HydroGEN: Photoelectrochemical (PEC) Hydrogen Production

Todd Deutsch, Nemanja Danilovic, Huyen N. Dinh, Adam Z. Weber
June 13, 2018
Annual Merit Review
Advanced Water-Splitting Materials (AWSM)
Relevance, Overall Objective, and Impact

AWSM Consortium
6 Core Labs:

Accelerating R&D of innovative materials critical to advanced water splitting technologies for clean, sustainable & low cost H₂ production, including:

- Photoelectrochemical (PEC)
- Solar Thermochemical (STCH)
- Low- and High-Temperature Advanced Electrolysis (LTE & HTE)

Production target <$2/gge

HydroGEN: Advanced Water Splitting Materials
Synopsis of Photoelectrode-based Approaches

**Approach 1:** Stabilize High Efficiency Systems

**Approach 2:** Enhance Efficiency in Thin-Film Materials

**Approach 3:** Develop 3rd Generation Materials and Structures

**DOE Targets:**
- >1000h @ STH 10-25%
- Projected PEC Cost: $2 - 4/kg H₂

**Theory & Characterization**
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

- **DOE**
  - FOA Proposal Process
    - Proposal calls out capability nodes
    - Awarded projects get access to nodes

- **HydroGEN**
  - Core labs capability nodes
  - Data Hub

- **EMN**

https://www.h2awsm.org/capabilities
Approach – EMN HydroGEN

PEC: Photoelectrochemical Electrolysis

- Support through:
  - Personnel
  - Equipment
  - Expertise
  - Capability
  - Materials
  - Data

PEC Node Labs
- NREL
- Berkeley Lab
- Sandia National Laboratories
- Lawrence Livermore National Laboratory

PEC Projects
- Rutgers
- University of Michigan
- Stanford University
- Los Alamos National Laboratory

Barriers
- Cost
- Efficiency
- Durability
Collaboration: 57 PEC Nodes

- 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

<table>
<thead>
<tr>
<th>Category Readiness Level</th>
<th>Analysis</th>
<th>Characterization</th>
<th>Computation</th>
<th>Synthesis</th>
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Example node: LLNL - LTE 2, PEC 1
Ab initio modeling of electrochemical interfaces

**Solid-liquid interfacial chemistry**
- *Ab initio* molecular dynamics of semiconductor-water and metal-water interfaces
- Bulk and interfacial properties of aqueous electrolytes

**Electronic properties of interfaces**
- Electric properties of electrode-electrolyte interfaces (from GW)
- Simulations under applied bias or photobias

**Electrocatalysis and photocatalysis**
- Charge-transfer barriers for H₂ evolution
- Catalytic activity predictions using *ab initio* descriptors

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HydroGEN: Advanced Water Splitting Materials


*JPCC* 117, 21772 (2013); *JPCC* 118, 4 (2014)

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

*JPCC* 120, 7332 (2016)

*PCCP* 17, 25379 (2015)


*PCCP* 17, 25379 (2015)

*JPCC* 118, 26236 (2014)

*PCCP* 17, 25379 (2015)
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

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

17 Nodes utilized
14 Lab PIs engaged
1 User facility proposal submitted
26 samples exchanged
100’s of files on Data Hub
# Collaboration: HydroGEN PEC Node Utilization

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<th>Lab</th>
<th>Node</th>
<th>Hawaii</th>
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<th>Rutgers</th>
<th>Michigan</th>
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**Processing & Scale Up**

**Computation**

**Material Synthesis**
Collaboration: HydroGEN PEC Node Utilization

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Photocathode: thin films $\text{Ni}_5\text{P}_4$/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 $\text{Ni}_5\text{P}_4$/TiN on np-GaInP/GaAs

J-V performance 1st trial

CONCLUSION:

TiN protection layer & $\text{Ni}_5\text{P}_4$ hydrogen electrocatalyst on GaInP are more stable, efficient and spectrally as good as PtRu.
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.
Develop innovative technologies to synthesize and integrate chalcopyrites into efficient and low-cost PEC devices.

**Theory**

- Synthesis Charac.
  - Thin film chalcopyrite “printed” with molecular inks
  - Theoretical Modeling
  - 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

**U. Hawaii Project Accomplishments**

- Defect identification in known gallium-based wide Eg chalcopyrites (LLNL)
  - Mo CuInSe₂ Crystallization in Se atmosphere
  - High quality polycrystalline chalcopyrites via printing Q1 milestone achieved
  - Crystallization in Se atmosphere
  - Identifying new Ga free materials
  - Identifying new Ga free materials

- Spectroscopic analysis of printed CuInSe₂ (UNLV)

- Transparent conductive (TC) binder for semi-monolithic tandem PEC integration Q2 Milestone achieved

- HydroGEN: Advanced Water Splitting Materials
U. Michigan Project Accomplishments

Controlled synthesis of BCTSSe, InGaN and T$_3$N$_5$ photoelectrodes (~1.7-2.0 eV bandgaps)

Unassisted overall pure water splitting on InGaN nanowires on Si

![Image of controlled synthesis of BCTSSe, InGaN and T$_3$N$_5$ photoelectrodes]

![Image of CBTS film]

![Graph showing current density vs. applied bias]

![Graph showing evolved H$_2$ and O$_2$ over time]

See Poster PD163
PI: Zetian Mi
LANL Project Accomplishments

- 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/cm² with stability 100 h
- Ni-Fe@MW-rGO OER catalyst with overpotential < 200mV and 1 mA/cm²

See Poster PD164
PI: Aditya Mohite
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

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

**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

**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

1. NREL: MOVPE

NREL synthesizes III-V sample

- n-GaInP (25 nm)
- p-GaInP (1 µm)
- p'-GaAs substrate (~500 µm)

Sent to Rutgers: ¾

Kept at NREL: ¼

PtRu sputtering

3. NREL: PEC Characterization

NREL: Surface Mods

Material Synthesis

Characterization

Electrode fabrication and baseline testing

PtRu/np-GaInP Baseline

n-GaInP (25 nm)

p-GaInP (1 µm)

p'-GaAs substrate (~500 µm)

Gold back contact

25 mm

0.5 M H₂SO₄

Potential (V vs RHE)

Current Density (mA/cm²)

Rutgers

NREL

HydroGEN: Advanced Water Splitting Materials
Rutgers modifies III-V sample surface

**Ni**

**Ni₅P₄**

Phosphidation

**PEC Characterizations**

PEC data taken at Rutgers compared with NREL baseline

**NREL**

Performs additional measurements on the modified samples

Incident photon-to-current efficiency (IPCE)

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

NREL: PEC Characterization

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

Modified samples sent back to NREL
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

### Authors

- Adam Weber
- Todd Deutsch
- Nemanja Danilovic
- Huyen Dinh

### PEC Project Leads

- Eric Garfunkel
- Tom Jaramillo
- Nicolas Gaillard
- Zetian Mi
- Aditya Mohite

### Research Teams

- University of Hawai‘i at Mānoa
- UNLV
- Los Alamos National Laboratory
- Stanford University
- Rutgers University
- University of Michigan
- NREL
- Lawrence Livermore National Laboratory
- Sandia National Laboratories
- Idaho National Laboratory
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 Ta₃N₅ 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 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. Planned 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

  **Impact on project:** 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
Academia-EMN Node interaction

**Integrated Theory, Analysis, Synthesis and Testing**

- **THEORY / ANALYSIS**
  - Interfaces modeling
  - Adv. spectroscopy
  - Novel chalcopyrites
  - Development of new buried p-n junctions

- **DEVICE INTEGRATION**
  - Surface passivation
  - Tunable buffers
  - PEC Benchmarking

- **PHOTOELECTROCHEM.**
  - Durability validation
  - Absorbers modeling
  - Tunable buffers
  - Novel chalcopyrites

- **SOLID STATE MATERIALS / 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.

- **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.

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


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.