seattle (May 13, 2018)

Future Work

- Leverage HydroGEN Nodes at the labs to enable successful Go/No-Go of Phase 1 projects
  - Increased durability and lifetime
  - Utilization of PGM-free catalysts
  - Novel photoelectrode materials
- Enable research in Phase 2 work for some projects and enable new seedling projects
- Work with the 2B team and PEC working group to establish testing protocols and benchmarks
- Utilize data hub for increased communication, collaboration, generalized learnings, and making digital data public
- Leverage JCAP resources and work done with the solar fuel hub

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

Summary

- Supporting 5 FOA projects with 17 nodes and 14 PIs
  - Synthesis, benchmarking, modeling, characterization
  - 26 sample sets exchanged between PEC nodes and seedling projects including 100's of files on the data hub
  - 1 joint user proposal to Advanced Light Source
  - Personnel exchange: 2 visits of PI 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
- Future work will include continuing to enable the projects technical progress and develop & utilize lab core capabilities

Acknowledgements

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HydroGEN
Advanced Water Splitting Materials

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

Technical Backup Slides

PEC HydroGEN Node Participants

- PIs:
  - NREL: Dan Friedman, Myles Steiner, Todd Deutsch, Andriy Zakutayev, Kai Zhu, Mike Ulsh, Glenn Teeter, Genevieve Sauer
  - LBNL: Francesca Toma, Adam Weber, Nemanja Danilovic
  - LLNL: Joel Varley, Tuan Anh Pham, Tadashi Ogitsu
- Contributing Staff:
  - NREL: James Young, Rachel Mow, Chase Aldridge, Isabel Barraza, Chris Muzzillo, Elisabetta Arca, Kristin Munch, Conor Riley, Karen Heinselmann, Yun Xu, Imran Khan, Dylan Hamilton
  - LBNL: Johanna Eichhorn, Guosong Zeng, David Larson

Collaboration: U Michigan/Node Interactions

G. Teeter, NREL

- **Surface Analysis Cluster Tool**

- Performed XPS measurements and revealed that the conduction band offset between Si and GaN is negligibly small, which forms the basis for the design of GaN/Si tandem photoelectrode.

T. Ogitsu, LLNL

- **Ab initio modeling of electrochemical interfaces node**
- **Materials diagnostics node**

- Developed surface structural models of N/Ga rich GaN surfaces to elucidate the atomic origin of the long-term stability of GaN photoelectrodes.
- Developed defect structural models of GaN to identify types of defects responsible for the saturation of open circuit voltage.

T. Deutsch, NREL

- **Surface modifications and protection**

- Performed co-catalyst deposition and PEC characterization of GaN and Ta_3N_5 photoelectrode samples, which provide critical feedback for the PEC device design, synthesis, and performance improvement.

F. Toma, LBNL

- **Probing and mitigating chemical and photochemical corrosion of electrochemical and PEC assemblies**

- Submitted a joint proposal to Advanced Light Source (ALS) at LBNL for in operando characterization of of GaN photoelectrodes.
- Intensified sample exchange will take place in Q3 and the results will be correlated with theory and PEC testing.

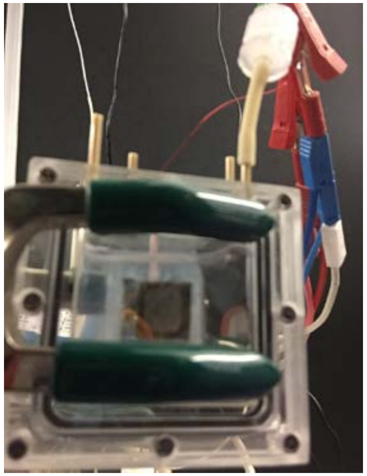
Collaboration: LANL/Node Interactions

- **LBNL: PEC measurements and benchmarking**
  Dr. Nemanja Danilovic & Dr. Francesca Toma
  1. Site-visit (2-full days) to establish detailed protocols for hybrid perovskite PEC measurements
  2. Established device design and interface layers for photocathode & anode
  3. Design of complete PEC cell and validated design by loading perovskite/Pt photocathodes
  4. Three batches of perovskite solar cells exchanged with different barrier layers
- **LBNL: Understanding degradation mechanisms in PECs through in-situ characterization techniques – Dr. Francesca Toma**
  1. Planed work to perform in-situ degradation studies before and after PEC testing using in-situ scanning probe techniques such as conducting AFM
  2. Planned work on measuring in-situ charge transfer using dynamic optical probes
- **LBNL: Multiscale modeling of PECs – Dr. Adam Weber**
  1. Discussions to understand interfacial degradation processes using modeling

  <u>Impact on project:</u> Critical for development of first of its kind perovskite-based PEC platform for testing, characterization and benchmarking performance and stability.
- **NREL: Techno economic analysis of perovskite based PEC system**
  Working to develop a rough techno-economic evaluation of the perovskite-based PEC

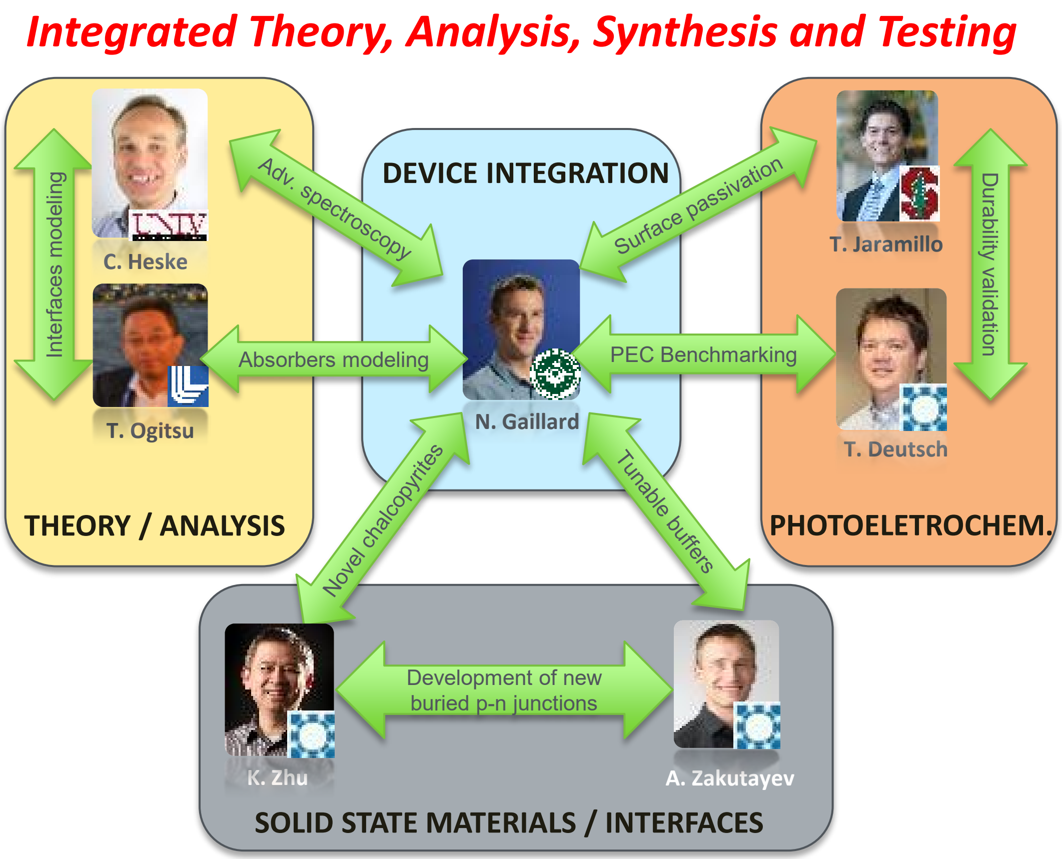
Front surface of photocathode/anode

Full assembled cell



Collaboration: U Hawaii/Node Interactions

Academia-EMN Node interaction



Computational Materials Diagnostics and Optimization Node (T. Ogitsu).

- **Role:** theoretical modeling of novel materials.
- **Benefit to this program:** defines synthesis conditions and thermodynamic stability of chalcopyrite candidates.

I-III-VI Compound Semiconductors for Water-Splitting Node (K. Zhu)

- **Role:** synthesis of high-purity material systems.
- **Benefit to this program:** "ideal" vacuum-based chalcopyrites used to test alloying/doping strategies.

High-Throughput Thin Film Combinatorial Capabilities Node (A. Zakutayev)

- **Role:** develop n-type buffers with tunable 'energetics'
- **Benefit to this program:** accelerates material discovery for improved interfaces.

Corrosion Analysis of Materials Node (T. Deutsch)

- **Role:** supports development of surface passivation against photo-corrosion.
- **Benefit to this program:** provide access to unique instrumentation to identify corrosion mechanisms.

Collaboration: Stanford/Node Interactions

This project advances towards <$2/kg hydrogen by:

- Improving efficiency and durability of state-of-the-art photoelectrodes using earth-abundant protection layers towards > 20% solar-to-hydrogen (STH) efficiency with long-term, on-sun operation. Techno-economic modeling (B. Pinaud et. al. *Energy & Environmental Science*, 6 (2013) 1983-2002) shows that with high-efficiency, durable, low-cost photoelectrodes, cost effective production of H_2 is feasible.

Leveraging EMN Resource Nodes:

- **NREL EMN Node: Characterization of Semiconductor Bulk and Interfacial Properties, Todd Deutsch**
  - Characterization of fundamental semiconductor properties and growth defects before and after testing
- **NREL EMN Node: Corrosion Analysis of Materials, Todd Deutsch**
  - Pre- and post- failure analysis and improved understanding of catalyst corrosion and interfaces
- **NREL EMN Node: III-V Semiconductor Epi-structure and Device Design and Fabrication, Daniel Friedman**
  - Fabrication of III-V materials and systems and improved understanding of growth defects
- **NREL EMN Node: On-Sun Solar-to-Hydrogen Benchmarking, Todd Deutsch**
  - Testing station for collection of on-sun data for unassisted water splitting devices

This project is heavily engaged with the EMN nodes, which are absolutely necessary for the success of this project; the HydroGEN Consortium R&D model is working extremely well. Furthermore, we expect that our node utilization is helping to improve node capabilities by generating expertise such as improved understanding of catalyst corrosion and interface energetics in the PEC node as well as improved understanding of growth defects in the III-V fabrication node. We expect that the on-sun solar-to-hydrogen benchmarking node will also be of greater benefit to the community as we gain knowledge on testing our devices when the time comes.