HydroGEN: Photoelectrochemical (PEC) Hydrogen Production

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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
HydroGen Consortium

III-V PEC systems
- Bandgap tuning
- Buried junctions
- Durability testing
- Bubble management
- Non-PGM catalysts
- Membranes

Particle PEC systems
- Reactor designs
- Selective catalysis
- Gas separation
- Mass transfer

Thin-film PEC systems
- Absorbers and interfaces
- Processing compatibility

Sunlight to H₂
- Interfaces
- Catalysts
- STH efficiency
- Stability
- Balance of plant
- Reactor designs
- Techno economics
- Life cycle assessment

Looking Inward: Crosscutting challenges that bind us together

Looking Outward: Unique materials development frontiers

Higher TRL

Lower TRL
Synopsis of Photoelectrode-based Approaches

Approach 1: Stabilize High Efficiency Systems

Approach 2: Enhance Efficiency in Thin-Film Materials

DOE Targets: >1000h @STH 10-25%

Projected PEC Cost: $2 - 4/kg H₂

Approach 3: Develop 3rd Generation Materials and Structures

Theory & Characterization

HydroGEN: Advanced Water Splitting Materials
Approach – HydroGEN EMN

DOE

EMN

HydroGEN

Core labs capability nodes

Data Hub

FOA Proposal Process

• Proposal calls out capability nodes
• Awarded projects get access to nodes

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

PEC: Photoelectrochemical Electrolysis

Barriers
- Cost
- Efficiency
- Durability

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

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

PEC Projects
- University of Hawaii
- Rutgers University
- Stanford University
- University of Michigan
Collaboration: 56 PEC Nodes, 2 Supernodes

- Analysis: 2
- Characterization: 15
- Computation: 8
- Synthesis: 5

Analysis: 2
Computation: 8
Characterization: 15
Synthesis: 5

Analysis: 2
Computation: 6
Characterization: 13
Synthesis: 5

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

HydroGEN: Advanced Water Splitting Materials
### Collaboration: HydroGEN PEC Node Utilization

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<th>Node</th>
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**Computation**

**Material Synthesis**

Electrolyte potential (V) and current density (stream line)
# Collaboration: HydroGEN PEC Node Utilization

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**Characterization**

HydroGEN: Advanced Water Splitting Materials
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 that can provide a path toward electrodes that cost $200/m² by incorporating earth-abundant protective catalysts and novel epitaxial growth schemes.

Accomplishments in BP1

Go/No-Go #1: Photoelectrode that achieves >10mA/cm² 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

Go/No-Go #1:

Photos in BP1 and BP2 show progress towards the goals.

https://h2awsm.org/capabilities/sun-photoelectrochemical-solar-hydrogen-benchmarking
HydroGEN: Advanced Water Splitting Materials

Best-in-class Platinum Group Metal-free Catalyst Integrated Tandem Junction PEC Water Splitting Devices
Rutgers University #P160

**High-Performance (HP) devices**

Goal: >10% STH, > 100h durability

- Electolyte
  - 4H⁺ O₂
  - 2H₂2H₂O

- Ni₅P₄ TF-eCAT HER
- LiCoO₂ TF-eCAT OER

- GaInP₂/GaAs Tandem devices
- TiN thin film (TF) protection layer

**Goals:**

**High-Value (HV) devices**

Goal: ~10% STH, > 100h durability

- Light
- p-i-n
- p-n⁺

- LiCoO₂ TF catalyst
- TF Protection layer
- Silicon

- Perovskites (Inorganic-organics or oxynitrides)

**Accomplishments in BP1**

Successful TF integration of Ni₅P₄/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.
Project Vision
Strengthen theory, synthesis and advanced characterization “feedback loop” to accelerate the development of efficient materials for H₂ production.

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

Accomplishments in BP1
1) Materials efficiency/cost barriers
   - Printable CuInSe₂ with high conversion efficiency
   - Photoconversion efficiency > 70% of theoretical max (GNG #1/2)

2) Materials durability barrier
   - WO₃ ALD coatings (3 nm) on 1.8 eV CuGa₃Se₅
   - WO₃
   - CuGa₃Se₅
   - Mo
   - Glass

Focus of BP2
1) Materials efficiency/cost barriers
   - Expend printable CuInSe₂ baseline process to novel wide bandgap chalcopyrites e.g. Cu(In,B)Se₂ with 40-60% B content
   - Cu(In,Al)Se₂ with 20-40% Al content
   - Theoretical prediction of Cu(In,B)Se₂ bandgap as a function of boron content

2) Materials integration barrier
   - Demonstrate chalcopyrite-based tandem device integration with exfoliation/transfer techniques

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

Project Team
- 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)
**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

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**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
**Goal:** Validated multiscale modeling to understand OER across pH scale using a modeling framework on IrO₂ informed and validated by experiments

- AP XPS
- RDE
- Microelectrode

**OER rates and mechanism**

- Surface intermediate coverage
- $E_a$ and $\Delta G_{rxn}$ for each elementary step

**Catalyst surface structure**

**Species activity near the catalyst**

**DFT calculations**

**Microkinetic model**

**Species flux at catalyst surface**

**Continuum transport**

**Concentration profiles**

**MD/DFT simulations**

**Species concentration near double layer**

**Double-layer structure**
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\textsubscript{2}
OER Supernode: Future Work

• Experiments on \( \text{IrO}_2 \)
  – 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 \( \text{IrO}_2 \)

• Incorporate the knowledge gained in the multiscale modeling framework and compare to experimental data
**Goal:** Understand integration issues and emergent degradation mechanisms of PEC devices at relevant scale, and demonstrate an integrated and durable 50 cm² PEC panel.

**PEC Supernode Approach**

**LBNL**
- PEC Cell Scale up
- Commercial PVs
  - 1 cm²
  - 4 cm²
  - 8 cm²

**NREL**
- PV Cell Scale up
  - 0.1 cm²
  - 1 cm²
  - 4 cm²
  - 8 cm²

**Benchmarking**
- In situ degradation and characterization
- Emerging Degradation Pathways
- Modeling
PEC Supernode: Results

Scale up of LBNL PEC Devices
1 cm² PEC

Scale up of NREL PV/PEC Cells
0.1 cm² PV

Accomplishments:
• Benchmarking PV and PEC cell performance between Labs
• PV fabrication scale up from 0.1 to 1 cm²
• 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 cm² and 8 cm² devices
- Characterize freshly prepared PVs and after PEC testing

**PEC scale up**

- Continue scale up and evaluation of 4 cm² vapor and liquid PEC cells
- Translate to 8 cm² 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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Huyen Dinh

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PEC Supernode Team

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