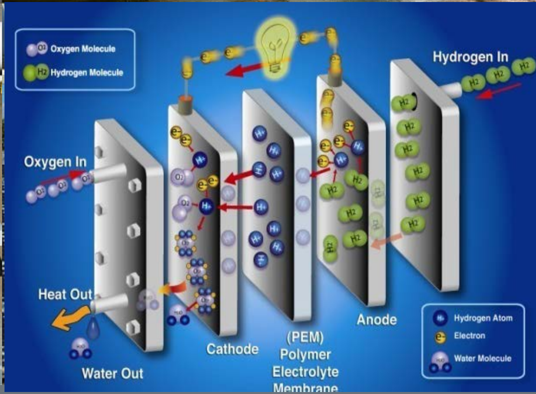
Fuel Cell Technologies Office Webinar

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy





HydroGEN – AWSM: Photoelectrochemical (PEC)

November 10, 2016

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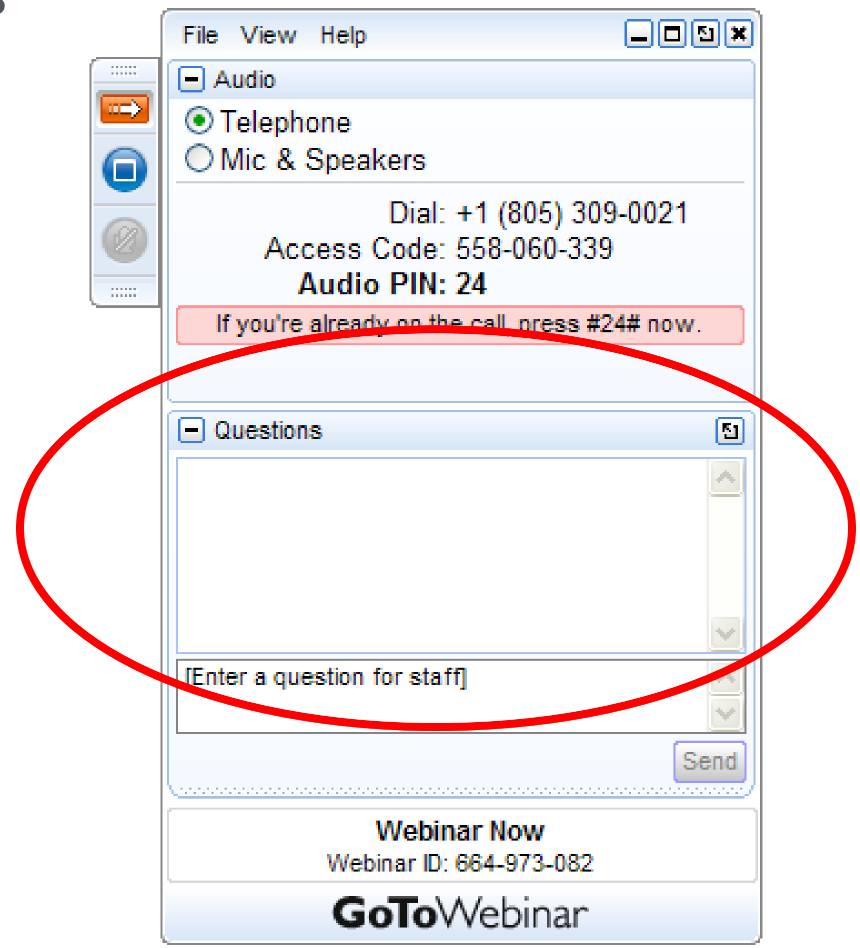
Staff Scientist
Leader, Energy Conversion Group
Fuel Cell Technologies Program Manager

Question and Answer

- Please type your questions into the question box



Consortium Services

How do I find the right resource to accelerate a solution to my materials challenge?

How do I engage with the National Labs quickly and effectively?

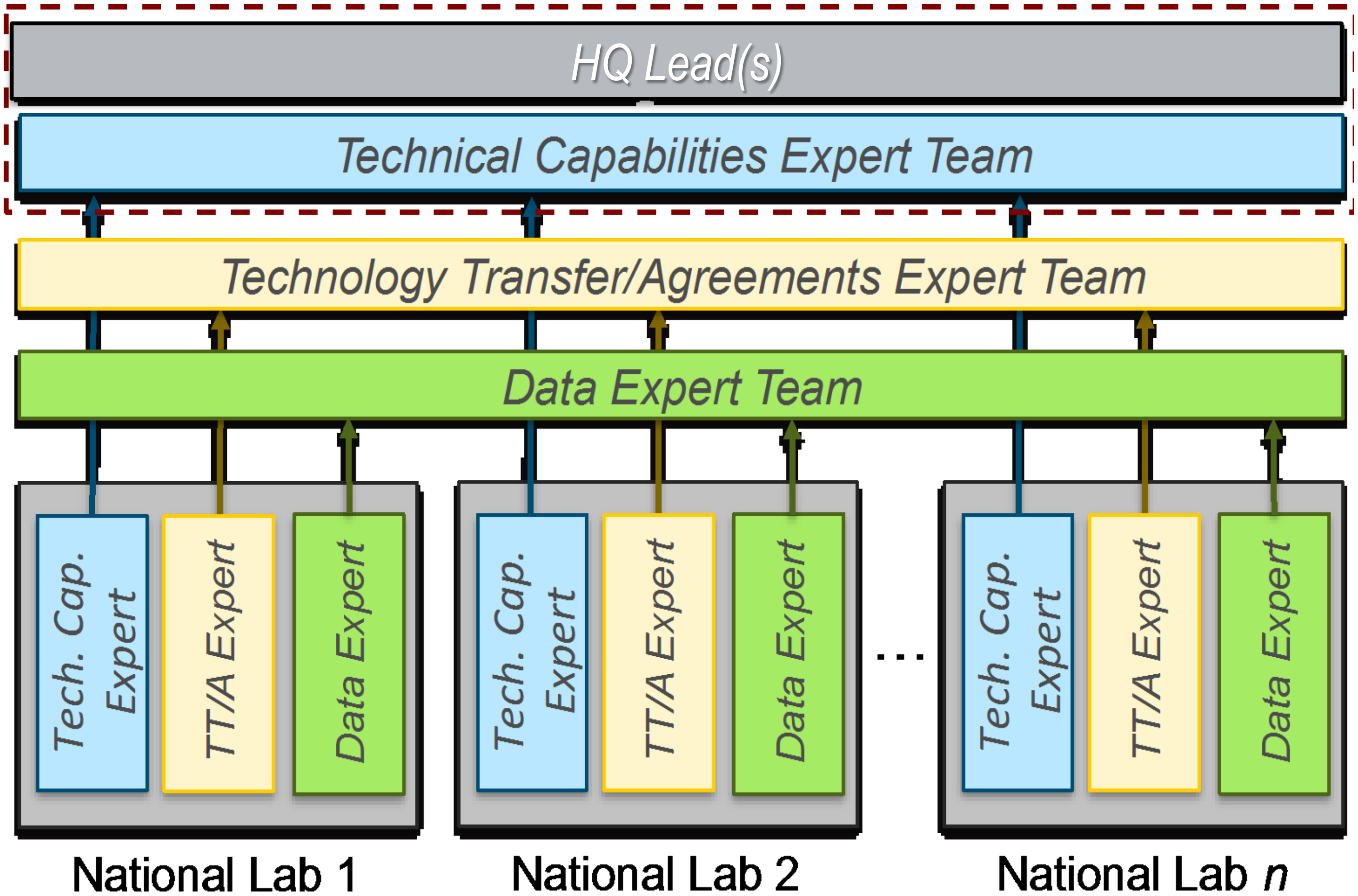
The EMN offers a common yet flexible RD&D consortium model to address key materials challenges in specific high-impact clean energy technologies aimed at accelerating the tech-to-market process

Consortium Requirements

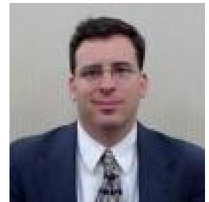
- **World Class Materials Capability Network:** *Create and manage a **unique, accessible set of capabilities** within the DOE National Laboratory system*
- **Clear Point of Engagement:** *Provide a **single point-of-contact** and concierge to direct interested users (e.g. industry research teams) to the appropriate laboratory capabilities, and to **facilitate efficient access**.*
- **Data and Tool Collaboration Framework:** *__Capture data, tools, and expertise__ developed at each node such that they can be **shared and leveraged** throughout the EMN and **in future programs**. Establish data repositories and, where appropriate, distribute data to the scientific community and public. Accelerate learning and development through data analysis using advanced informatics tools.*
- **Streamlined Access:** *Facilitate **rapid completion of agreements** for external partners, and aggressively pursue approaches to reduce non-technical burden on organizations seeking to leverage the EMN for accelerated materials development and deployment.*

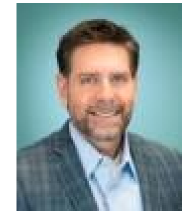
Ensuring Transparency

Consortium Steering Teams



HydroGEN Steering Committee





NREL NATIONAL RENEWABLE ENERGY LABORATORY

Huyen Dinh

BERKELEY LAB

Adam Weber

Sandia National Laboratories

Anthony McDaniel

INL Idaho National Laboratory

Richard Boardman

Lawrence Livermore National Laboratory

Tadashi Ogitsu

SRNL SAVANNAH RIVER NATIONAL LABORATORY

Héctor Colón-Mercado

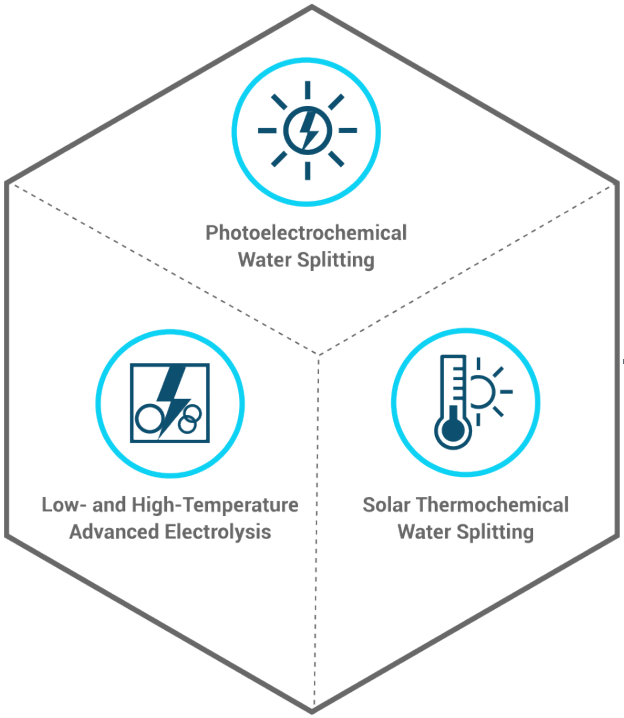
Eric Miller, DOE-EERE-FCTO

HydroGen Energy Materials Network (EMN)

Aims to accelerate the RD&D of advanced water splitting technologies for **clean, sustainable hydrogen production**, with a specific focus on **decreased materials cost**, **intermittent integration**, and **durability** :

Advance Electrolysis	Photoelectrochemical	Solar Thermochemical
Low & High Temperature		Hybrid thermochemical

RD&D from different water splitting pathways is critical to reducing renewable H_2 production cost



Production target <$2/gge

H_2 Cost at Pump

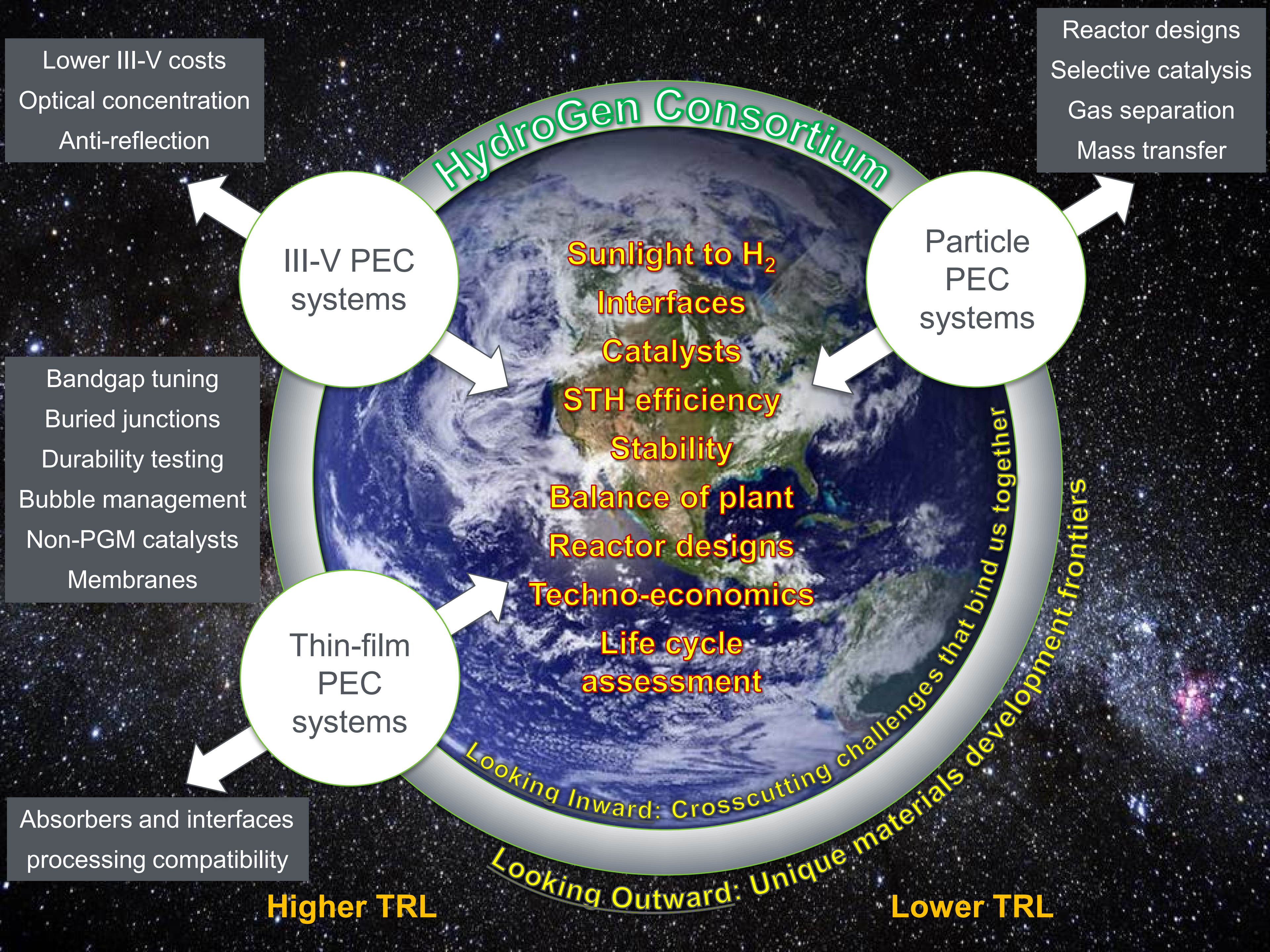
<$4/gge

<$7/gge (early market)

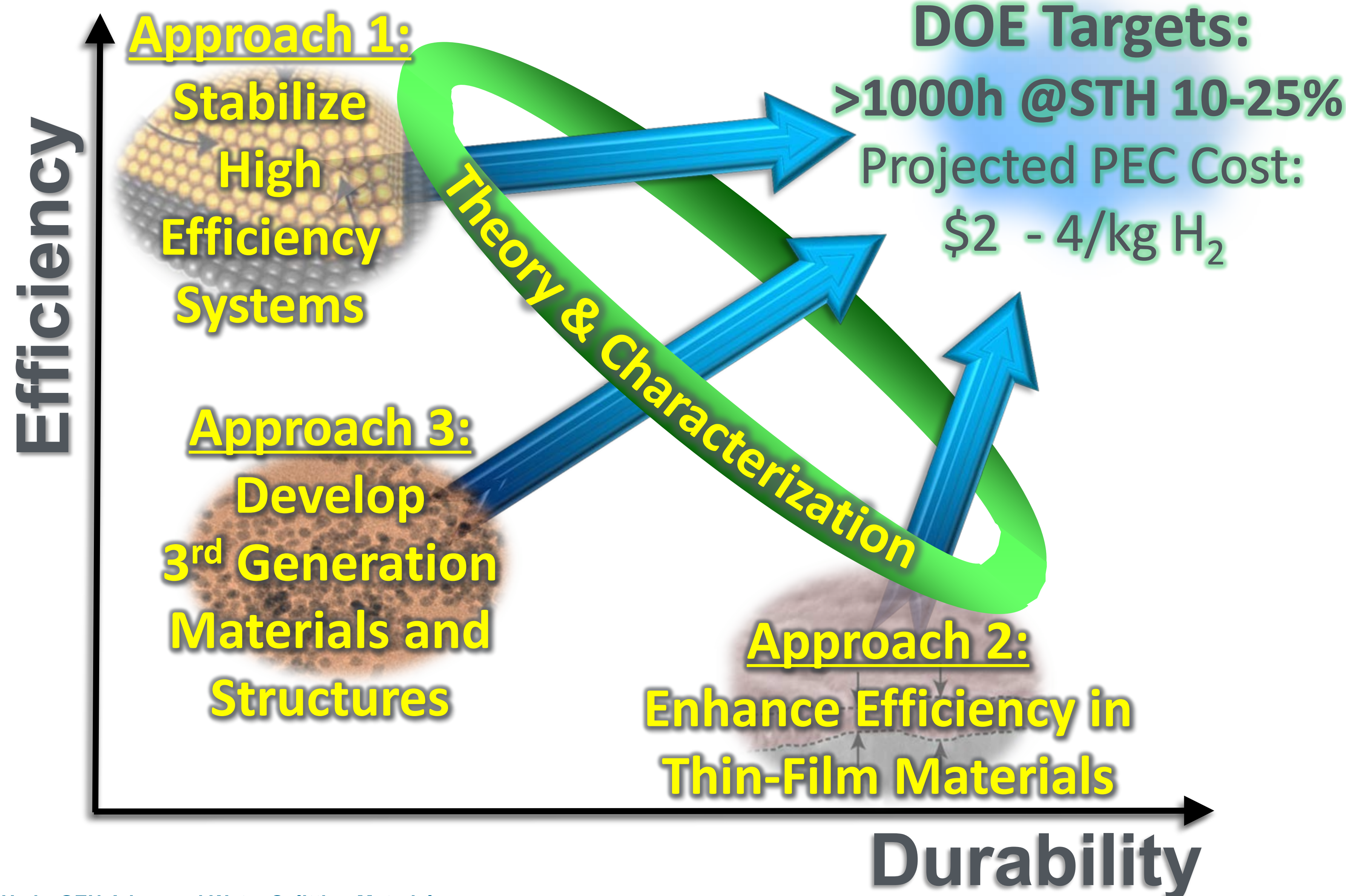
Technology Abbreviations:

- AE: Advanced Electrolysis
- LTE: Low-Temperature Electrolysis
- HTE: High-Temperature Electrolysis
- HT: Hybrid Thermochemical
- PEC: Photoelectrochemical
- STCH: Solar Thermochemical

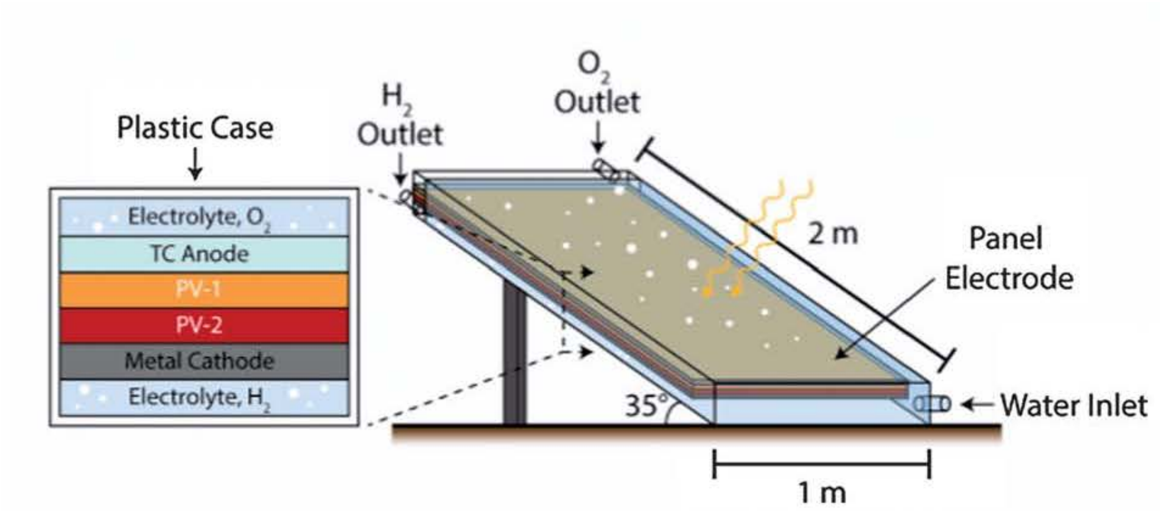
https://www.h2awsm.org/

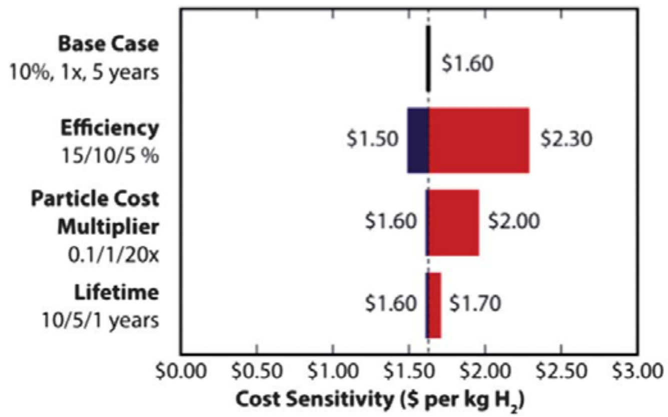

HydroGen Consortium
Lower III-V costs
Optical concentration
Anti-reflection
Reactor designs
Selective catalysis
Gas separation
Mass transfer
III-V PEC systems
Particle PEC systems
Thin-film PEC systems
Bandgap tuning
Buried junctions
Durability testing
Bubble management
Non-PGM catalysts
Membranes
Sunlight to H_2
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
Absorbers and interfaces processing compatibility
Higher TRL
Lower TRL

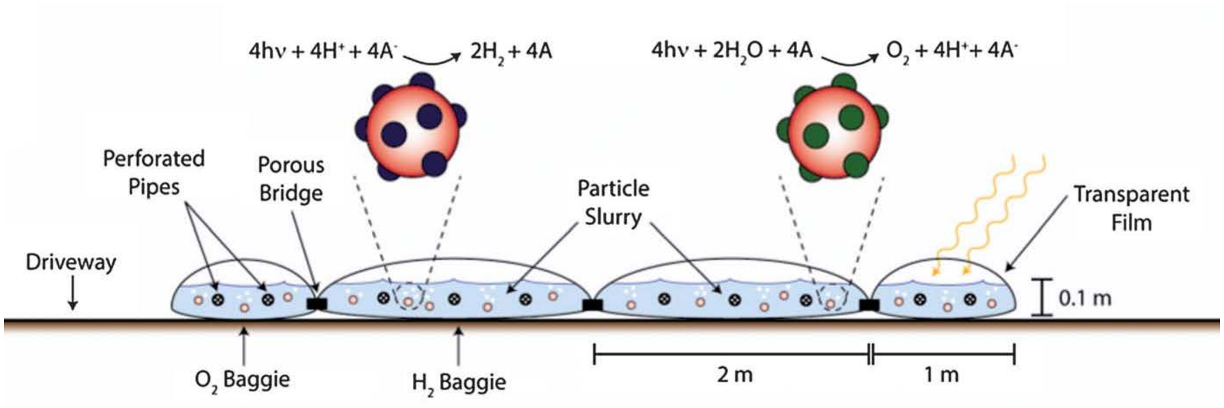
Synopsis of Photoelectrode-based Approaches

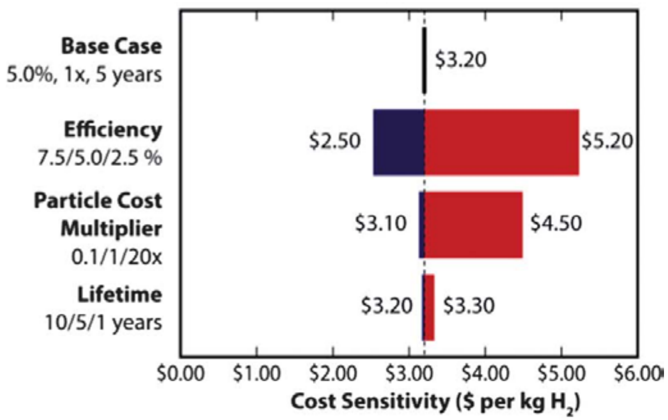


Approaches to PEC Hydrogen



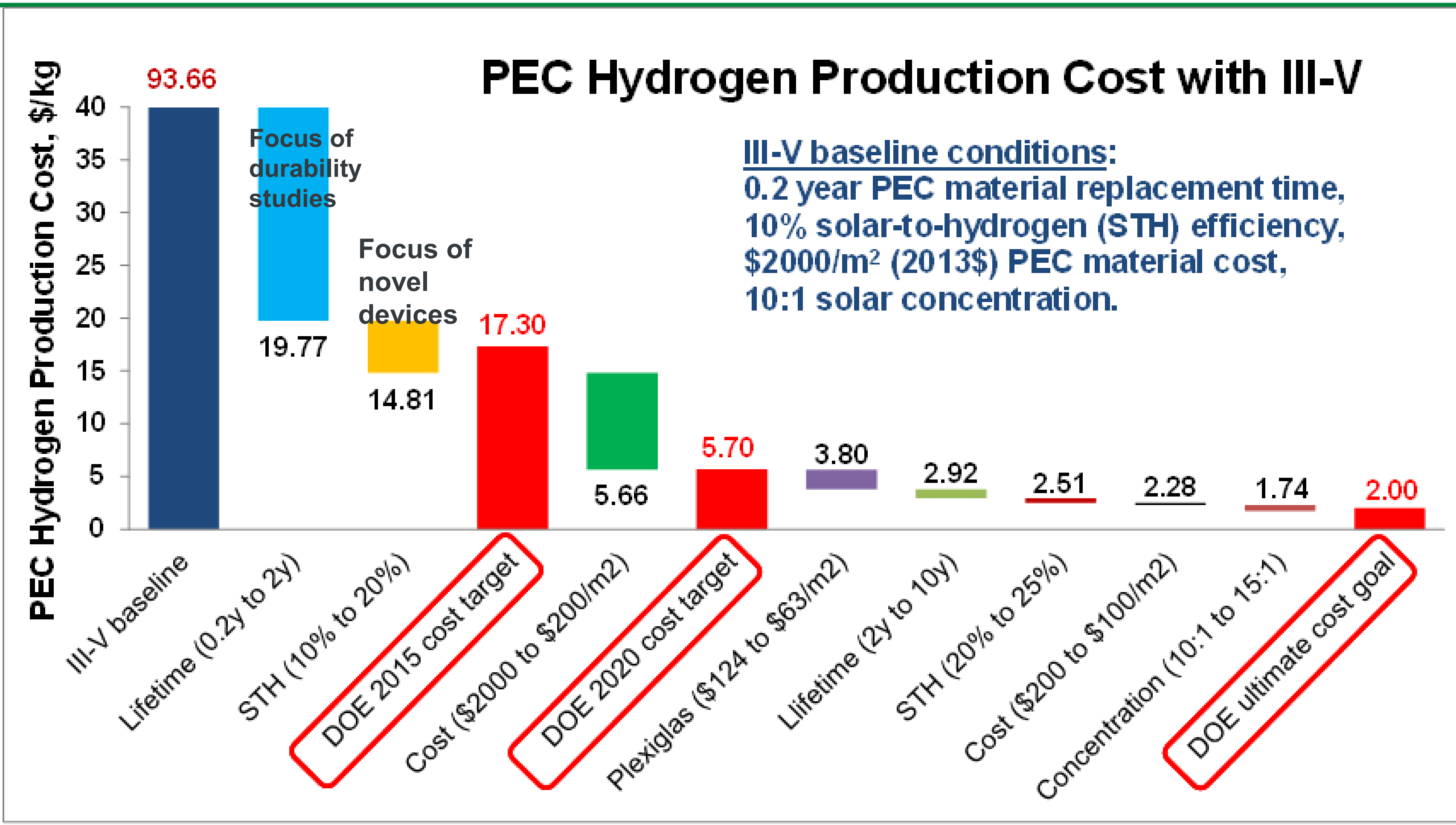






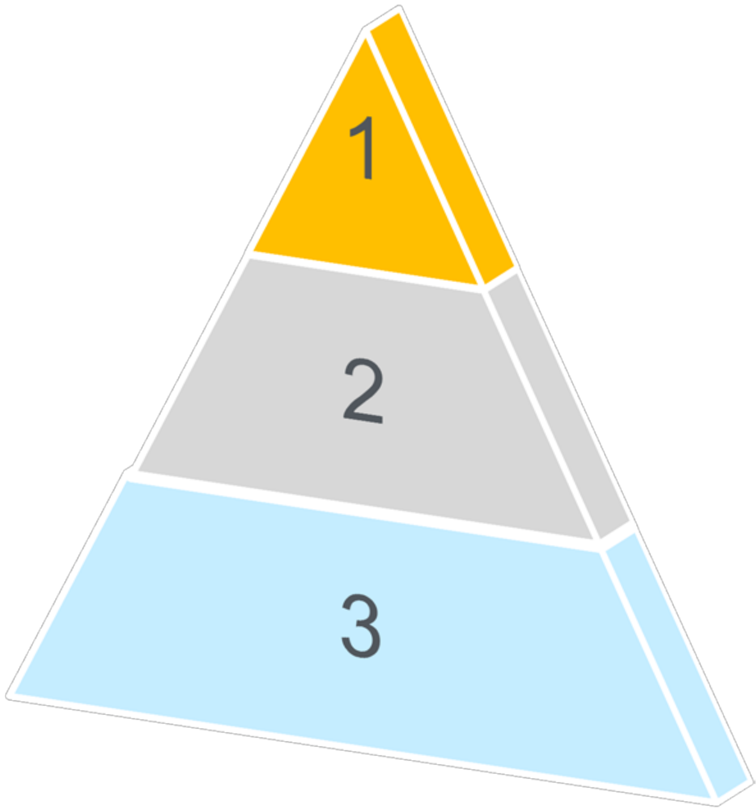
Energy Environ. Sci., **2013**, 6, 1983

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.

Node Readiness Category Chart



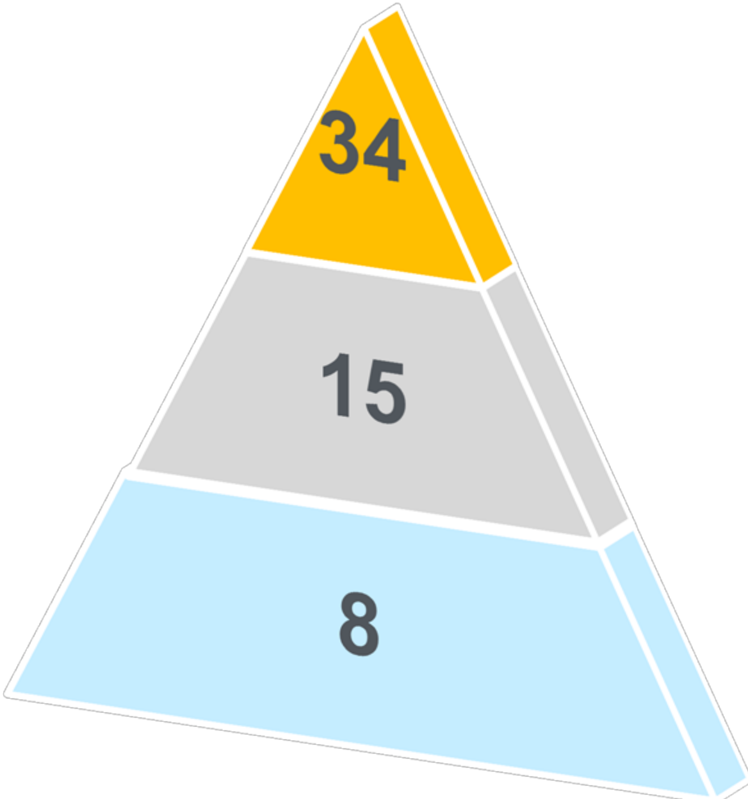
Category 1
Node is fully developed and has been used for PEC research projects

Category 2
Node requires some development for PEC

Category 3
Node requires significant development for PEC

- Nodes comprise tool, technique, and expertise including uniqueness
- Category refers to availability, readiness and relevance to AE and not necessarily the expense and time commitment

57 PEC Nodes



Classification:

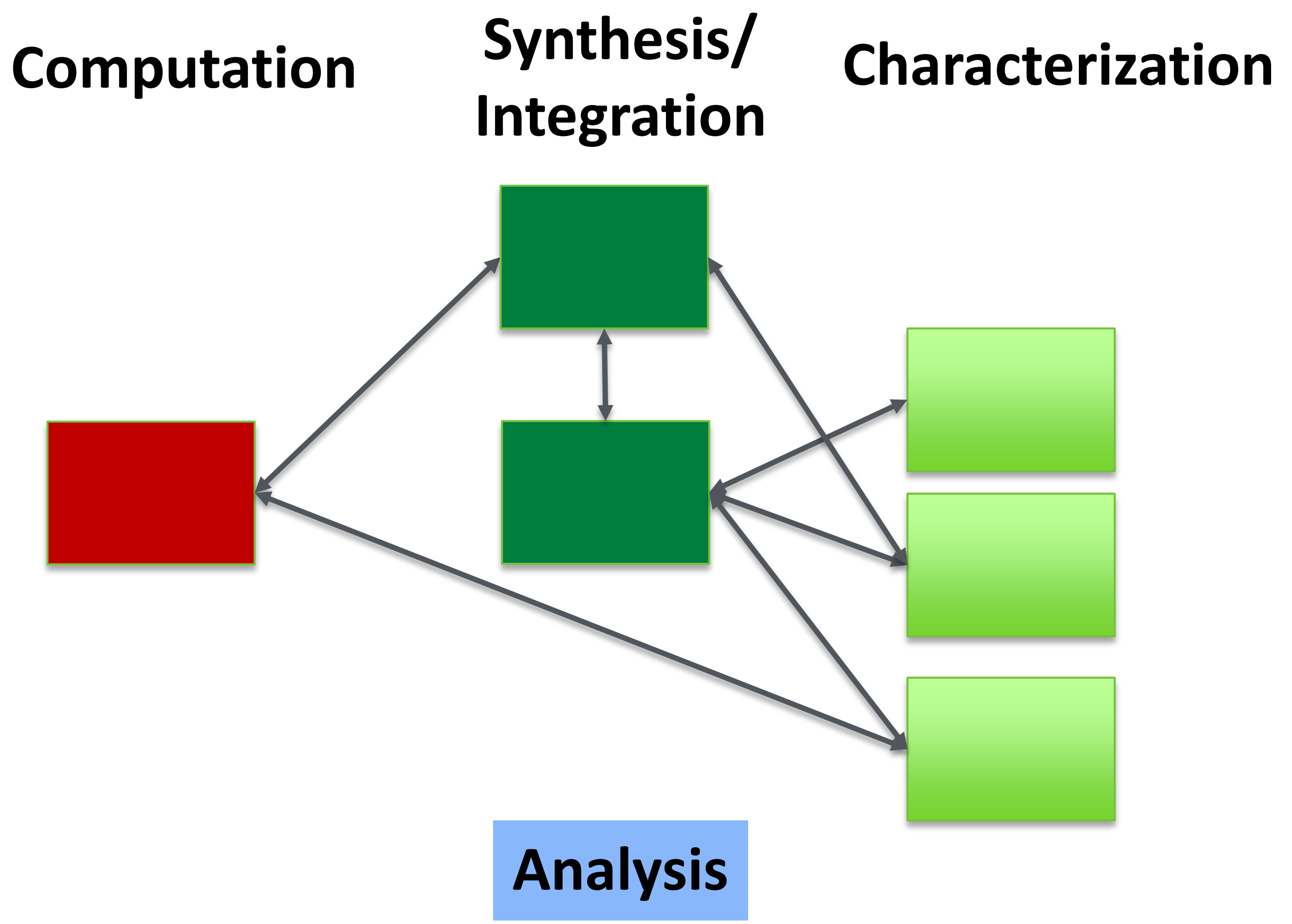
Analysis: 2
Computation: 11
Characterization: 13
Synthesis/Process: 8

Analysis: 0
Computation: 3
Characterization: 7
Synthesis/Process: 5

Analysis: 1
Computation: 3
Characterization: 2
Synthesis/Process: 2

- Nodes comprise tool, technique, and expertise including uniqueness
- Category refers to availability, readiness and relevance to AE and not necessarily the expense and time commitment
- Note that many nodes span classification areas (analysis, synthesis, computation, characterization, etc.)

Node Usage



- Projects can/should use multiple nodes to leverage national laboratory capabilities and progress the project
  - Not all types of nodes have to be used

Simplified Example Flow Diagram for Multijunction III-V Photoelectrochemical Water Splitting

Ideal tandem bandgaps identified by modeling

What is the optimal III-V semiconductor tandem design for total photovoltage generated, optical absorption of water, and current matching?

↓

MOVPE node: Design growth recipe and perform synthesis run

Can this material combination be grown? Does a new tunnel junction or transparent buffer layer need to be developed?

↓

Corrosion Analysis node: Characterize material durability

What is the intrinsic stability of the material under operating conditions? Can a post-growth surface modification improve the durability? Can an alternative III-V alloy with the same bandgap achieve greater stability? What elements end up in the electrolyte?

↓

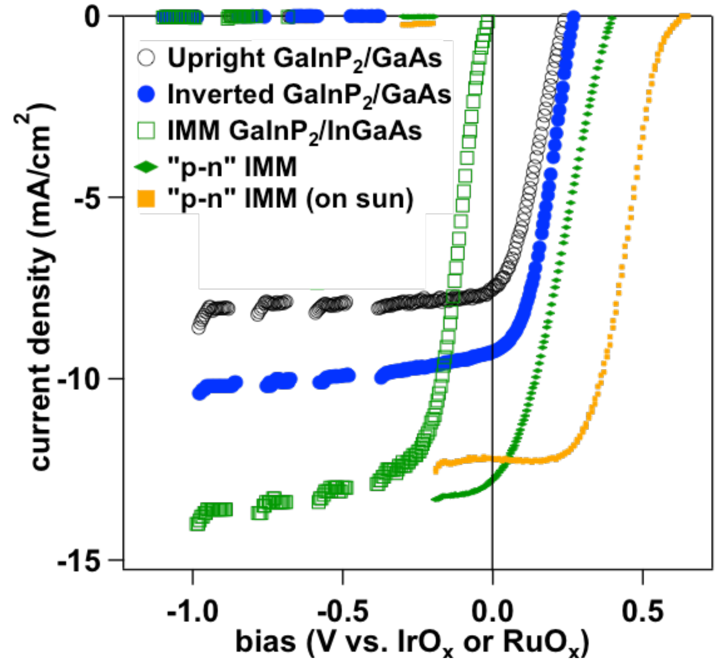
Efficiency Benchmarking node: Determine the STH efficiency under standard reference conditions

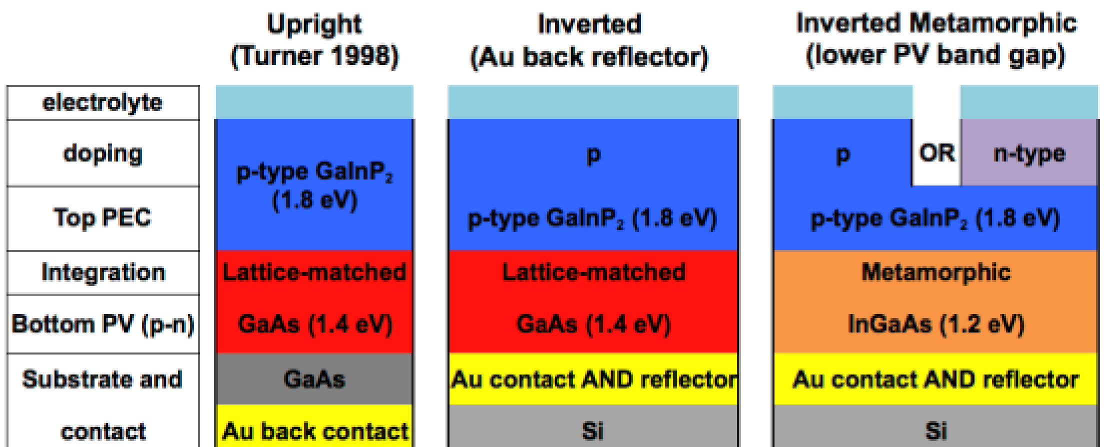
What is the intrinsic solar-to-hydrogen efficiency of the tandem material? Do the corrosion mitigation modifications to the surface or bulk decrease the efficiency? What is the performance over several days when mounted on a solar tracker?

MOVPE Cost Case Study

Developing new inverted metamorphic multijuction III-V structures

- Grow 2cm x 3cm sample per fortnight within range of alloy compositions and substrates/form factors that the III-V group has experience with
- Processing
  - Contacts, mesa isolation, etc.
- 25% FTE Labor
  - Consumables
    - Substrates, precursor reactor parts





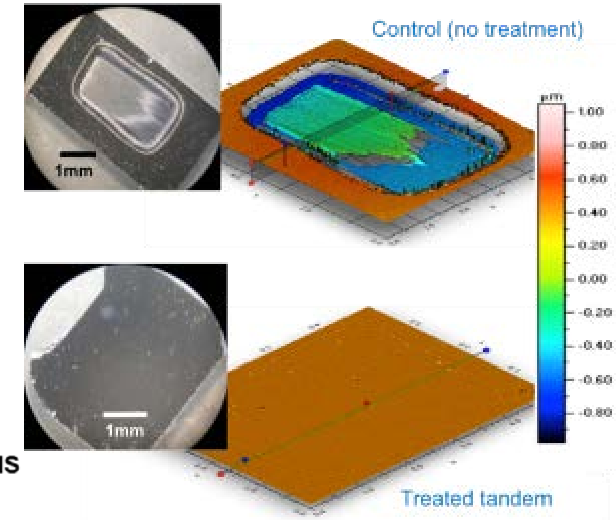
Corrosion Analysis Cost Case Study

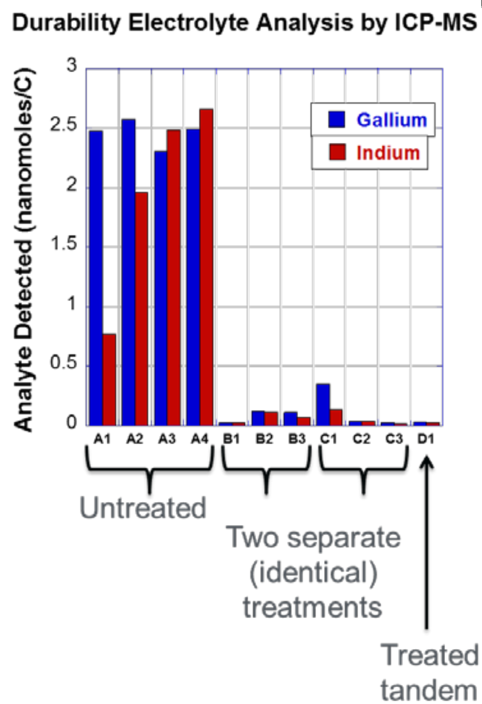
Durability testing and post-mortem optical profilometry

- Understand the influence of surface/bulk mods on a reasonable sample size within three months including degradation products
  - Detailed understanding of corrosion mechanism would require additional nodes
- Testing
  - Long-term (10’s hours) durability testing
  - Pre-, intermediate, post J-V
  - Analysis of electrodes
  - Analysis of electrolyte

– 15% FTE labor

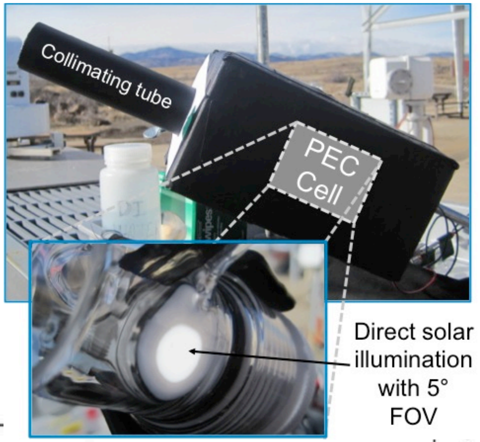
  – Consumables

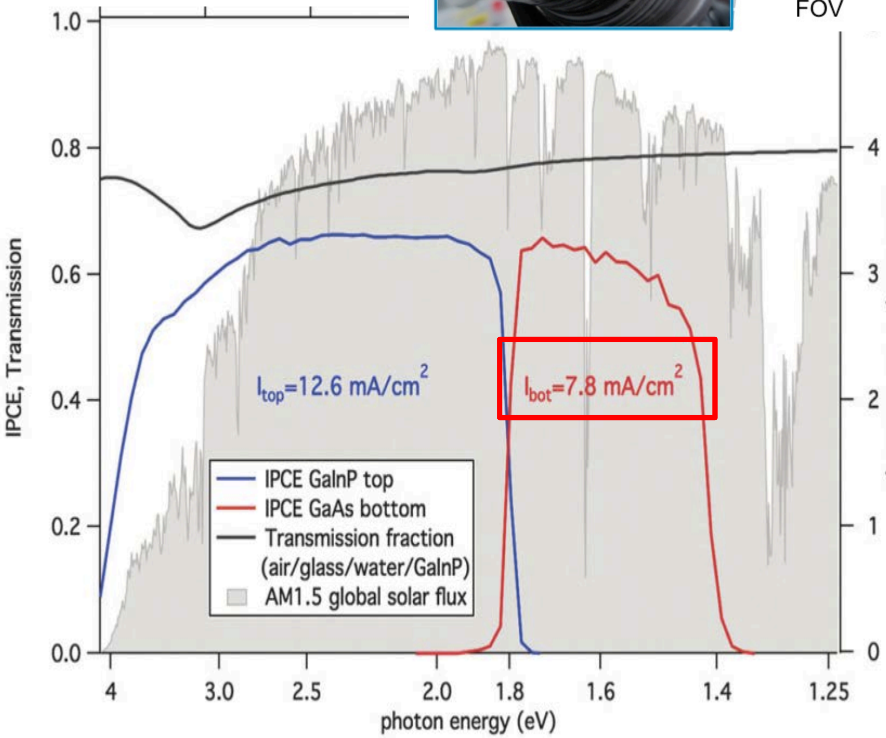




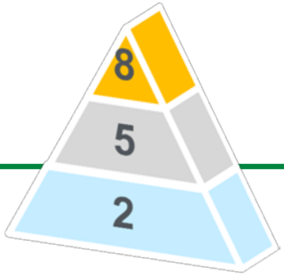
IPCE and outdoor testing to validate STH efficiency at short-circuit

- Determine STH efficiency of ~10 smaller samples (1 cm^2) per week
- Testing
  - Sample mounting
  - IPCE of both junctions
    - Integrated over reference spectrum
  - Outdoor measurements
- 2% FTE Labor





Synthesis Capabilities



1. Large area, nanoimprinted Al substrates for plasmon-enhanced PEC
2. Spray pyrolysis
3. III-V semiconductor epi-structure and device designs and fabrication
4. I-III-VI Compound semiconductors for water splitting
5. Novel membrane fabrication and development
6. Clean rooms with surface preparation
7. Surface modifications for catalysis and corrosion mitigation
8. Photoelectrochemical device fabrication

1. CdTe Photovoltaic growth
2. High-throughput combinatorial experimental thin films
3. Electrolysis catalyst synthesis, characterization, and standardization
4. High-throughput approaches for scaling electrodes
5. Fabrication of designer catalyst electrodes

1. ALD based surface functionalization
2. Novel materials and characterizations for electrocatalysis

Light absorbers, catalysts, integration, other components

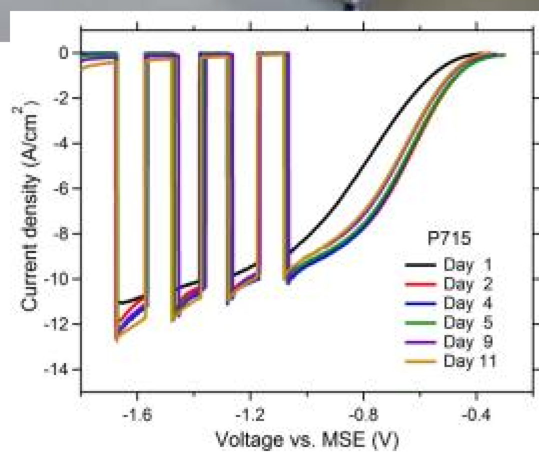
Note that many capabilities span different classification areas

I-III-VI Compound Semiconductors

State-of-the-art ultrahigh vacuum (UHV) CIGS cluster tool at NREL:

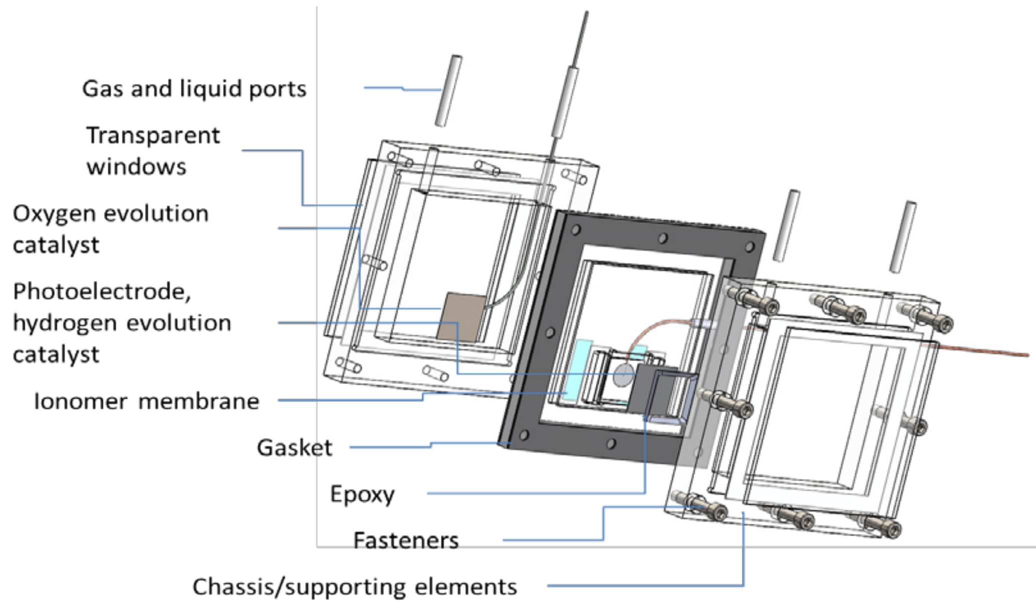
- Integrated chambers enabling capability to fabricate PEC and other photonic devices
  - 6"x6" substrate sizes, evaporation, RF/DC/pulsed DC sputtering/reactive sputtering capabilities
  - Metallic contacts (Mo and other refractory metals)
  - Growth of I-III-VI wide bandgap gap semiconductors
  - Device fabrication, photolithography, e-beam evaporation
- Material testing & characterization
  - Access to chemical and surface analysis
  - Access to PEC characterization equipment

<ins>**Preliminary PEC result:**</ins> Good intrinsic stability of a bare $CuGa_3Se_5$ (1.85 eV) PEC electrode (one sun light soaking, continuous galvanostatic testing)

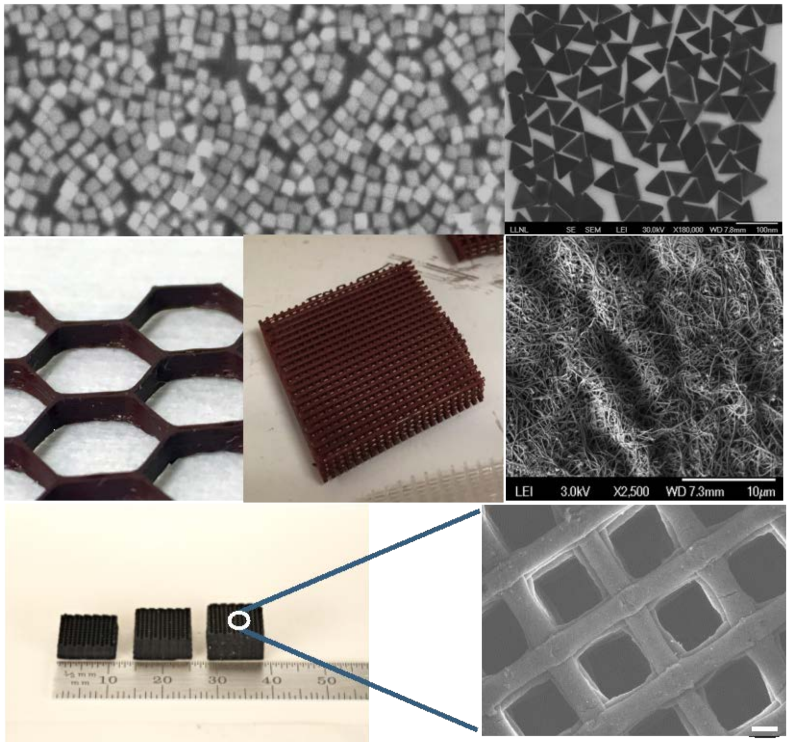


Photoelectrochemical device fabrication facility

- Design and Fabrication
  - Extensive expertise in designing and assembling cells
    - Guided by modeling
  - Equipment
    - Connex 350 inkjet 3D-printer
      - Resolution 16 microns z-axis and 600 microns x-y axis
      - Working volume 30 x 30 x 30 cm
      - Printing materials: acrylic acrylates
    - Database for compatible materials plastics and epoxies
    - Custom tooling for mounting device components during assembly
    - Othermill milling machine
      - CAD to CAM software
      - Resolution 25 microns
      - Working volume 14 x 11.4 x 4.06 cm

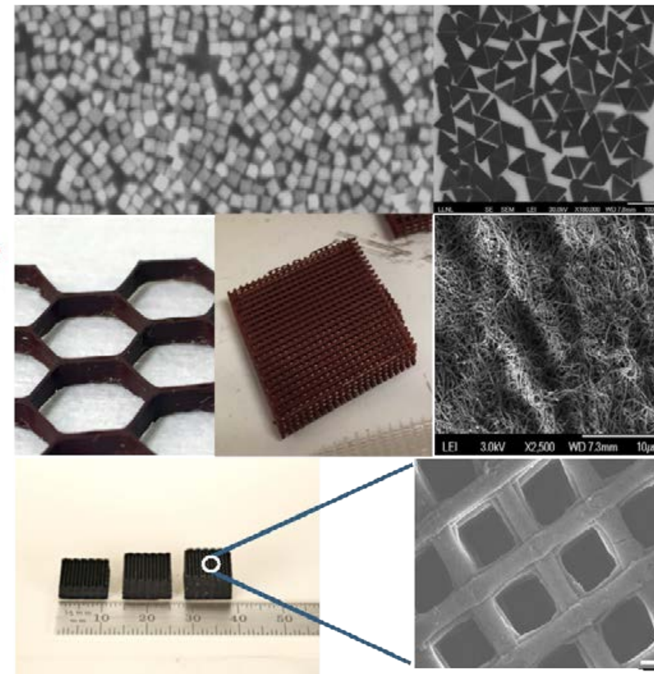


Fabrication of Custom Electrodes at Multiple Length Scales using Additive Manufacturing



Custom Materials Synthesis

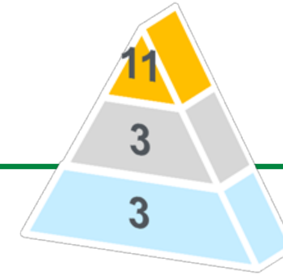
Scale-Up



Additive Manufacturing

Combining abilities to ***synthesize*** and ***scale-up*** custom materials (i.e. conductive high surface area electrodes/catalysts) to formulate unique feedstock materials for ***additive manufacturing*** processes, including direct-ink writing, electrophoretic deposition and projection micro-sterolithography, opens up the design space to create optimized catalysts and electrodes for water splitting.

Computation Capabilities



1. Multiscale modeling
2. Albany: Open-source multiphysics platform
3. Mesoscale kinetic modeling of water splitting and corrosion
4. Real-time DFT and ab initio calculations
5. Ab-initio modeling of electrochemical interfaces
6. SeqQuest: Quantum electronic structure code for DFT
7. Socorro: highly scalable DFT code
8. LAMMPS: open-source MD code
9. Computational materials diagnostics and optimization of PEC devices
10. Uncertainty quantification in computational models
11. Experimental and computational Materials Data infrastructure

1. Real-world modeling of PEC devices
2. Beyond-DFT Simulation of Energetic Barriers and photexcited dynamics
3. First principles materials theory for reaction pathways

1. Moab:particle-based mesh-freee code for modeling heat transfer, phase transition
2. Peridigm: code for peridynamic modeling for material failure
3. SPPARKS: Mesoscale modeling for microstructural evolution

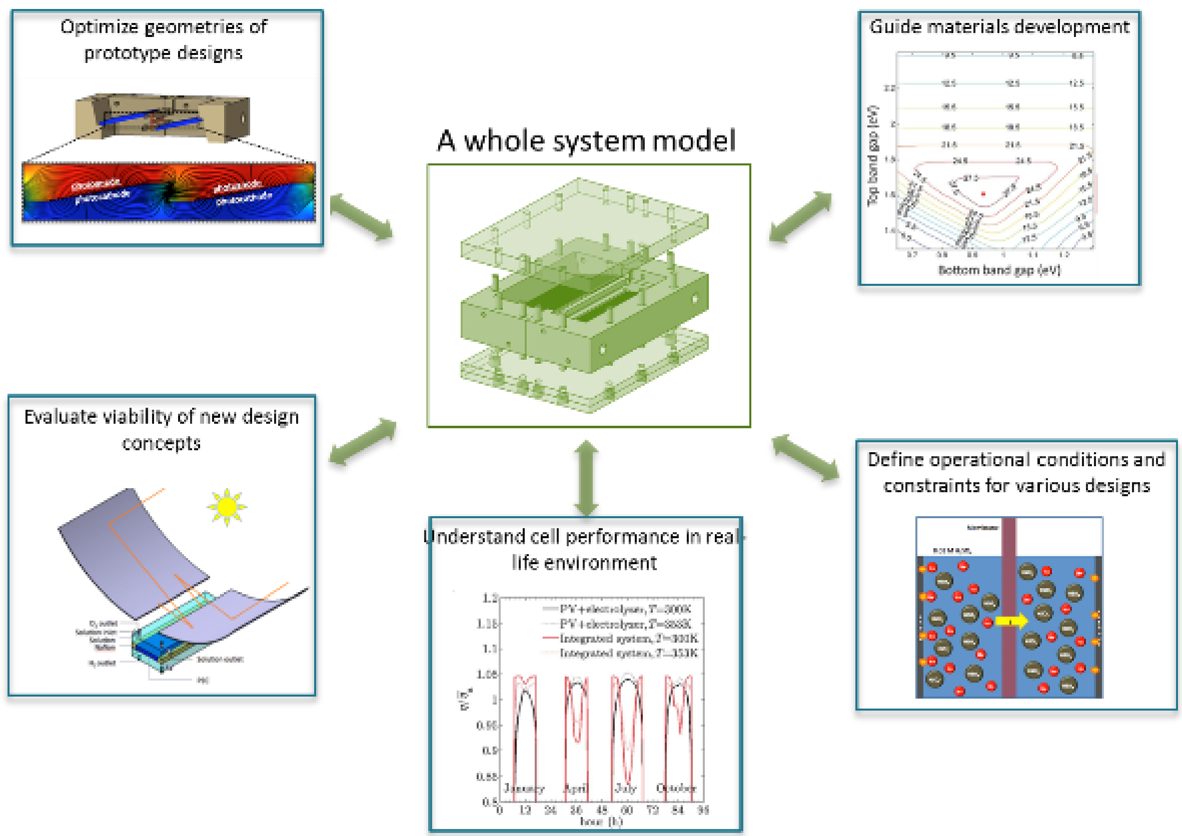
Ab-initio, other, multiphysics

Note that many capabilities span different classification areas

Multiscale, Multiphysics Modeling

Use continuum multiphysics mathematical modeling to predict and optimize cell performance

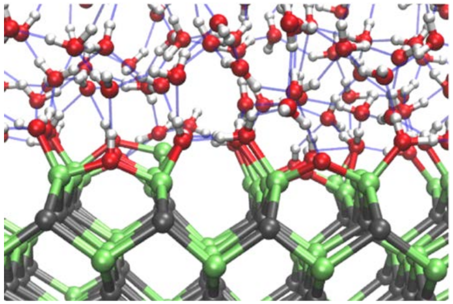
- Extensive experience in modeling electrochemical and water-splitting technologies
  - Models ready to go
  - Help with parameter estimation
  - Sensitivity and optimization studies
- Help develop models for specific materials set and conditions



*Ab initi*o modeling of electrochemical interfaces

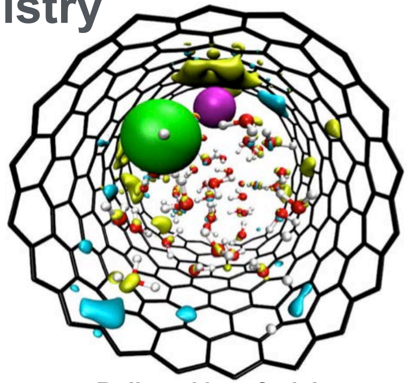
Solid-liquid interfacial chemistry

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



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

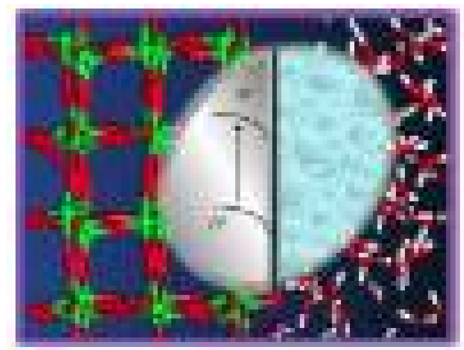
JPCC 120, 7332 (2016)



Bulk and interfacial properties of aqueous electrolytes

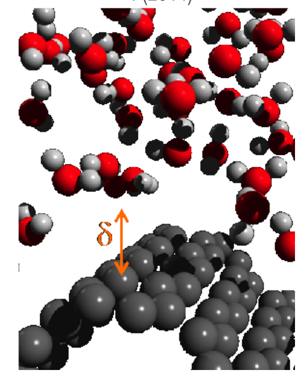
Electronic properties of interfaces

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



Electronic properties of electrode-electrolyte interfaces (from GW)

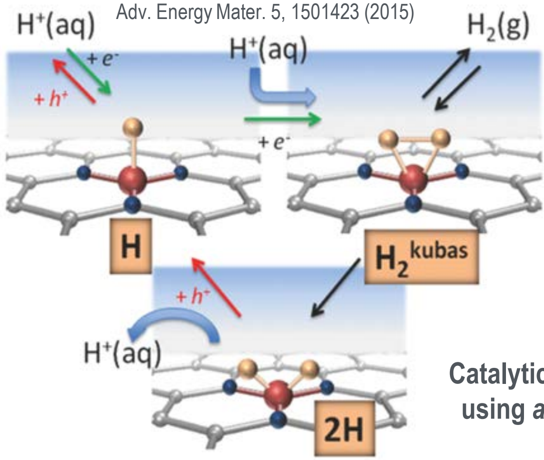
PRB 91, 125415 (2015); JPCC 118, 4 (2014)



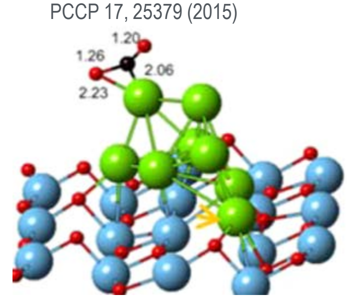
Simulations under applied bias or photobias

Electrocatalysis and photocatalysis

Adv. Energy Mater. 5, 1501423 (2015)

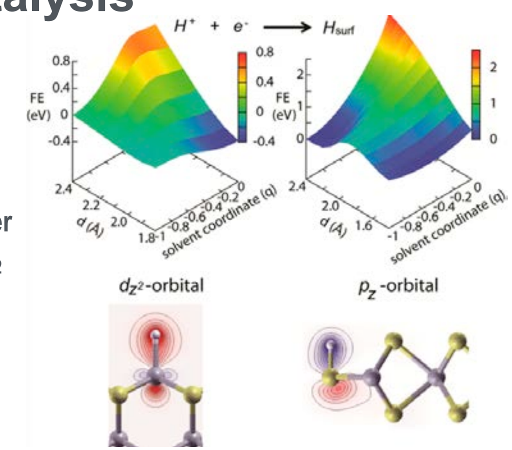


JPCC 118, 26236 (2014); PCCP 17, 25379 (2015)



Catalytic activity predictions using *ab initio* descriptors

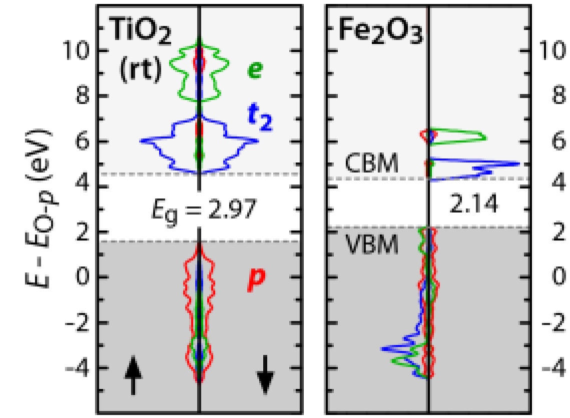
Charge-transfer barriers for H_2 evolution

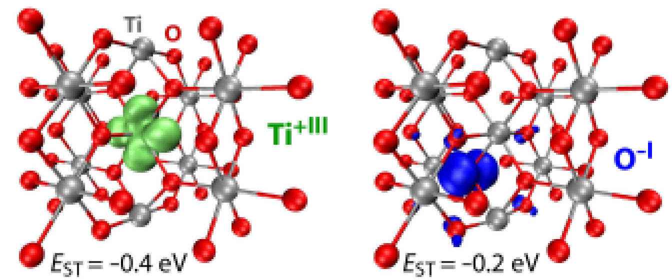


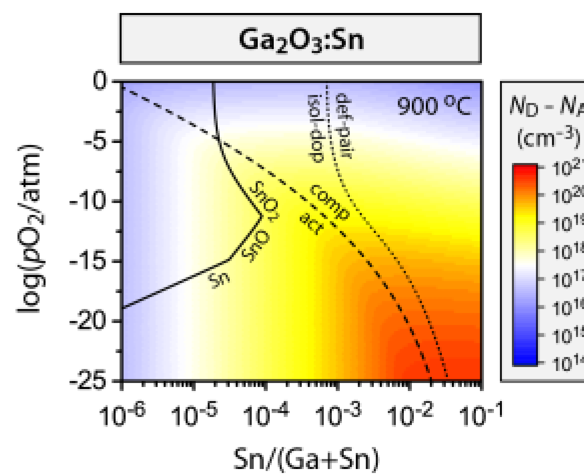
JPCC 117, 21772 (2013)

First Principles Materials Theory for Advanced Water Splitting Pathways

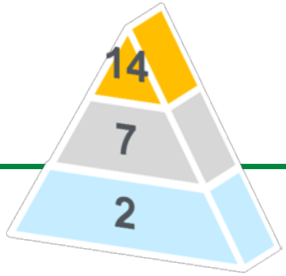
- Electronic structure prediction
  - Accurate band gap prediction for semiconductors, including transition metal compounds
  - Band-structure, effective masses, density of states, ionization potential, band offsets, optical properties
- Defects and alloys
  - Defect equilibria from first-principles, including effects due to defect-pair association
  - Small-polaron transport vs band-like transport
  - Alloys: Mixing enthalpy and phase diagrams
  - Ionic diffusion pathways, energy barriers
- Materials Design and Discovery
  - Structure prediction for new compounds
  - Thermodynamic stability range







Characterization Capabilities



1. Ionomer characterization
2. Photoelectrochemical device in situ and operando using x-rays
3. In situ and operando x-ray characterization of electronic structure
4. Compound semiconductor S&T
5. Characterization of degradation processes at PEC interfaces
6. Corrosion analysis
7. Probing and mitigating corrosion of photoelectrochemical assemblies
8. Characterization of semiconductor bulk and interfacial Properties
9. Advanced electron microscopy
10. E-beam and in-situ proton beam
11. Water splitting device testing
12. On-sun PEC STH benchmarking
13. Outdoor testing

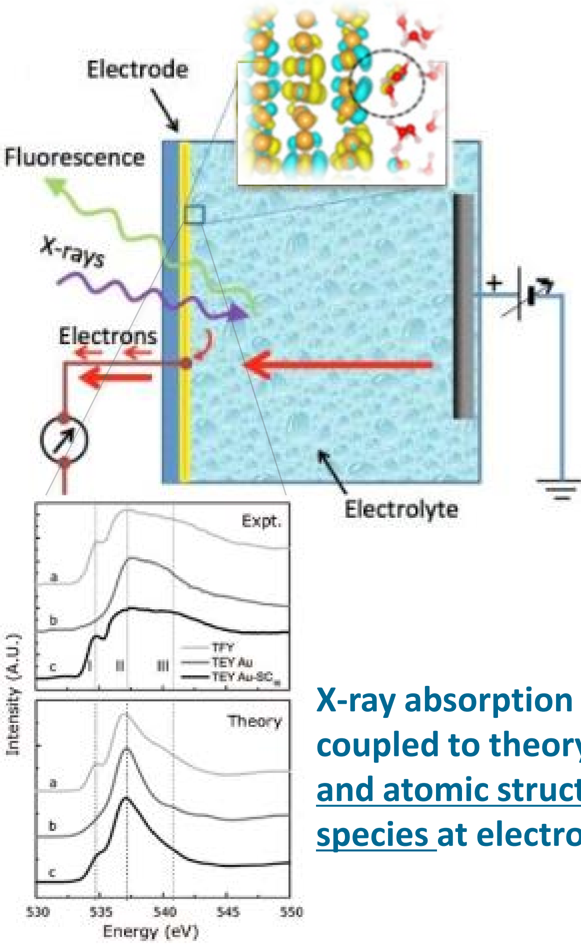
1. In-situ and operando nanoscale characterizations
2. Photophysical characterization
3. SIMS
4. Surface analysis cluster tool
5. Ex-situ spatial characterization
6. Nanoscale characterization capabilities for PEC
7. Concentrating solar-power furnace

1. Contamination related capabilities
2. Near-ambient electrochemical XPS

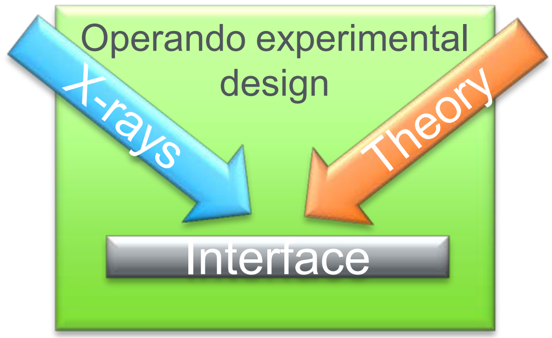
Note that many capabilities span different classification areas and techniques

X-ray Approaches for Understanding (photo)electrochemistry at Interfaces

Operando XAS

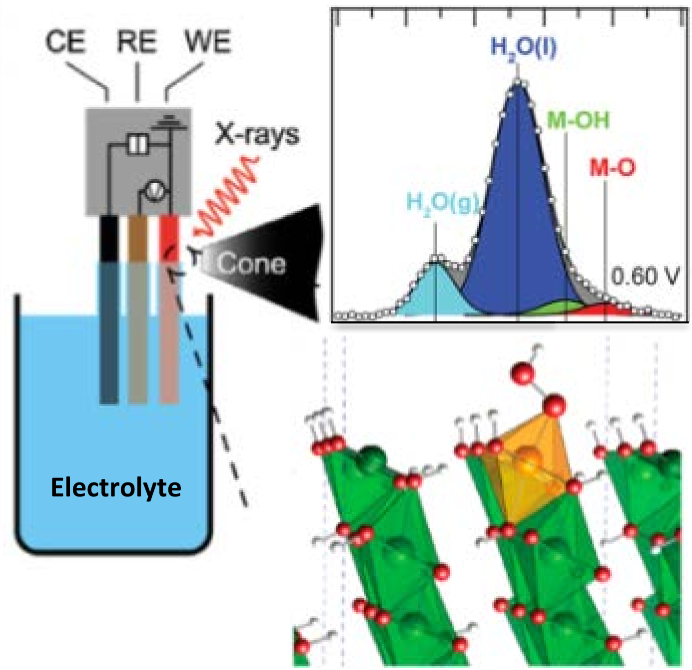


X-ray absorption spectroscopy, coupled to theory, reveals <u>electronic and atomic structure of chemical species</u> at electrode interface



Expertise combining operando instrumentation, X-ray spectroscopy, and theory to uncover molecular-scale chemical details at operating electrode interfaces

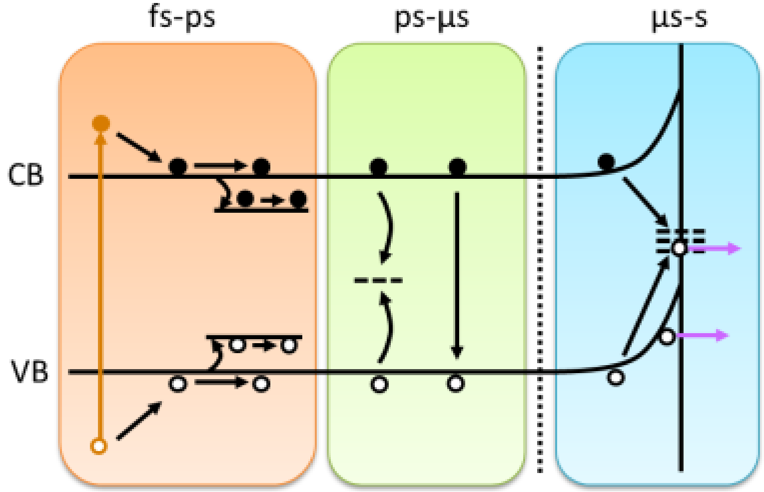
Operando ambient pressure XPS



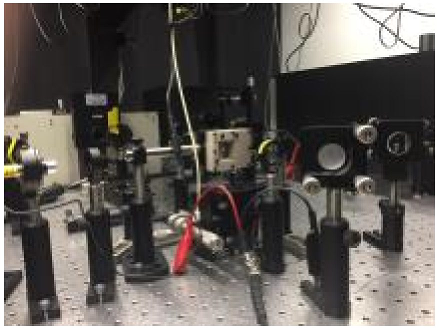
X-ray photoelectron spectroscopy and molecular simulations reveal <u>atomic concentration, chemical speciation, and potential profile</u> at electrode interface

Photophysical characterization of photoelectrochemical materials and assemblies

Complete capabilities and expertise for correlating function with basic optoelectronic properties, photocarrier dynamics, and chemical transformations



Understanding the mechanisms that govern photochemical transformations , define efficiencies, and contribute to stability



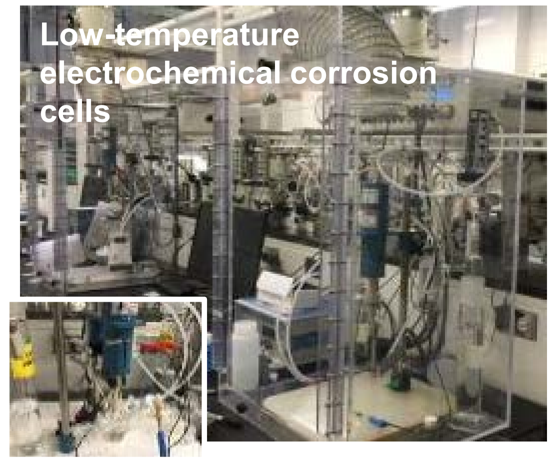
In situ and *operando* characterization of solar fuels components and assemblies. A range of testing cells are available and custom cell design and fabrication is done in-house.

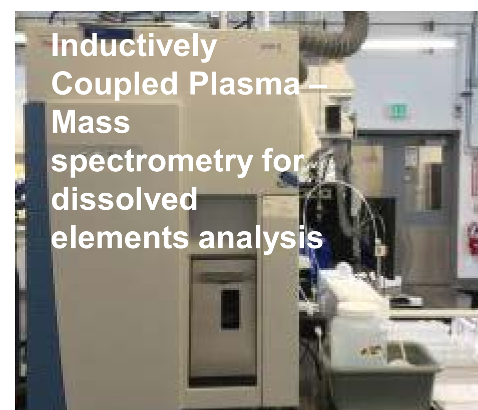
- **Pump-probe optical spectroscopy**
  - Transient absorption and reflectivity
  - Time resolved (fs – s)
  - In situ, temperature-dependent
  - UV – IR spectral range
- **Photoluminescence spectroscopy**
  - Time resolved (ps – steady state)
  - UV to IR spectral range, 10 – 500 K
- **Spectroscopic ellipsometry**
  - *in situ* (photo)electrochemical, environmental, and temperature-dependent characterization
- **Confocal Raman spectroscopy**
  - *in situ* (photo)electrochemical, mapping
- **Fourier transform infrared spectroscopy**
  - Time resolved (ns – steady state)
  - Stopped flow, laser-initiated, *in situ*, etc.
  - Reflection, transmission, ATR
- **Photo-/electro-reflectance**

Fully equipped spectroscopy labs, with experience for custom optoelectronic measurements. *Contact for more information about techniques not listed here.*

Corrosion Analysis

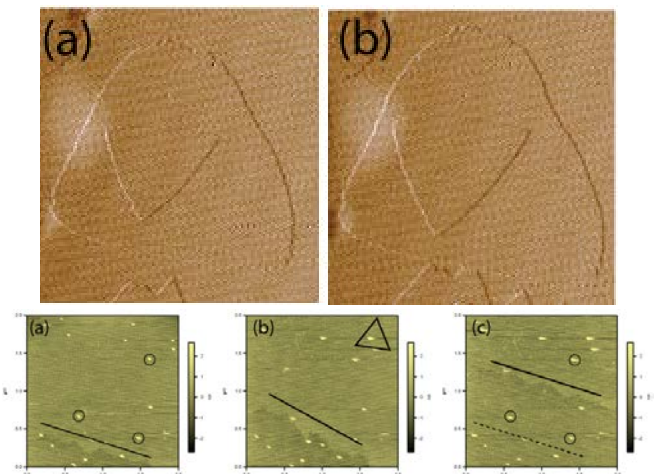
- *Electrochemical corrosion and long-term immersion weight-change evaluations at low- and high- temperature in controlled environments*
- *Strict protocols followed for sample handling*
- *Characterization before and after degradation for microstructure, chemical and physico-chemical evaluations*





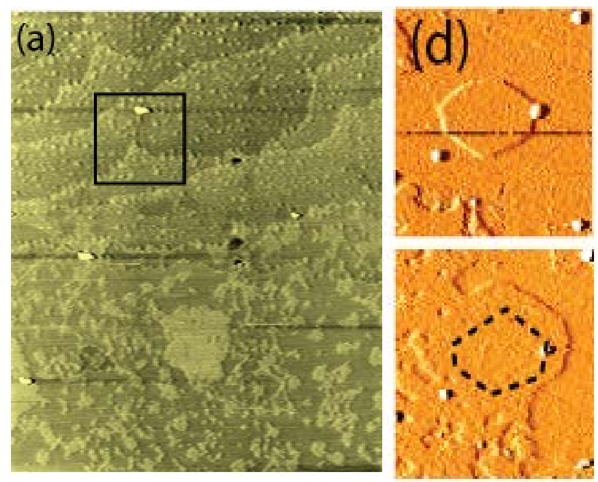
Characterization & Mitigation of Corrosion During Photoelectrochemical Hydrogen Production

Etch pit formation & corrosion rates under electrochemical control



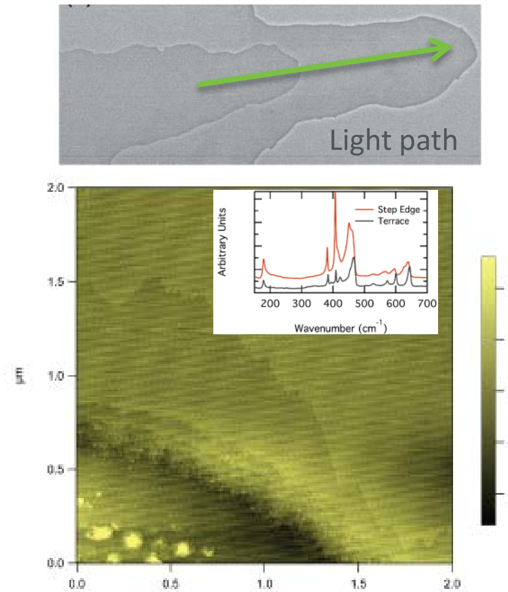
Etching of MoS_2 atomic steps

Chemical & electrochemical reactions during cycling



Precipitation and oxide growth on MoS_2

Photo-induced corrosion



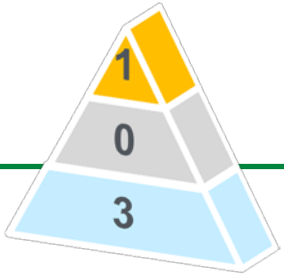
Orme (2012) Surface Reactions on Molydisulfide (MoS_2) in Aqueous Environments, Report to Chevron ETC

Provide information using a suite of *in situ* experimental tools (EC SPM, SECM, Raman, IR, SAXS):

- **change of surface morphology induced by relevant factors (potential, pH, light etc)**
- **identify chemical activities**
- **identify corrosion mechanisms and assist developing a corrosion mitigation strategy**

Technique: Qiu and Orme, Chem. Rev. **108**, 4784 (2008); Keist et al, Electrochemica Acta **152**, 161 (2015)

Analysis Capabilities



1. Prospective LCA modeling
2. Technoeconmic Analysis

1. Advanced water-splitting materials requirements using flowsheet development and technoeconomic analysis

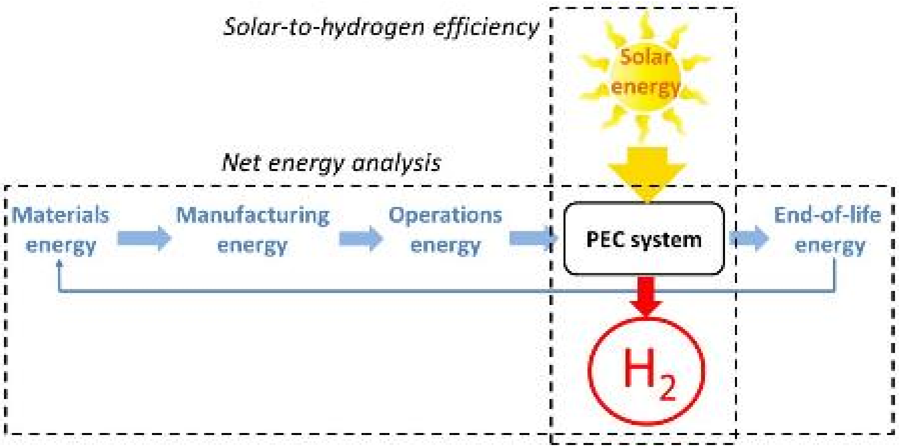
Note that most if not all projects will utilize these nodes

Prospective LCA modeling for water-splitting technologies

Extensive experience in energy analysis for water-splitting technologies

- Estimates of material and energy flows across entire plant life-cycle including total cost of ownership and externalities
- Ability to add costs or other metrics to model

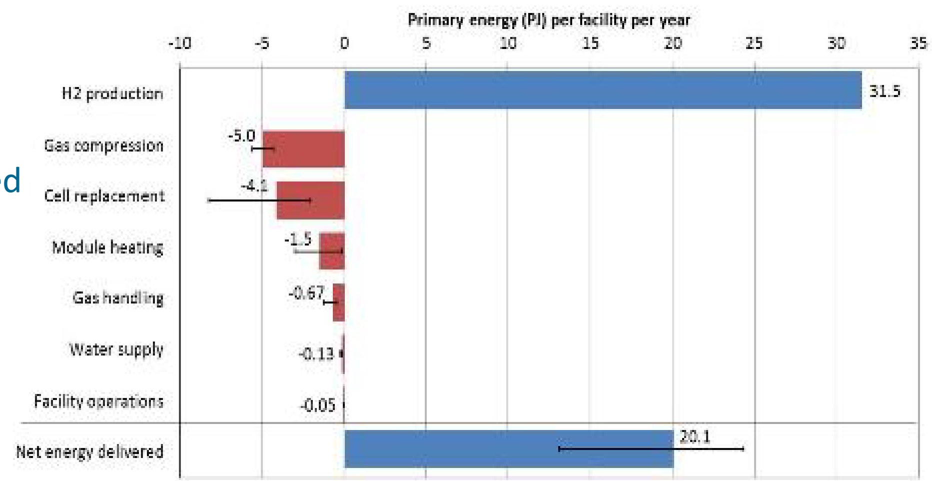
PEC example:

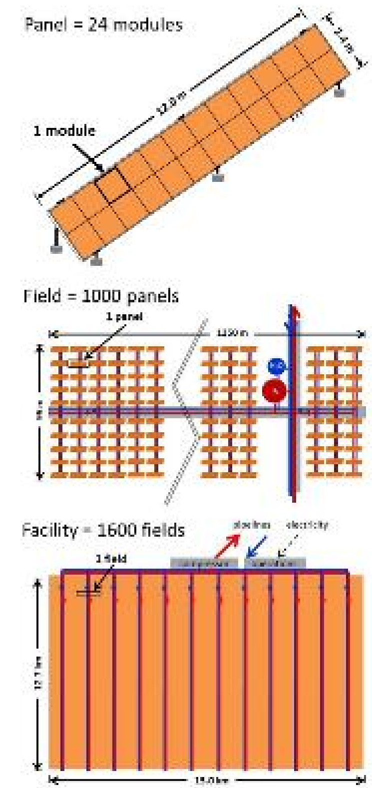


Calculated energy metrics:

- **Net energy**
- **Energy return on energy invested (EROEI)**
- **Energy payback time**

- New materials, components and processes can easily be incorporated
- Perform sensitivity analysis of key parameters
- Monte Carlo simulation capability
- Synergistic with technoeconomic analysis





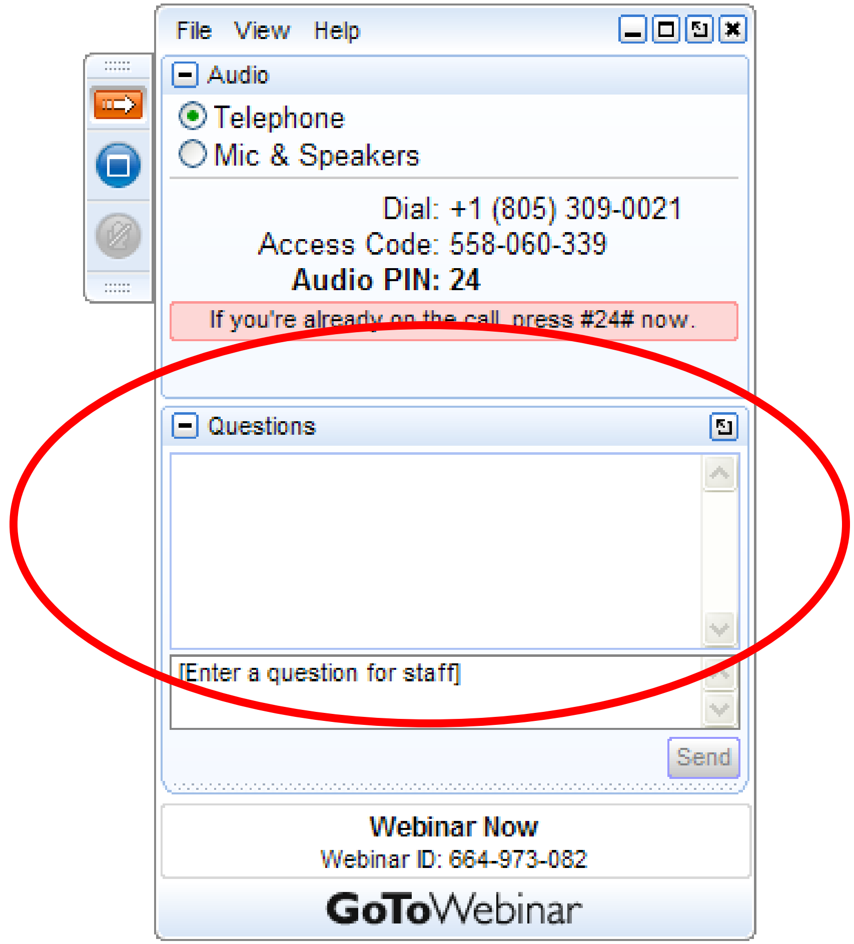
Upcoming Webinars on HydroGEN EMN Consortia

Webinar	Links to register for webinar	Date and Time
FCTO's HydroGEN Consortium Webinar Series, Part 1 of 3: Photoelectrochemical (PEC) Water Splitting	https://attendee.gotowebinar.com/register/4254096628056359684	Thursday, November 10th, 2016; 4 – 5 PM EST
FCTO's HydroGEN Consortium Webinar Series, Part 2 of 3: Electrolysis	https://attendee.gotowebinar.com/register/1213908600370749848	Tuesday, November 15th, 2016; 4 – 5 PM EST
FCTO's HydroGEN Consortium Webinar Series, Part 3 of 3: Solar Thermochemical (STCH) Hydrogen Production	https://attendee.gotowebinar.com/register/3983369483529561648	Thursday, November 17th, 2016; 4 – 5 PM EST

Eric Miller, DOE-EERE-FCTO

Question and Answer

- Please type your questions into the question box



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Thank you

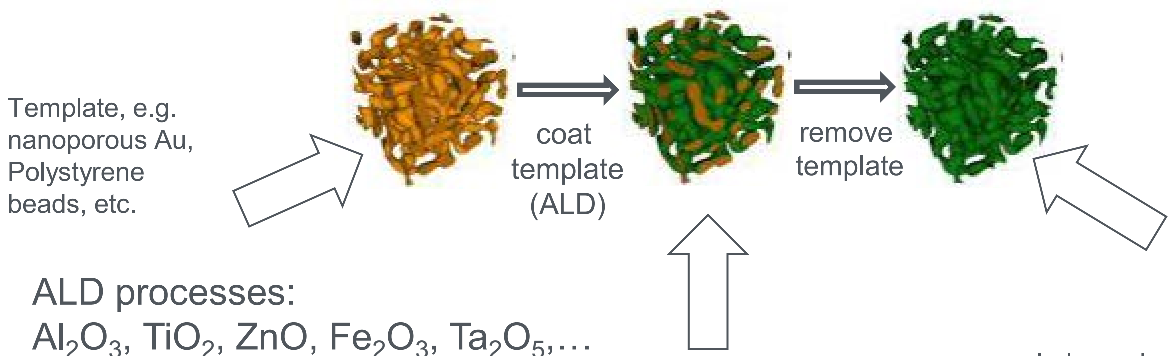
Eric Miller
(eric.miller@ee.doe.gov)

Adam Weber
(azweber@lbl.gov)

hydrogenandfuelcells.energy.gov

ALD based surface functionalization and porosity control: PEC Cat 3

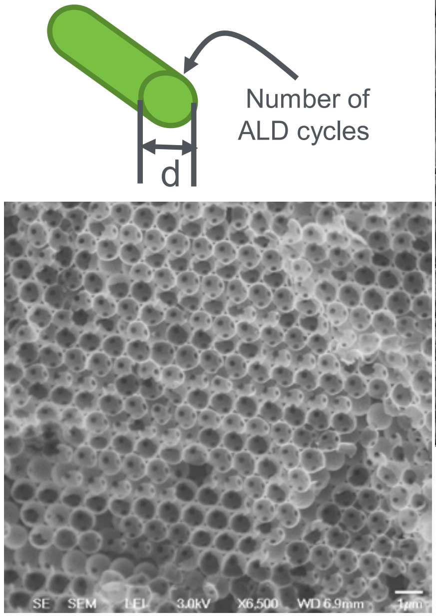
3D templated bulk materials with deterministic control of composition, density, and pore size/morphology:

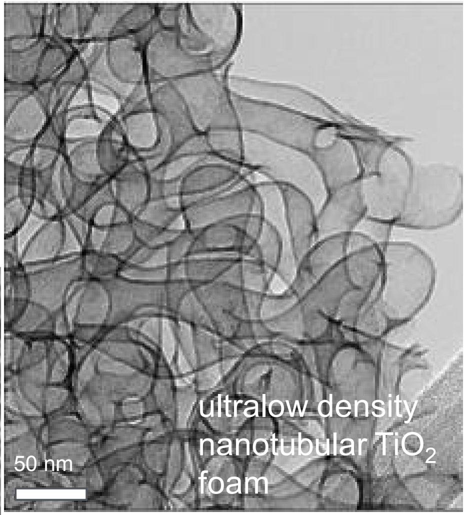


freestanding ALD coatings that are fully tunable in density and porosity

ALD processes:
Al_2O_3, TiO_2, ZnO, Fe_2O_3, Ta_2O_5,…

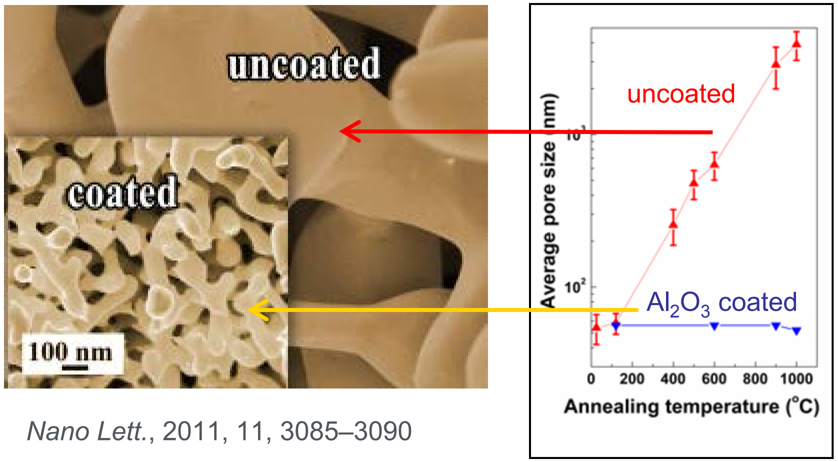
Independent control of pore size *and* density





Adv. Mat. 26 (2014) 4808

Surface functionalization/stabilization by ALD:

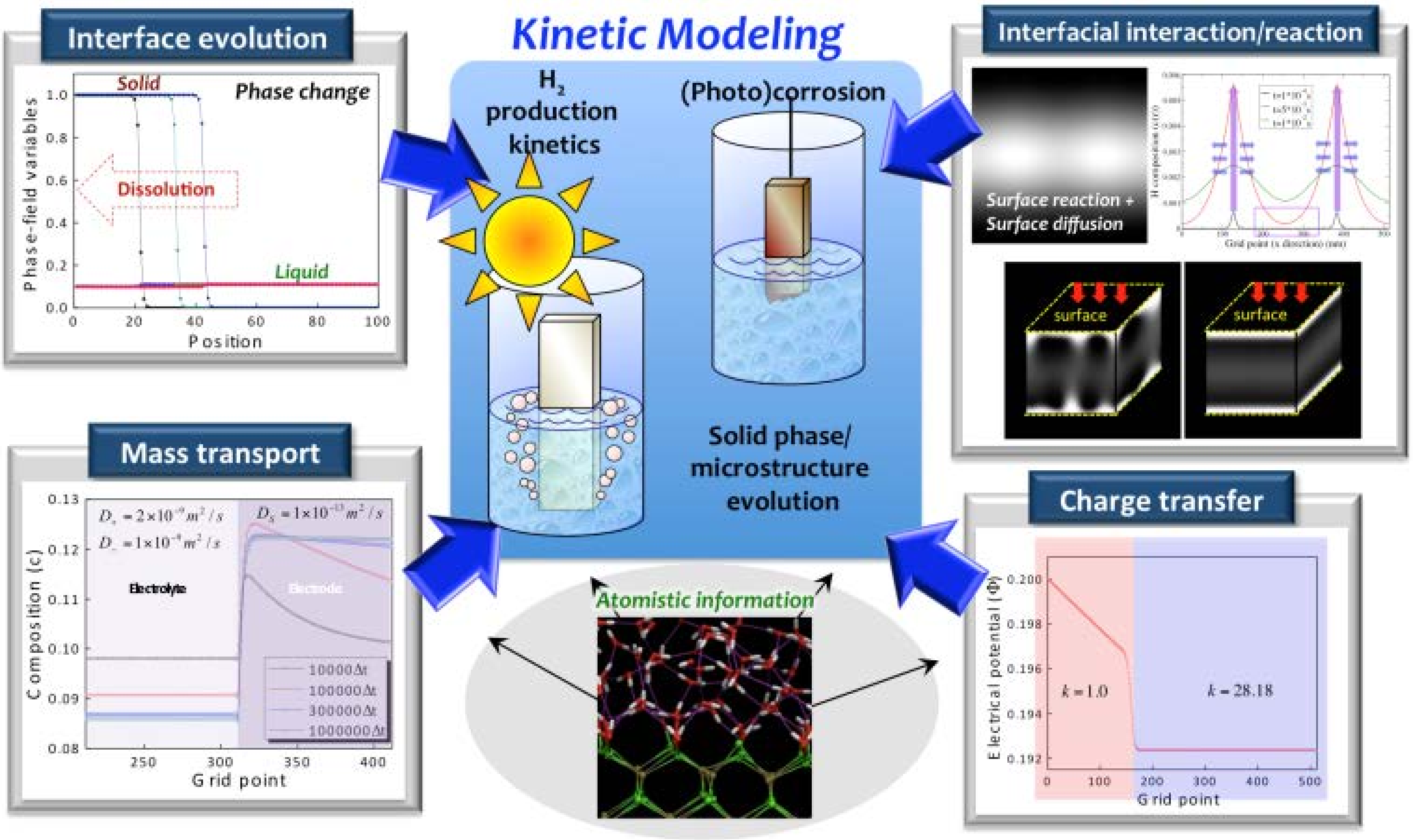


Nano Lett., 2011, 11, 3085–3090

Monika Biener

Mesoscale Modeling of Kinetic Processes and Interface Evolution: PEC Cat 1; LTE Cat 2

- **Multi-physics continuum modeling** integrating relevant **kinetic processes** at or across water-splitting interfaces (mass transport, charge transfer, photon harvesting, recombination, *etc.*)
- **Interface evolution** during (photo)electrochemical corrosion or upon solar thermochemical H_2 production from phase field models
- Parameterization **informed by atomistic mechanisms** and precisely derived **physical parameters**



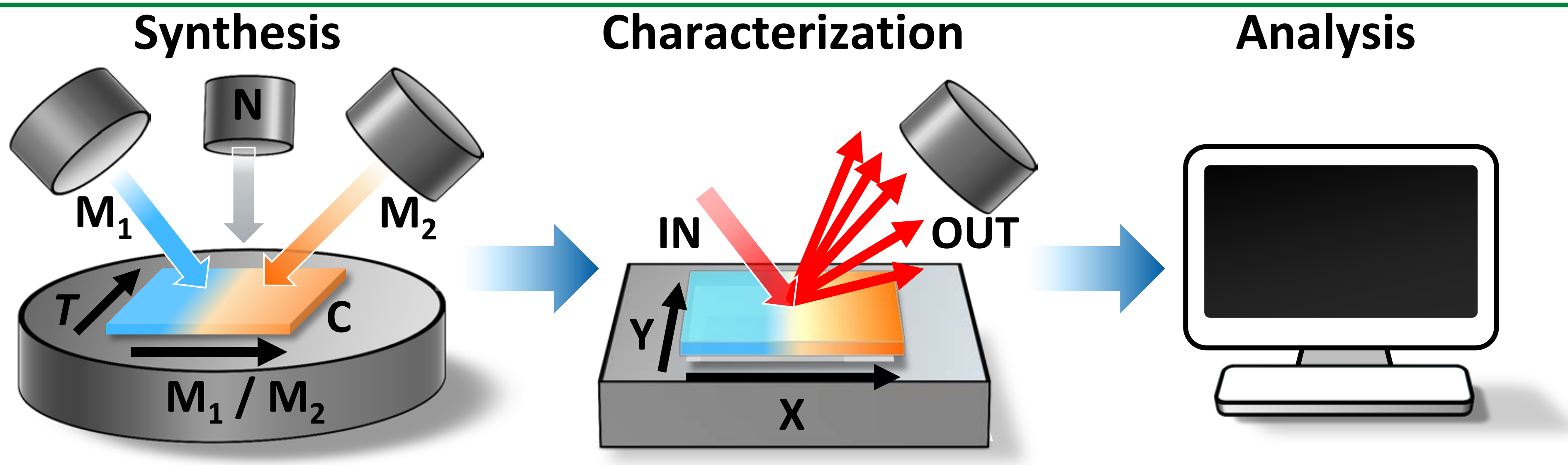
CdTe Capability Node

Wide range of deposition capabilities

- **Transparent (front) contacts by MOCVD or sputtering**
  - Conducting oxides including SnO_2:F (FTO), In_2O_3:Sn (ITO), Cd_2SnO_4 (CTO), ZnO:Al (AZO)
  - Insulating oxides including SnO_2, zinc tin oxide (ZTO), ZnO, ZrO_2
  - Buffer layers including CdS, CdS:O, CdS:In, CdSe, CdSe:O, $Mg_{1-x}Zn_xO$
- **Absorber layer (CdTe)**
  - Close-space sublimation (CSS)
  - Molecular beam epitaxy (MBE)
  - Vapor transport deposition (to come online by end of fiscal year)
- **Back contacts by sputtering and/or evaporation**
  - Cu, MoO_x, Cu_xTe, ZnTe, ZnTe:Cu, Sb_xTe, Ti, Au, Mo, Ni, carbon paste
- **Sample details**
  - Sample size capabilities vary depending on deposition system (12 deposition systems available)
  - 1.5x1.5” capability for all deposition steps – smaller sample sizes can be generated, upon request
  - Some steps allow large sample sizes (e.g. 4x12” for MOCVD; 3x3”, 4x4”, 6x6” for certain sputtered layers)
  - Samples can be grown on various substrates (e.g. Soda lime glass, Corning® 7059, Corning® Willow® Glass)
  - 6x6” capability planned to come online by end of fiscal year
- **Photovoltaic cell efficiencies**
  - Superstrate geometry ~ 15% [baseline process]
  - Substrate geometry ~ 10% [baseline process]
- **Other**
  - Other material layers are available
  - Different architectures can be generated upon request
  - Numerous material and device characterization techniques available

Primary Contact: Matthew O. Reese (matthew.reese@nrel.gov)

High-Throughput Experimental (HTE) Thin Film Combinatorial Capabilities



Combinatorial Synthesis

- multi-element thin films of nanoparticles (metals, oxides, nitrides, sulfides)
- gradients (composition, temperature, film thickness, nanoparticle size etc)
- physical vapor deposition techniques (sputtering, pulsed laser deposition)
- substrates (highly oriented pyrolytic graphite, metals, glass etc)

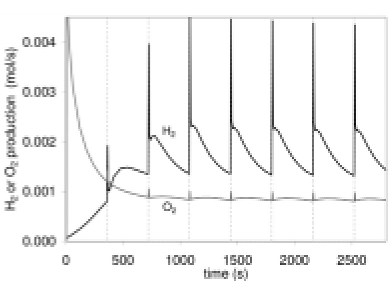
Spatially-resolved characterization

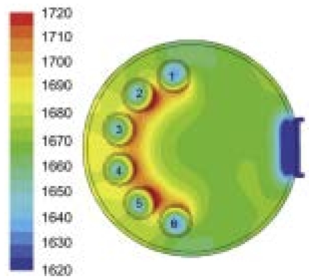
- chemical composition (XRF, RBS)
- crystallographic structure (XRD, Raman)
- microstructure (SEM, AFM)
- surface properties (PES, KP, PYS)
- optical (UV/VIS/FTIR absorption, PL)
- electrical ((photo)conductivity, Seebeck)
- electrochemical (SECM, scanning droplet cell under development)

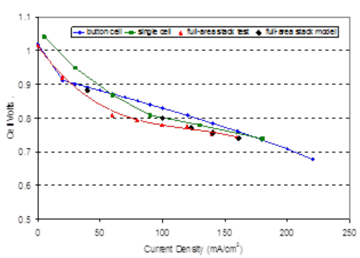
+ Automated data analysis (Igor PRO, HTE materials database)

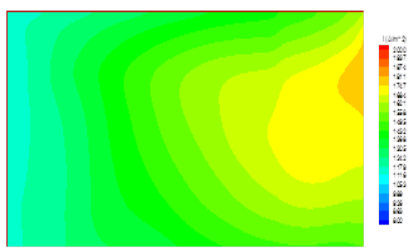
Contact: Andriy.Zakutayev@NREL.gov

Multi-scale thermochemical and electrochemical modeling for material scale-up to component design









Purpose: This capability develops computational tools to enable the implementation of materials into a component (cell, stack, or reactor) and to assess their performance, lifetime and reliability through high-fidelity modeling of a component design.

Key Features:

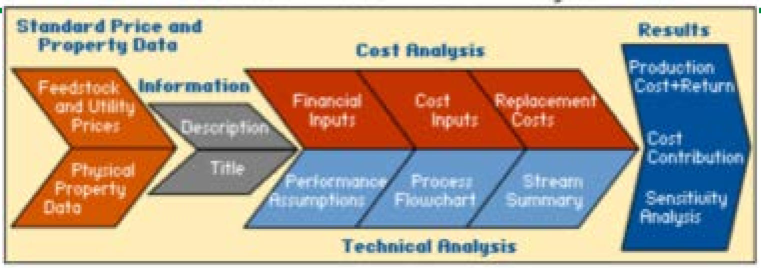
- NREL component and system modeling expertise can support material integration into the hydrogen generation devices and system configuration.
- The component modeling tools use ANSYS software as a solution framework, by adding fundamental thermochemical, electrochemical, and thermomechanical models in customized user defined functions.
- The modeling practices were previously successfully applied for fuel cell stack design and solar thermochemical hydrogen process (STCH).
- The capability can be used for advanced electrolysis and solar thermochemical hydrogen conversion development as a general tool for electrolyzer design or solar reactor performance optimization.

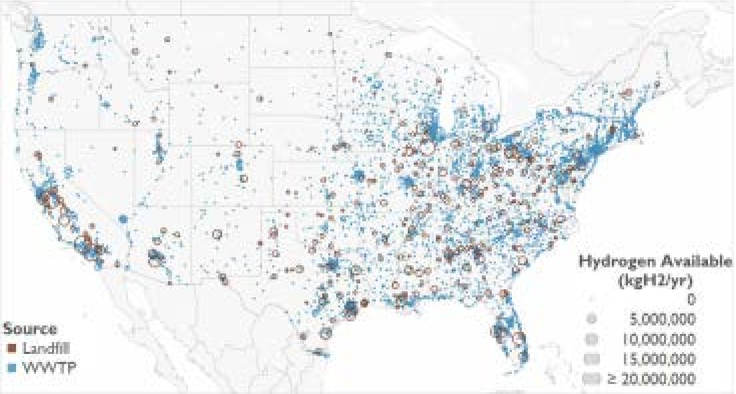
- Martinek, J., Viger, R., Weimer, A.W. (2014) “Transient simulation of a tubular packed bed solar receiver for hydrogen generation via metal oxide thermochemical cycles” Solar Energy 105 pp. 613-631.
- Ma, Z., Venkataraman, R., Farooque, M. (2009). “Modeling”, In J. Garche, C. Dyer, P. Moseley, Z. Ogumi, D. Rand and B. Scrosati, editors. Encyclopedia of Electrochemical Power Sources, Vol 2.Amsterdam: Elsevier; 2009. pp. 519–532.

Models supporting techno-economic analyses

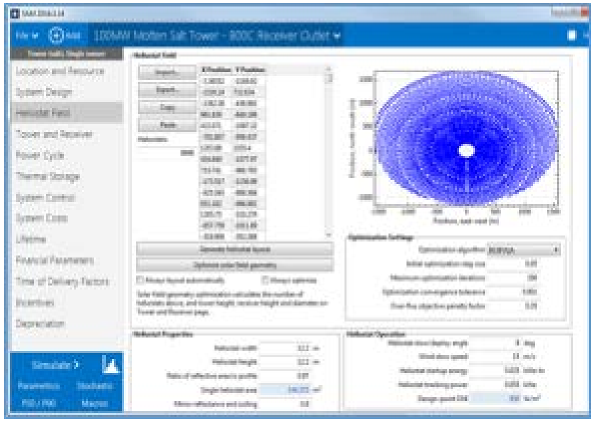
- Hydrogen Analysis (H2A) models
  - Production, Delivery, and Fuel Cells
  - Discounted cash flow framework
  - Models are transparent and public
    http://www.hydrogen.energy.gov/h2a_analysis.html

H2A Production Cash Flow Analysis Tool





- Scenario Evaluation and Regionalization Analysis (SERA)
  - Optimizes least cost spatial-temporal infrastructure in response to hydrogen demand
  - Optimization across all pathway options
  - Sub-models explore finance options
- NREL System Advisory Model (SAM)
  - Renewable resources including solar, wind, geothermal.
  - Economic and generation capacity models for planning
  - https://sam.nrel.gov/



- H2FAST
  - Standard financial accounting framework for H2A cost analysis models
  - Inform investment decisions by providing end users a tool to explore the financial aspects of station installations
  - Three ways to use H2FAST: Web, Spreadsheet, Business case scenario tool (BCS)

In situ/Operando Characterization of Electronic Structure in Photoabsorber Materials: PEC Cat 1; LTE Cat 2

Tightly coupled experimental and simulation capabilities:

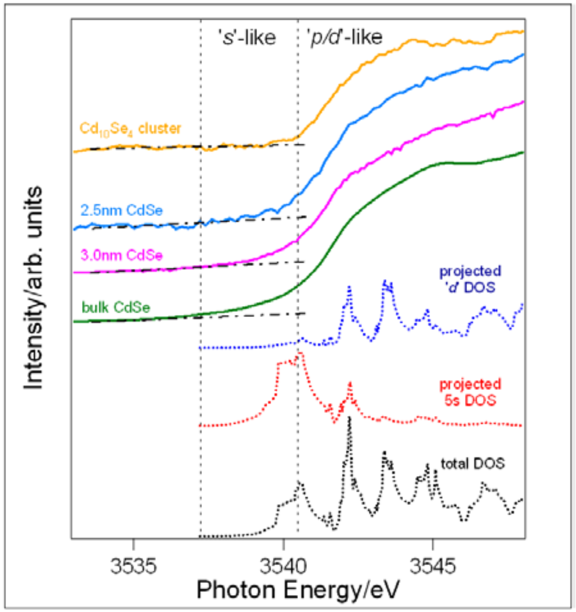
(1) *In situ/operando* x-ray emission and absorption spectroscopies (XES/XAS)*

(2) *Ab initio modeling of spectroscopic data: DFT-molecular dynamics framework with XCH approximation*

Element specific electronic structure:

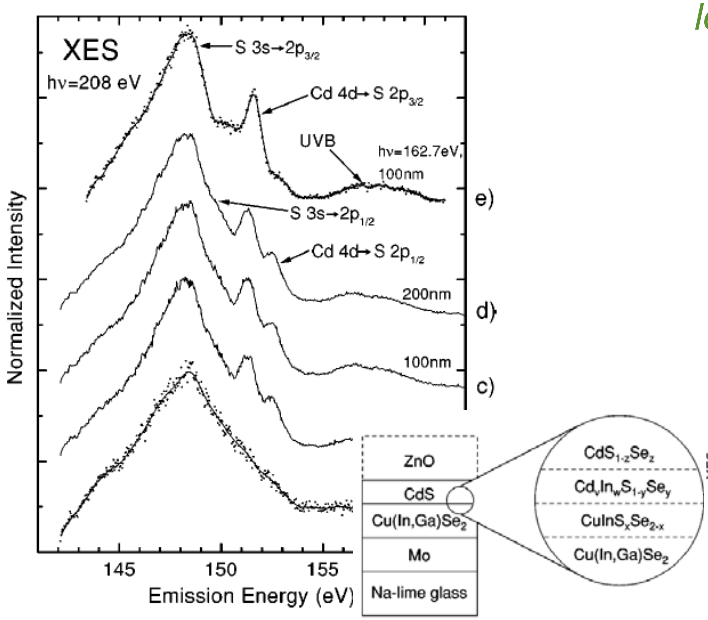
- *Band structure and band bending*
- *Band edge movement/alignment*
- *Exciton binding energies, band gaps*
- *Local chemistry/bonding*

XAS reveals conduction band edge movement in CdSe



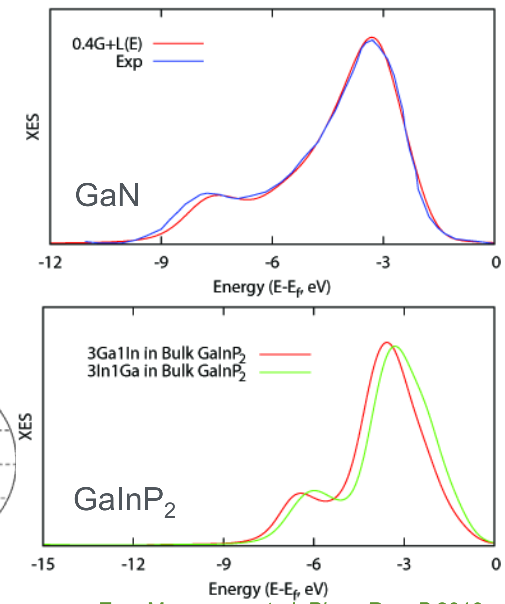
J.R.I. Lee *et al., Phys. Rev. Lett.* 2007

XES shows intermixing effects at buried interfaces in solar cell heterojunction



C. Hseke *et al., Appl. Phys. Lett.* 1999

Simulated XES of model PEC photoelectrodes help to elucidate local chemical environments



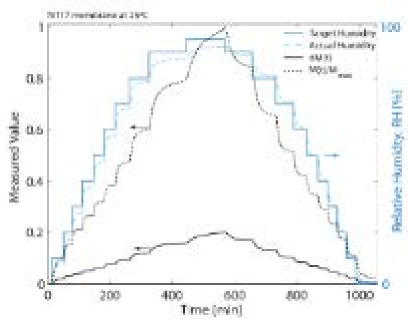
Exp: Magnuson *et al. Phys. Rev. B* 2010

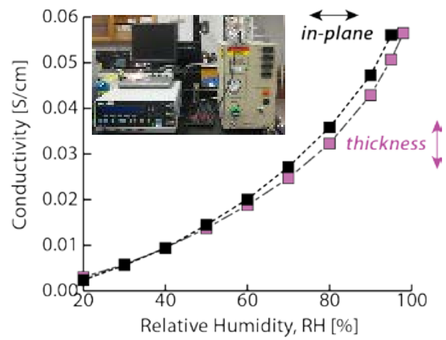
**cell designs can be developed for* in situ *studies of novel materials/device geometries*

Ionomer characterization and understanding

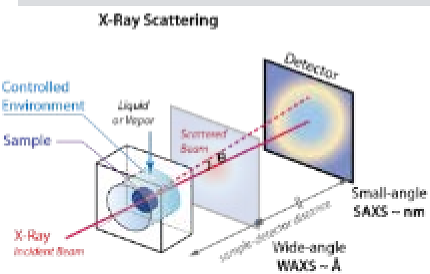
- **Characterization Tools for ionomers,** (ion-conductive polymers) that are used for water splitting

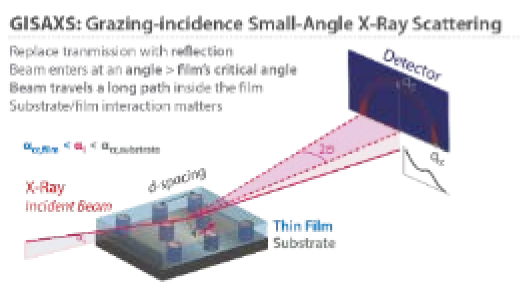
Water uptake/diffusion | ionic conductivity





Structural characterization using X-ray scattering





LBNL capabilities include:

– **thin-film fabrication**

spin casting, spray coating with a SONO-TEK Exacta Coat System)

– **Property characterization**

Thin Films: QCM and ellipsometry with RH /T control, profilometry, mechanical properties

Membranes: macroscale solvent uptake (dynamic vapor sorption), mechanical properties (DMA, Instron), titration, gas permeation (both single gas and mixtures, and dry/wet), density, conductivity and other transport properties in and through the plane as a function of solvent content

– **Structural characterization**

SAXS/WAXS and GISAXS (for thin films) cells and setups including heating, dry/wet imaging and mechanical testing setup for use in-line at a synchrotron. Also, various equipment to probe the formation of polymers and films including digital light scanning, rheometry, zeta potential.

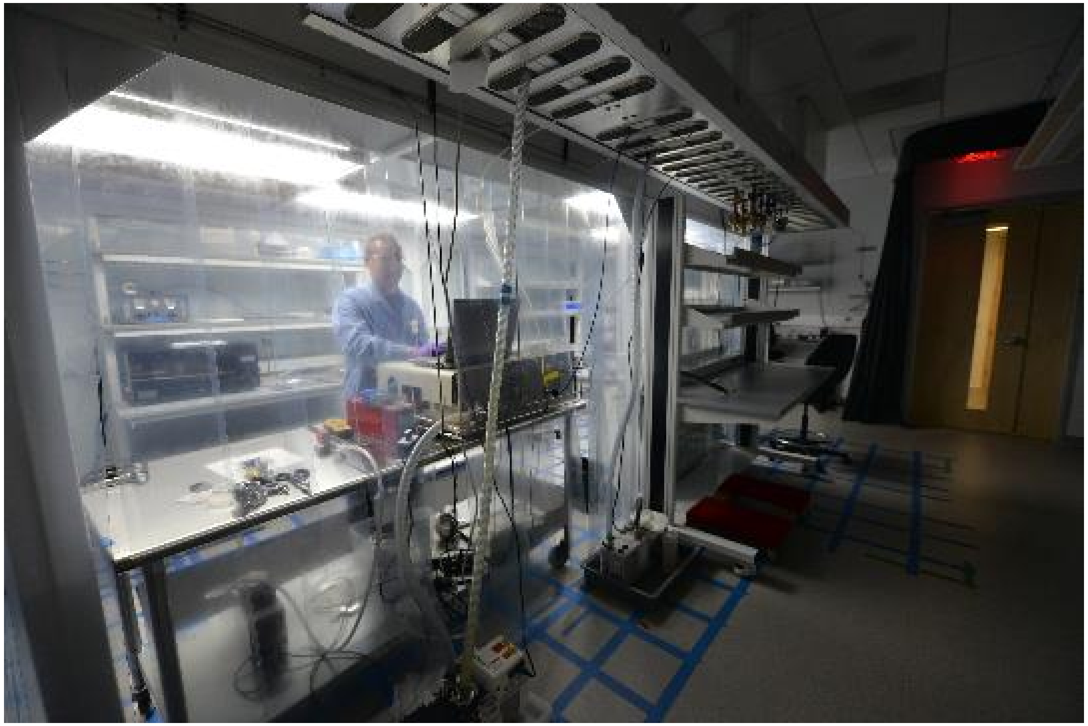
In accordance with the equipment, there is the associated expertise of using the equipment and analyzing the data

Cleanrooms with surface preparation

2 cleanrooms with facilities for surface cleaning and coating, sizes up to 150 mm

Room 1, softwall cleanroom in dedicated lab:

- GEMSTAR-6 Thermal Atomic Layer Deposition tool (model: GEMSTAR-6, vendor: Arradiance) for depositing highly conformal thin films with precise control of composition and thickness at relatively low temperatures (40 to 300°C)
- Plasma cleaner (model: PDC-32G, vendor: Harrick Plasma) and UV-ozone cleaner for removal of surface impurities
- Vacuum desiccator
- CO_2 sno-gun for particle removal
- Anti-static work surfaces
- Ellipsometer for film thickness measurements
- Custom large area optical-inspection tool for finding and mapping surface defects at the micron scale over large areas



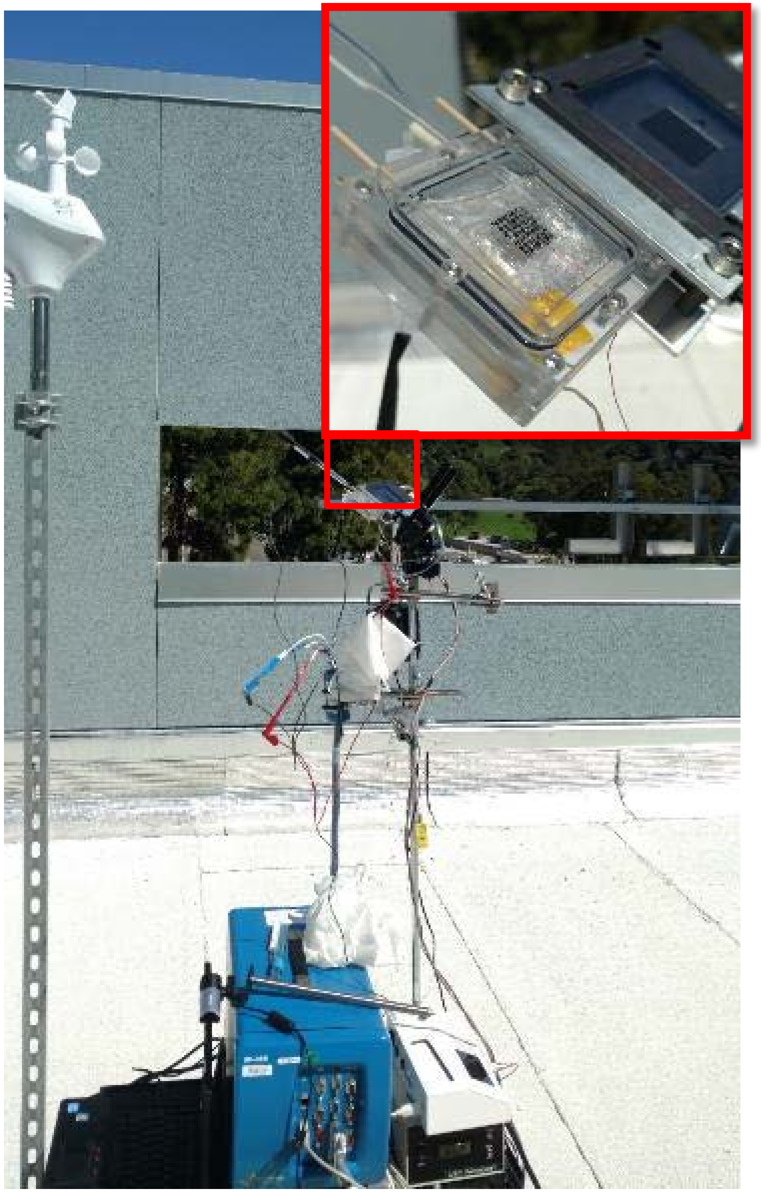
Room 2, dedicated wet process and assembly cleanroom:

- Wet benches for solvent and acid cleans including HF
- Laminar flow hood for substrate and component assembly and packaging

Outdoor solar water-splitting test station

Located on the roof of Chu Hall (Building 30) at LBNL

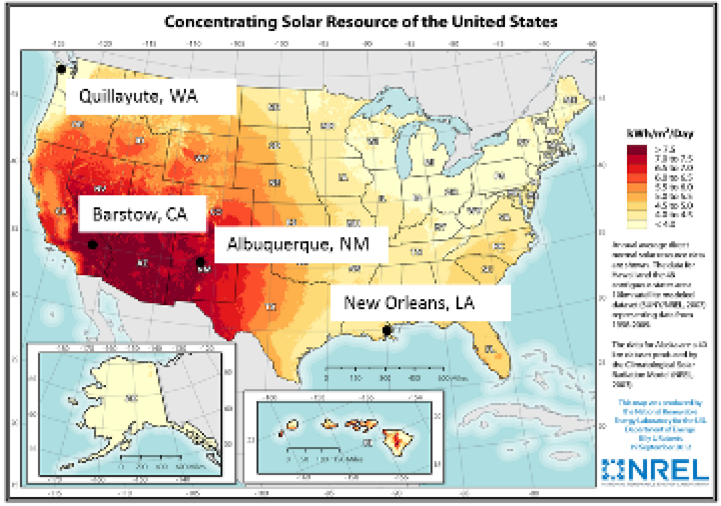
- Weather Underground weather station, Berkeley, California, at Weather Station ID: KCABERKE84, Latitude / Longitude: N 37° 52' 35", W 122° 14' 49" Elevation: 283m
- Solar tracker with platform for device
- Potentiostat and computer for data acquisition
- Calibrated Si reference cell (Newport 91150V)
- Thermocouples
- Video camera
- *GC to be added for product analysis*



Real-World Modeling for PEC Performance

Developed model framework to link multiphysics simulations with solar insolation and environmental data

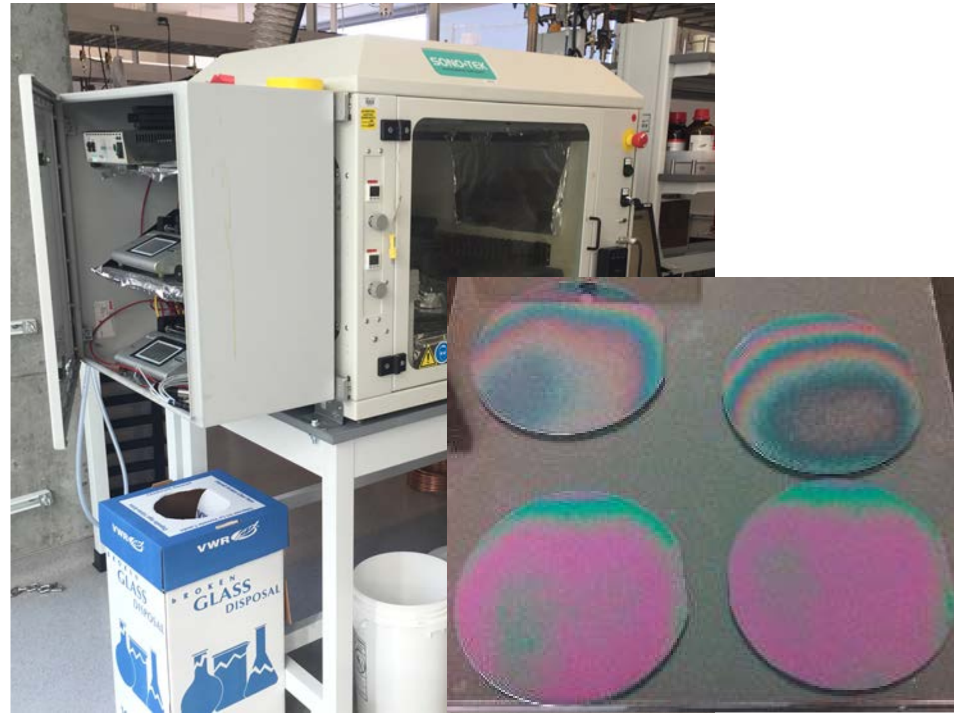
- Predict operation of PEC device based on location
  - Thermal management schemes
  - Solar to hydrogen on different time bases
  - Impact of solar concentration
- Will work to implement for different materials and designs



	Barstow	Albuquerque	New Orleans	Quillayute
Weighted Average Annual η_{STH} [%]	11.2	11.0	10.0	9.1
Annual kg of H_2 Produced per [sq. m] of Aperture	8.80	7.98	4.85	2.91

Spray pyrolysis tool

- Fully integrated Sono-Tek spray pyrolysis coating system
  - 2x syringe pumps
    - Ultrasonic and stir bar compatible
  - 2x ultrasonic nozzles
  - Wenesco 9000 W hot plate
    - 12x12 inches
    - Temperature 29 to 600 ^{o}C
  - Recipes available for transparent conducting oxides and metal oxide films

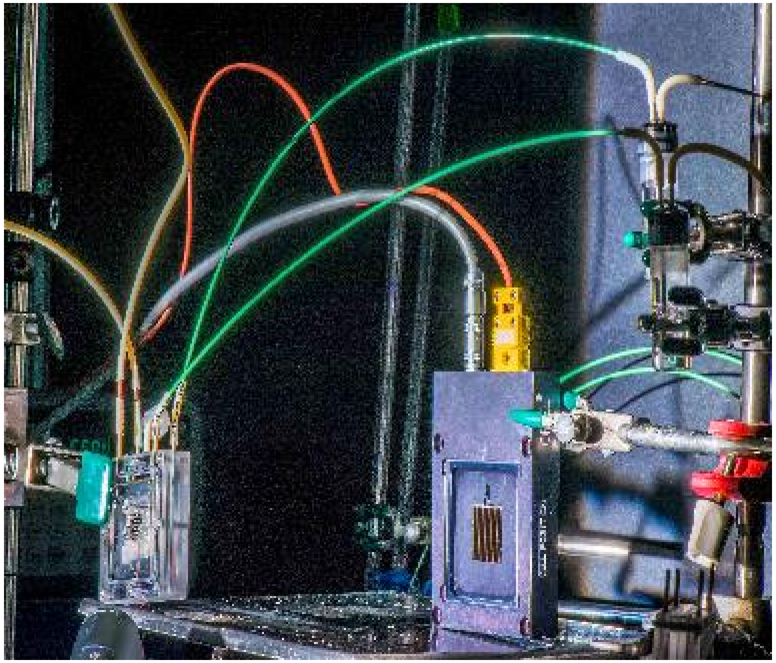


Reference:

K.A. Walczak, Y. Chen, C. Karp, J.W. Beeman, M. Shaner, J. Spurgeon, I.D. Sharp, X. Amashukeli, W. West, J. Jin, N.S. Lewis, and C. Xiang. Modeling, Simulation, and Fabrication of a Fully Integrated, Acid-stable, Scalable Solar-Driven Water- Splitting System, *ChemSusChem* **8**, 544 (2015).

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

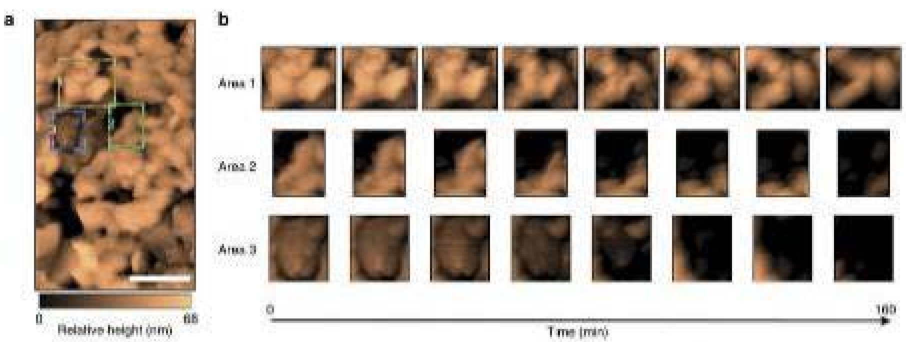


Probing and Mitigating chemical and photochemical corrosion of electrochemical and photoelectrochemical assemblies

Assessment of the chemical and photochemical stabilities of (photo)electrochemical assemblies

This suite of characterization techniques and expertise comprise:

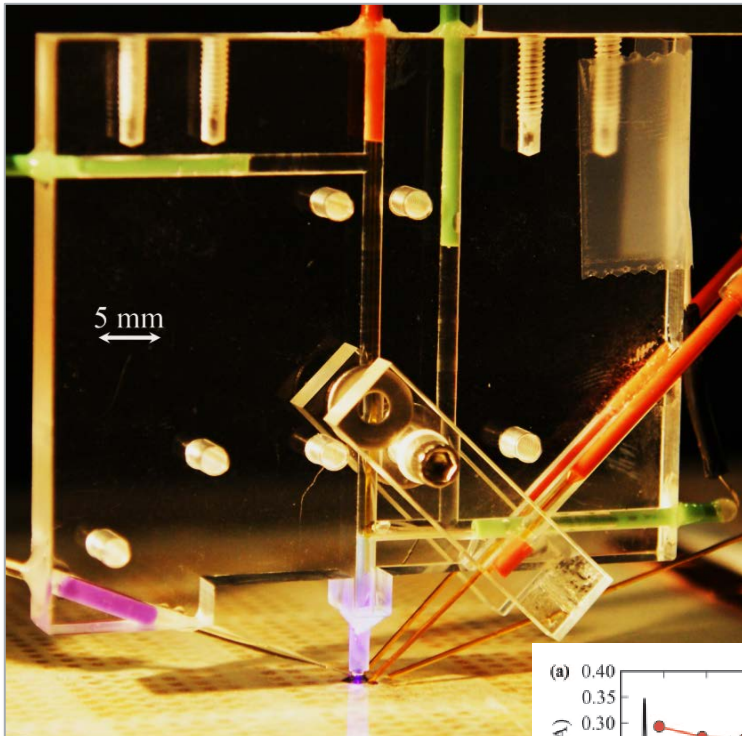
- Electrochemical (EC) and photoelectrochemical (PEC) measurements,
- Inductively coupled plasma mass spectrometry (ICP-MS),
- Electrochemical atomic force microscopy (EC-AFM)

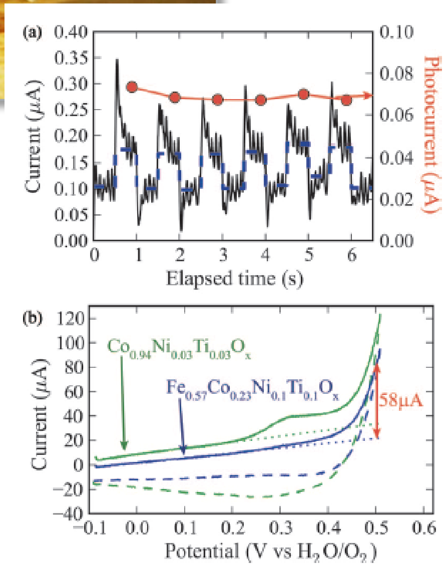


a) EC-AFM scan of $BiVO_4$. b) The three regions indicated in a) were used to monitor corrosion-induced changes to $BiVO_4$ morphology at 20 min increments in 1 M KPi (pH 12.3).

- The specific combination of all these characterization techniques and possible mitigation solutions offers a thorough and complete analysis of electrocatalytic and photoelectrocatalytic materials properties in their working environment
- These analyses are performed on the (photo)electrodes and on the electrolyte utilized to test the performance of the material, with a focus on **material degradation**
- Once identified, various **protection schemes** have been developed that can be used to easily protect the underlying substrates for PEC assemblies

Scanning droplet cell for high throughput electrochemical evaluation





J. M. Gregoire, CX Xiang, X. Liu, M. Marcin, J. Jin, Rev Sci Instrum 2013, 84, 024102

- Programmable raster over large areas
- Provides 3-electrode measurements, compatible with electrolytes across the pH scale
- Fiberoptics allow for PEC evaluation of materials
- Multiple measurements at each location (e.g., cyclic voltammetry, chronoamperometry, chronovoltammetry)
- Droplet constantly refreshed, eliminating cross contamination
- Applicable to a wide variety of high throughput synthesis methodologies
- Capability currently on loan, duplicate to be constructed

In-situ and *operando* nanoscale characterization capabilities for photoelectrochemical materials and integrated assemblies

A combination of different AFM techniques able to optimize (photo)electrochemical assemblies

This suite of characterization techniques comprises:

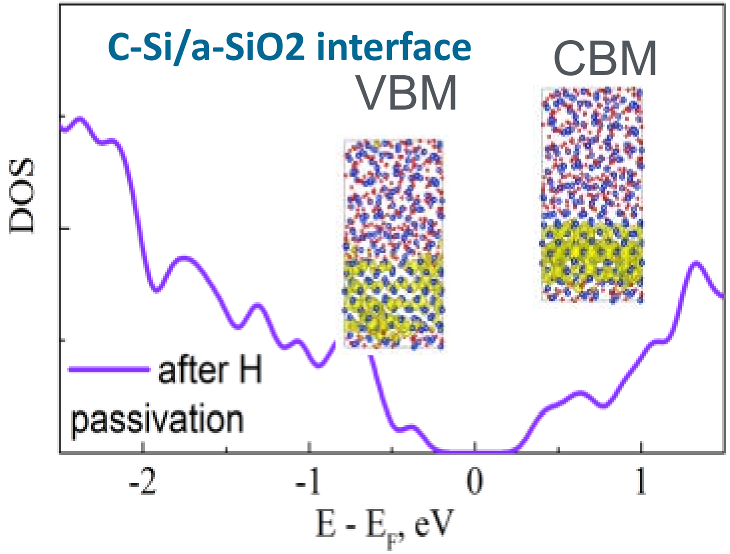
- Peak force AFM (PF-AFM)
- Photoconductive AFM (PC-AFM),
- Kelvin probe force microscopy (KPFM),
- Electrochemical AFM (EC-AFM)
- Photoelectrochemical AFM (PEC-AFM)

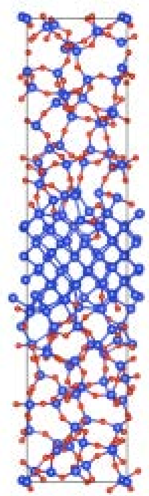
for in-situ and operando characterizations and with associated expertise for data acquisition and analysis

Left: setup for EC-AFM. Right: topography, contact current and electrochemical current of Au squares surrounded by a Si_3N_4 frame. 10 mM $[Ru(NH_3)_6]^{3+}$ solution as electrolyte.

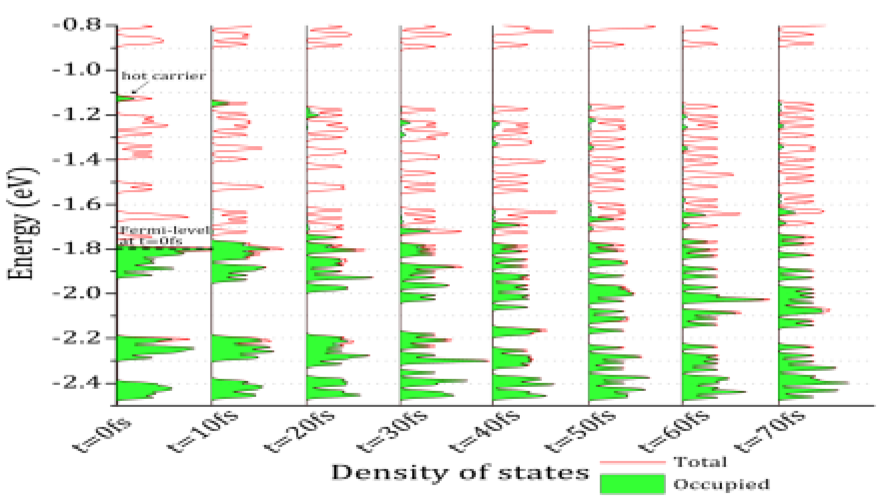
- *In-situ* and *operando* characterization of (photo)electrochemical systems using light illumination including from various lasers.
- These techniques are suitable to directly image local nm-scale PEC activity to understand the electrical mechanisms behind the PEC performance

Ab initio simulation of amorphous protection layer and rt-TDDFT simulation of carrier dynamics





Hot-carrier cooling in Al nanocluster

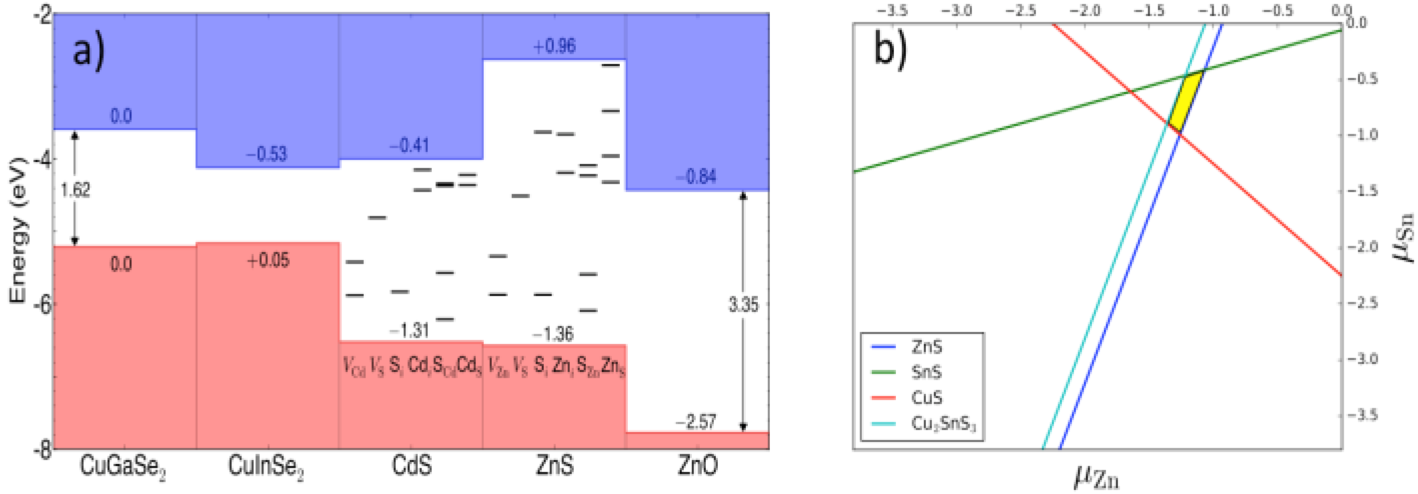


- Ab initio simulation of amorphous oxides electronic structures and defect states
- Using Marcus theory to calculate electron transport between trap states
- Linear scaling 3 dimensional fragment (LS3DF) method for DFT calculation of large (>10,000 atom) systems
- New algorithms for rt-TDDFT allowing calculation of carrier transport and other excited state dynamics for systems with hundreds of atoms for hundreds of fs

DFT applied for PEC and EC (ORR) but can be adapted for other technologies

Computational Materials Diagnostics and Optimization of Photoelectrochemical Devices: PEC&LTE Cat 1; STCH Cat 2

Varley and Lordi, J. App. Phys. 116, 063505 (2014)



Provide: (DFT/Hybrid functional/GW level)

- **Band alignment**
- **Character (malignant/benign) and position of gap levels**
- **Thermodynamics stability of alloys for a given condition (μ, T)**
- **Defect thermodynamics for a given condition (μ, T)**

Optimal choice of absorber/buffer pair including synthesis/process condition that minimizes detrimental effect

Beyond-DFT Simulation of Energetic Barriers and Photoexcited Dynamics: PEC Cat 2

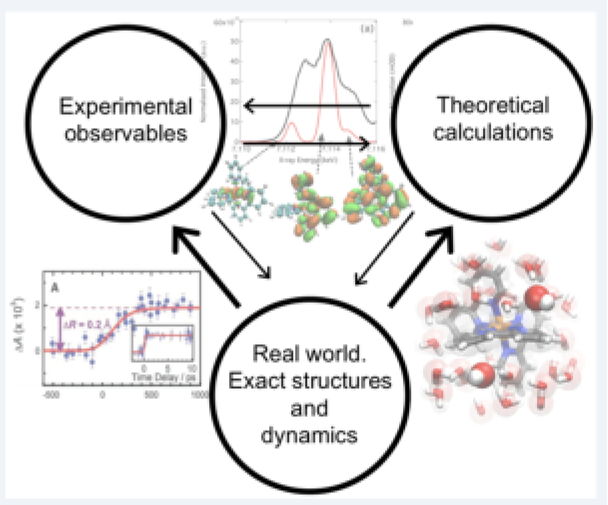
Table 2
A comparison of the observed band mapping of bulk silicon with that computed using correlated wavefunctions, perturbation theory, empirical and single-particle band theories

k-point	QMC[30]	GW[31]	HF[32]	LDA[33]	Emp.[34]	Expt.[35]	B3LYP
$\Gamma_{2'}$	4.6	3.89	9.0	3.19	4.23	4.1	4.68
Γ_{15}	3.7	3.36	8.0	2.55	3.40	3.05	3.78
$\Gamma_{25'}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Γ_1	−13.6	−11.95	−18.9	11.95	−12.5	−12.5	−13.08
X1c	1.51	1.43	5.3	0.63	1.25		1.57
X4	−3.35	−2.93	−4.7	−2.84	−3.3	−2.9	−3.69
X1v	−8.79	−7.95	−12.5	−7.81			−9.24
L1c	2.51	2.19	6.5	1.44	2.4	2.1	2.71
L3	4.55	4.25	8.7	3.31	4.15		5.34
L3'	−1.32	−1.25	−2.0	−1.19	−1.2	−1.5	−1.83
L1v	−7.81	−7.14	−11.1	−6.96	−6.96		−8.37
I2'	−11.05	−9.70	−15.4	−9.61	−9.3		−11.29

The data are in eV and have been aligned at $\Gamma_{25'}$.

Muscat et al. Chem. Phys. Lett. **342**, 397 (2001)

Kent et al. Phys. Rev. B **57**, 15293 (1998)



Tavernelli, ACC. Chem. Res. **48**, 792 (2015)

Provide:

- **QMC: Accurate energy of system**
- **QMC: Scalable up to several hundred atoms**
- **TD-DFT: Excited electron dynamics**
- **TD-DFT: May be used to study about recombination processes**

These will become useful tools when the limitation of DFT simulation becomes an issue for interpretation of experiments