Question and Answer

• Please type your questions into the question box
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.
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

HQ Lead(s)

Technical Capabilities Expert Team

Technology Transfer/Agreements Expert Team

Data Expert Team

National Lab 1

National Lab 2

National Lab n
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

Advanced Water Spitting Workshop April 2016 Stanford
RD&D from different water splitting pathways is critical to reducing renewable H₂ production cost

Production target <$2/gge

H₂ 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 Advanced Water Splitting Materials

**III-V PEC systems**
- Lower III-V costs
- Optical concentration
- Anti-reflection

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

**Thin-film PEC systems**
- Bandgap tuning
- Buried junctions
- Durability testing
- Bubble management
- Non-PGM catalysts
- Membranes

**Absorbers and interfaces**
- Processing compatibility

**Sunlight to H₂**
- Interfaces
- Catalysts
- STH efficiency
- Stability
- Balance of plant

**Techno-economics**
- Life cycle assessment

**Looking Inward: Crosscutting challenges that bind us together**

**Looking Outward: Unique materials development frontiers**
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
Approaches to PEC Hydrogen

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

- 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.)

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
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

1. Ideal tandem bandgaps identified by modeling
2. MOVPE node: Design growth recipe and perform synthesis run
3. Corrosion Analysis node: Characterize material durability
4. Efficiency Benchmarking node: Determine the STH efficiency under standard reference conditions

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

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

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?

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 multijunction 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
STH Efficiency Benchmarking Cost Case Study

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

- Determine STH efficiency of ~10 smaller samples (1 cm²) 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
6. ALD based surface functionalization
7. Novel materials and characterizations for electrocatalysis

Light absorbers, catalysts, integration, other components

Note that many capabilities span different classification areas
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

Preliminary PEC result: Good intrinsic stability of a bare CuGa₃Se₅ (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
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

Note that many capabilities span different classification areas

Ab-initio, other, multiphysics
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 initio modeling of electrochemical interfaces**

**Solid-liquid interfacial chemistry**

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

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

Bulk and interfacial properties of aqueous electrolytes

JPCC 120, 7332 (2016)

**Electronic properties of interfaces**

Electronic properties of electrode-electrolyte interfaces (from GW)

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

Simulations under applied bias or photobias

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

**Electrocatalysis and photocatalysis**

Catalytic activity predictions using *ab initio* descriptors

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

Charge-transfer barriers for $H_2$ evolution


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

JPCC 117, 21772 (2013); Nat. Mater. (In press)

**Electronic properties of electrode-electrolyte interfaces (from GW)**

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

JPCC 120, 7332 (2016)

JPCC 118, 4 (2014)

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

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### Additional Close-Up Summary

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

---

**Note that many capabilities span different classification areas and techniques**
X-ray Approaches for Understanding (photo)electrochemistry at Interfaces

Operando XAS

Operando ambient pressure XPS

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

X-ray photoelectron spectroscopy and molecular simulations reveal atomic concentration, chemical speciation, and potential profile at electrode interface.

Expertise combining operando instrumentation, X-ray spectroscopy, and theory to uncover molecular-scale chemical details at operating electrode interfaces.
Photophysical characterization of photoelectrochemical materials and assemblies

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

- 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

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.

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

Chemical & electrochemical reactions during cycling

Photo-induced corrosion

Etching of MoS₂ atomic steps

Precipitation and oxide growth on MoS₂

Orme (2012) Surface Reactions on Molydisulfide (MoS₂) 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

HydroGEN Advanced Water Splitting Materials

Analysis Capabilities

1. Prospective LCA modeling
2. Technoeconomic 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
- New materials, components and processes can easily be incorporated
- Perform sensitivity analysis of key parameters
- Monte Carlo simulation capability
- Synergistic with technoeconomic analysis

PEC example:

Calculated energy metrics:
- Net energy
- Energy return on energy invested (EROEI)
- Energy payback time
### Upcoming Webinars on HydroGEN EMN Consortia

<table>
<thead>
<tr>
<th>Webinar</th>
<th>Links to register for webinar</th>
<th>Date and Time</th>
</tr>
</thead>
</table>

Eric Miller, DOE-EERE-FCTO
Question and Answer

• Please type your questions into the question box
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:

- Template, e.g. nanoporous Au, Polystyrene beads, etc.
- Freestanding ALD coatings that are fully tunable in density and porosity

ALD processes:
- $\text{Al}_2\text{O}_3$, $\text{TiO}_2$, $\text{ZnO}$, $\text{Fe}_2\text{O}_3$, $\text{Ta}_2\text{O}_5$, etc.

Surface functionalization/stabilization by ALD:

- Independent control of pore size and density
- Number of ALD cycles


Adv. Mat. 26 (2014) 4808

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 H₂ production from phase field models
- **Parameterization** informed by **atomistic mechanisms** and precisely derived **physical parameters**
Wide range of deposition capabilities

- **Transparent (front) contacts by MOCVD or sputtering**
  - Conducting oxides including SnO$_2$:F (FTO), In$_2$O$_3$:Sn (ITO), Cd$_2$SnO$_4$ (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$_x$O

- **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$_x$Te, ZnTe, ZnTe:Cu, Sb$_x$Te, 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
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)
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.

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](http://www.hydrogen.energy.gov/h2a_analysis.html)

- **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/](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)*
   - Element specific electronic structure:
     - Band structure and band bending
     - Band edge movement/alignment
     - Exciton binding energies, band gaps
     - Local chemistry/bonding

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

XAS reveals conduction band edge movement in CdSe

XES shows intermixing effects at buried interfaces in solar cell heterojunction

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

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

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HydroGEN Advanced Water Splitting Materials
Ionomer characterization and understanding

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

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

Water uptake/diffusion | ionic conductivity

<table>
<thead>
<tr>
<th>Time [min]</th>
<th>Relative Humidity [RH]</th>
<th>Conductivity [S/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.000</td>
</tr>
<tr>
<td>200</td>
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<td>0.005</td>
</tr>
<tr>
<td>1000</td>
<td>100</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Structural characterization using X-ray scattering

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
- CO₂ 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
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
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
Spray pyrolysis tool

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

Reference:
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)

- 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

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).
Scanning droplet cell for high throughput electrochemical evaluation

- 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

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

- **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

Left: setup for EC-AFM. Right: topography, contact current and electrochemical current of Au squares surrounded by a Si$_3$N$_4$ frame. 10 mM [Ru(NH$_3$)$_6$]$^{3+}$ solution as electrolyte.
Ab initio simulation of amorphous protection layer and rt-TDDFT simulation of carrier dynamics

- 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
Provide: (DFT/Hybrid functional/GW level)

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

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

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
