

Characterization and Optimization of Photoelectrode Surfaces for Solar-to-chemical Fuel Conversion

PI: Tadashi Ogitsu

Presenter: Brandon C. Wood & Tadashi Ogitsu

Lawrence Livermore National Laboratory

May 12, 2011

Project ID# PD058

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start: March 2010
- End: October 2011
- Percent complete: 70%

Project continuation and direction determined annually by DOE

Barriers

- Z. Materials Durability
- Y. Materials Efficiency

Budget

Total project funding

- DOE \$200K
- Contractor \$280K
(5% of PI, 100% of postdoc)

Funding for FY10: \$100K

Funding for FY11: \$100K

Partners

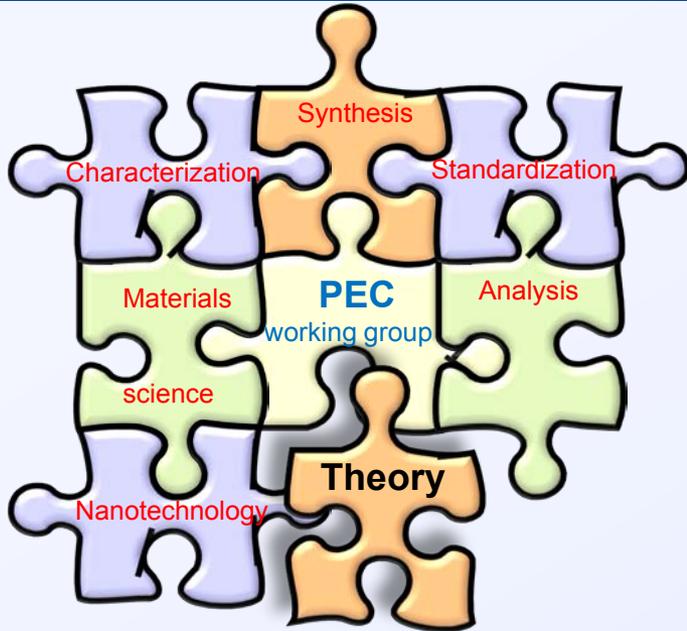
- DOE EERE PEC WG:
Deutsch/Wang/Turner/Kim
(NREL)
Heske (UNLV)

- Unfunded partners:
Prendergast (LBNL)
Otani (AIST Japan)

Project lead: T. Ogitsu, LLNL



III-V Surface Validation Team



PEC Working Group:
 Evaluating working directions
 Sharing and building-up knowledge
 Accelerating research progress

Theory and simulation

III-V Surface Validation

DOE Targets:
 >1000h @STH > 8% (2013)
 \$2 - 4/kg H₂ projected PEC cost
 (beating >\$10/kg H₂ for PV-electrolysis)



The collage includes a schematic of a photoelectrochemical cell with labels for Pt, p-GaAs, n-GaAs, p-GaInP₂, contact, photoelectrochemical cell, funnel diode interconnect, and Photoelectrochemical cell. It also features a photograph of a laboratory setup with a person's hand, a ball-and-stick molecular model, and logos for UNLV (University of Nevada Las Vegas) and NREL (National Renewable Energy Laboratory).

Relevance

■ Objectives

- Develop **theoretical tool chest** for modeling photoelectrochemical systems
- Compile **publications database** of research on relevant photoelectrode materials
- Uncover key **mechanisms of surface corrosion** of semiconductor photoelectrodes
- Understand **dynamics of water dissociation and hydrogen evolution** at the water-photoelectrode interface
- Evaluate **electronic properties** of the surface and water-electrode interface
- Elucidate relationship between **corrosion and catalysis**
- Provide **simulated X-ray spectra** to UNLV for interpretation of experimental results
- **Share research insights** with the PEC WG members

■ Specific relevance to H₂ program

- Inform experimental efforts to increase **durability** of photocatalyst (Barrier Z)
- Inform experimental efforts to increase **catalytic efficiency** (Barrier Y)



Approach

- Perform **large-scale interfacial simulations** of III-V semiconductor surfaces in contact with water
 - Leverage *unique massively parallel **supercomputing capability** of LLNL*
 - Use **quantum molecular dynamics** for truly accurate interfacial modeling
 - Examine different **surface treatments, geometries, and solution chemistries**
 - **Look for correlations** of corrosion and water dissociation with surface morphology, chemistry, and dynamics
 - **Extract model surface geometries** for further analysis
- Calculate **simulated X-ray spectra** of model surfaces
- Participate in **feedback cycle** between synthesis, characterization, and theory teams to accelerate progress toward DOE goals
- Recruit external **collaborators** to extend theoretical tool chest
 - *AIST, Japan: First-principles modeling of charge transfer reaction (ESM)*
 - *Northwestern U.: Thermodynamics of electrode surfaces (CEMC)*
 - *LBNL: Computational spectroscopy (e.g., XAS, XES)*

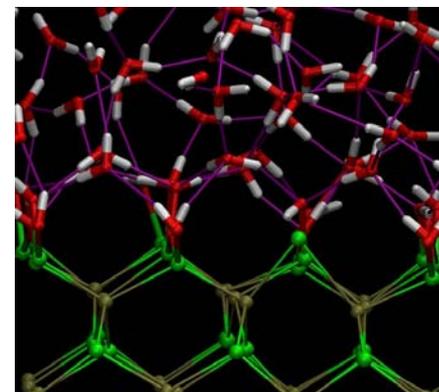
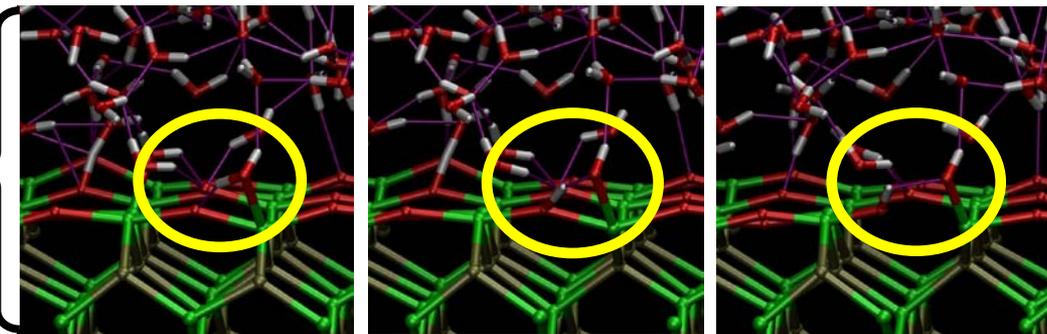
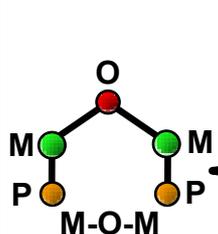
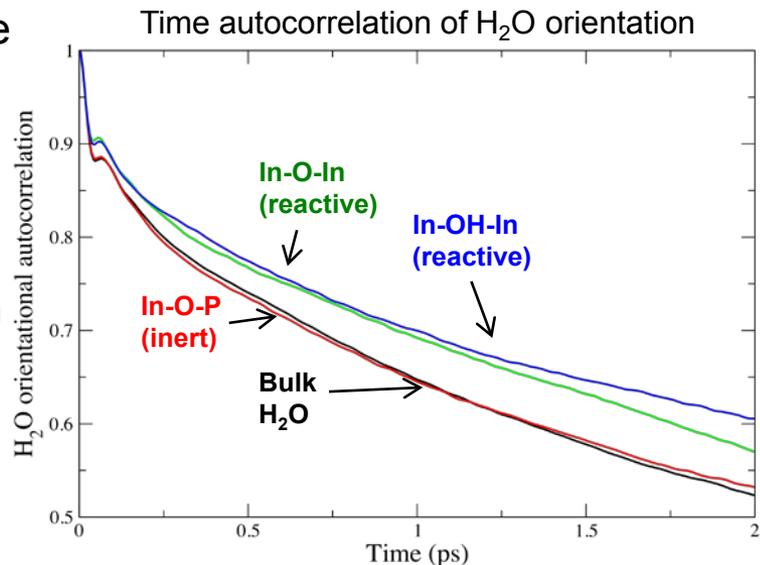


Milestones and Deliverables

Milestone	Description	% Completed
1	Modeling of clean, O-decorated, and OH-decorated III-V surfaces and electrode-electrolyte interfaces	90
2	Implementation of tools for modeling of surfaces under bias	100
3	Examine energetics of nitrogen incorporation	70
4	Investigate precursor states for surface photocorrosion processes	80
5	Study mechanisms of dissociative adsorption of water as a first step in photo-induced hydrogen evolution	60
6	Deliver simulated spectra of model surfaces to experimental III-V characterization team at UNLV	30

Review: Structure and reactivity of InP(001)-H₂O interface

- *Ab-initio* investigation of InP(001) surface & interface
 - Clean surface is chemically inert
- Experiment + theory show importance of surface oxygen/hydroxyl
 - Oxygen topology connected to reactivity
- Dynamics: dissociative adsorption of H₂O on In-O-In
- Hydrogen bonding is important for surface structure
 - Unusually strong water-water bonding at reactive interface
 - Facilitates hydrogen diffusion along surface and first adsorption layer



Water structure: InP(001) w/OH

Overview of new technical accomplishments

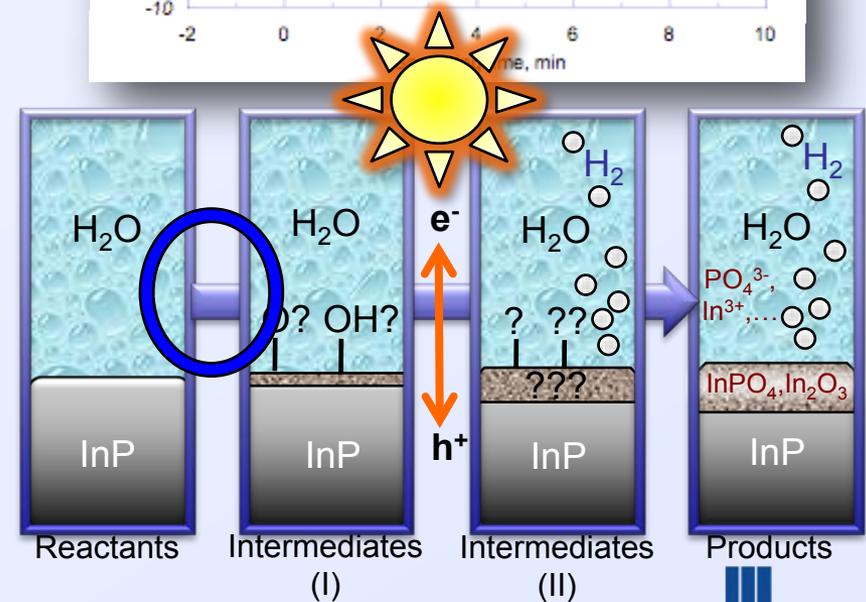
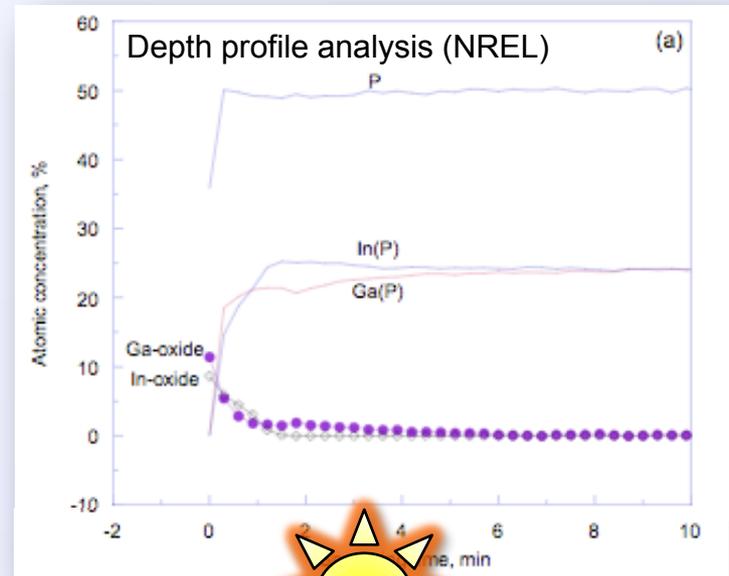
Project has met all target milestones

- Performed literature search to understand science of III-V oxides (idea of oxygen relevance dates to 1980s)
- Theory + characterization: oxygen is relevant
- Shifted focus to understanding **precursor oxygen-rich states** of GaP, InP, and GaInP₂

LLNL Theory Team focus:

- Structure of surface and bulk oxides*
- Relationship of surface structure to electronic structure of oxide surfaces*
- Implications for understanding and controlling corrosion and catalysis*

- With partners at NREL and UNLV, formulated corrosion mechanism hypotheses (being verified)
- Comparison of calculated and measured X-ray spectra (partnership with UNLV)



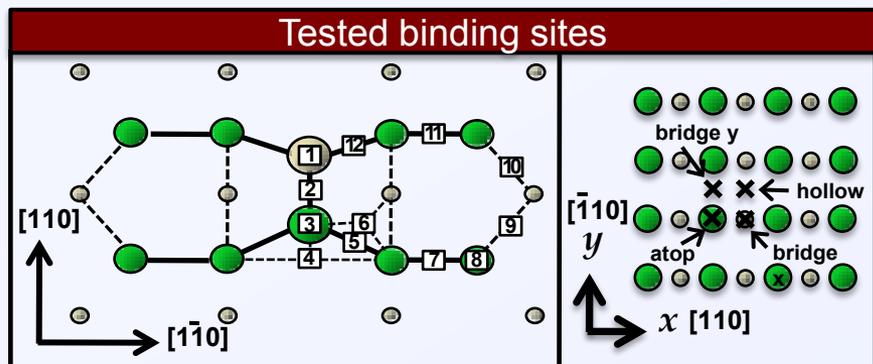
Technical Accomplishment: Database of PEC Research

(in progress)

- Approximately 700 papers (1960-present) have been collected, indexed, and stored as of March 2011
- Information on relevant papers is shared among WG members using online collaboration tools
- Completed detailed review on surface and interfacial properties of GaInP₂ (89 papers total), shared with WG members
 - Discovered literature explaining the relevance of ordered and disordered surface phase competition, which rationalizes inconsistencies in device performance
 - Discovered additional literature on relevance of oxide
- Currently extending review to surface and interfacial properties of native oxides of III-V semiconductors

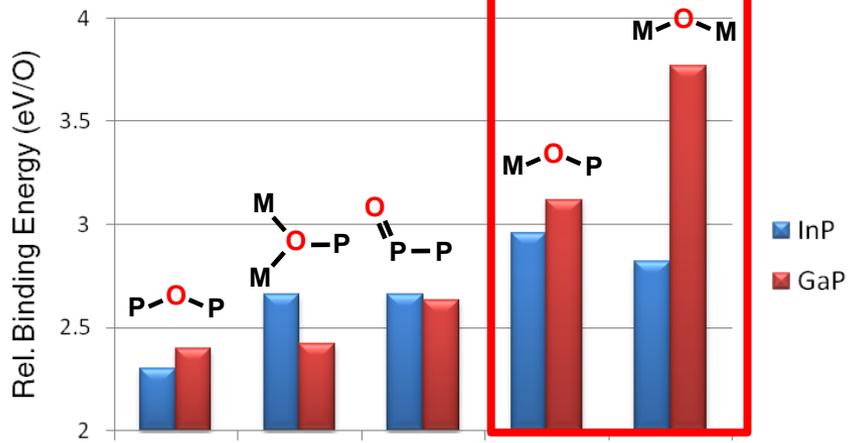
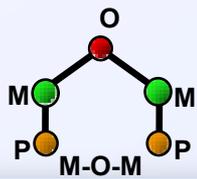
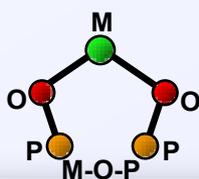


Technical accomplishment: Surface structure

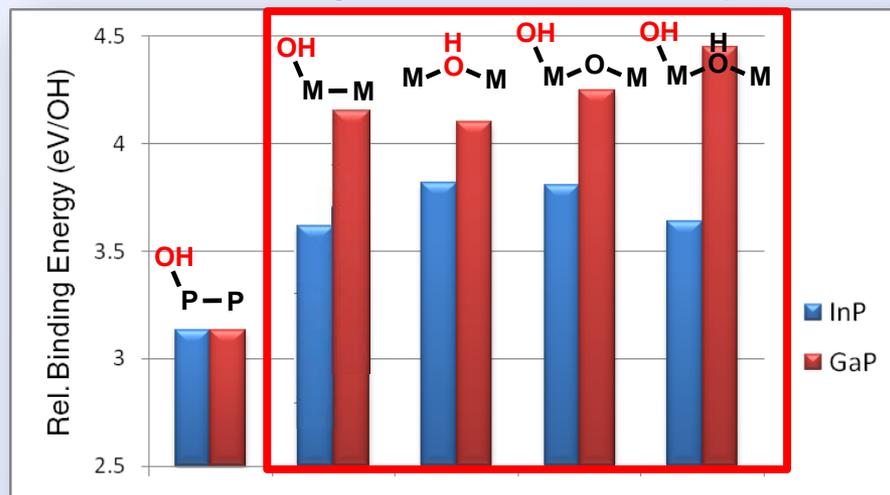
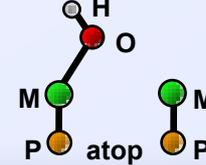
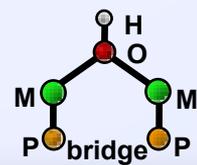


- Wide study of oxygen binding on GaP, InP
- Identified common local structural motifs
 - Oxide: M-O-P, M-O-M, P=O
 - Hydroxide: M-[OH]-M, P-OH, M-OH
- Features resemble motifs in bulk oxides
 - Connects local oxygen binding to bulk oxide nucleation

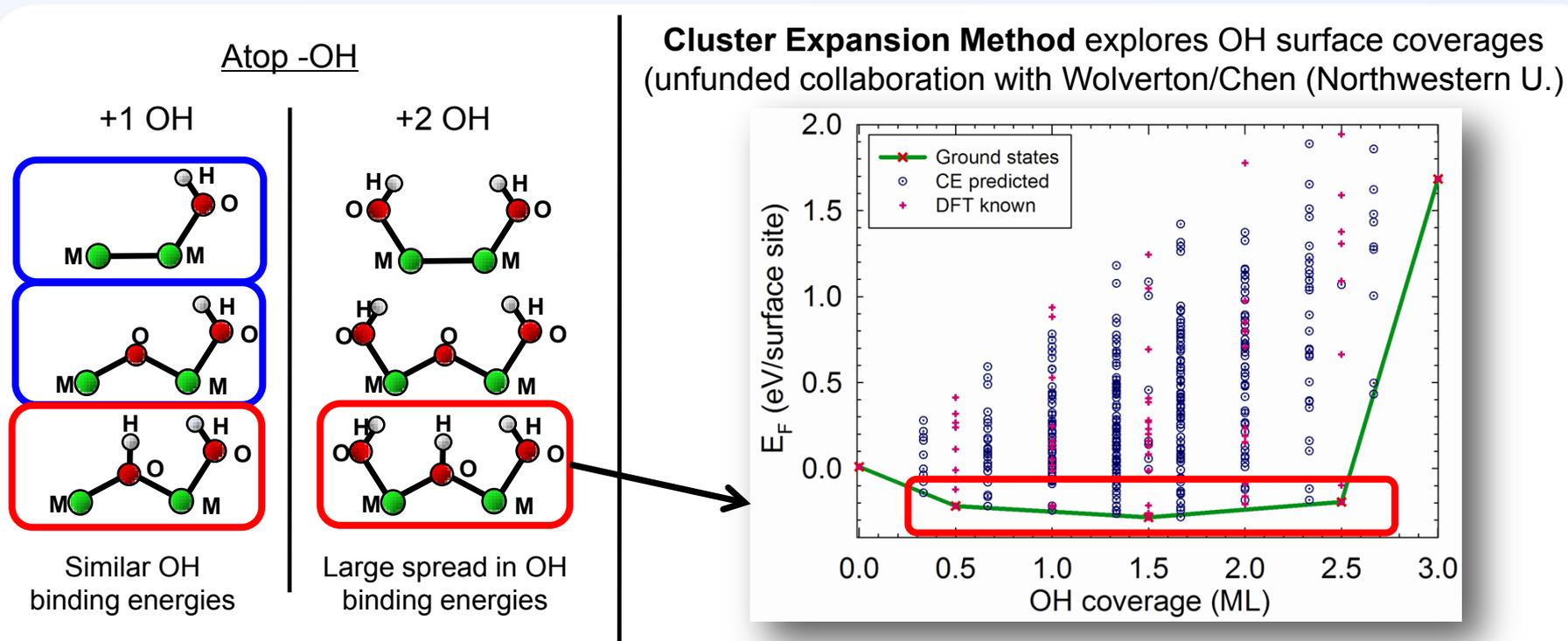
Oxygen



Hydroxyl



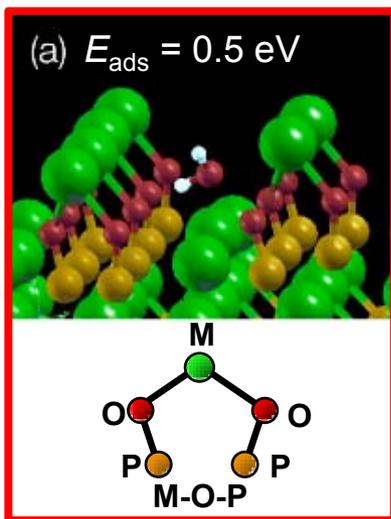
Technical accomplishment: Surface structure



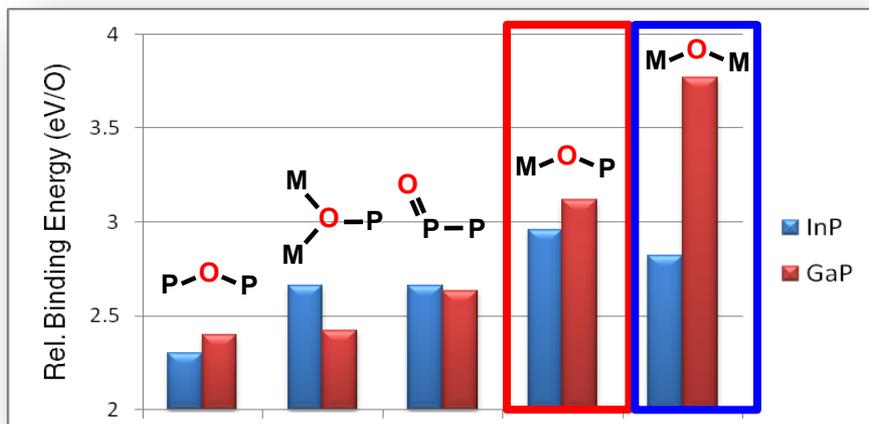
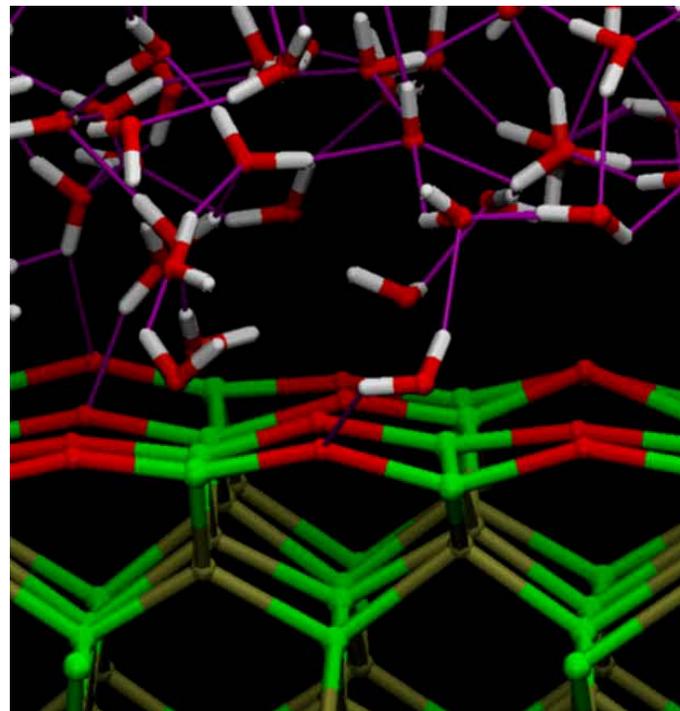
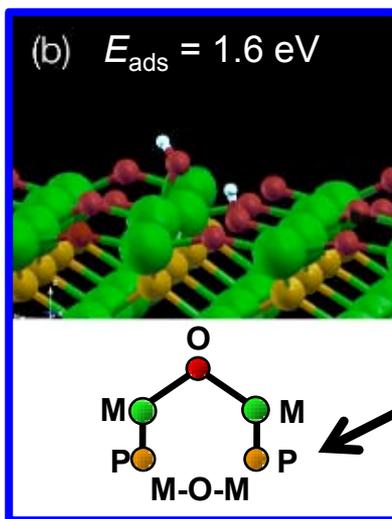
- OH binding shows strong site correlation in presence of surface dimer or oxygen
 - Binding energy of first atop OH is independent of host topology but second is not
- Cluster expansion of atop OH shows surface energy has little coverage dependence
 - System is not governed by octet rule

Technical accomplishment: Electronic structure

Inert (M-O-P)



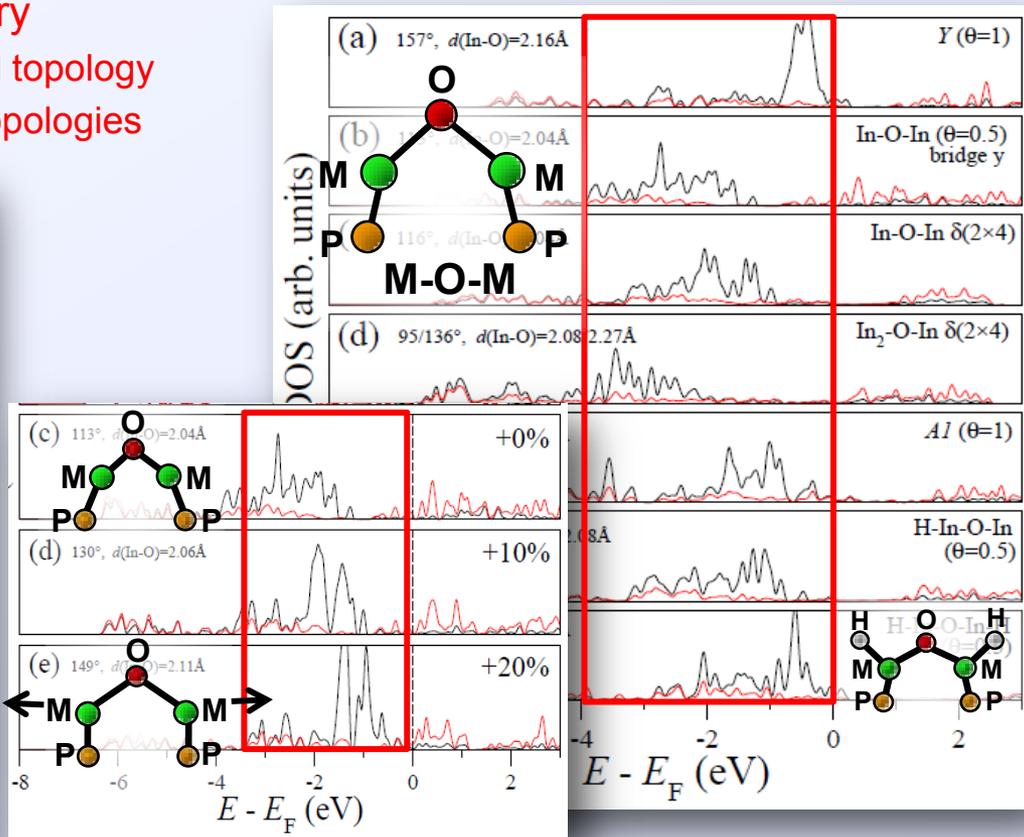
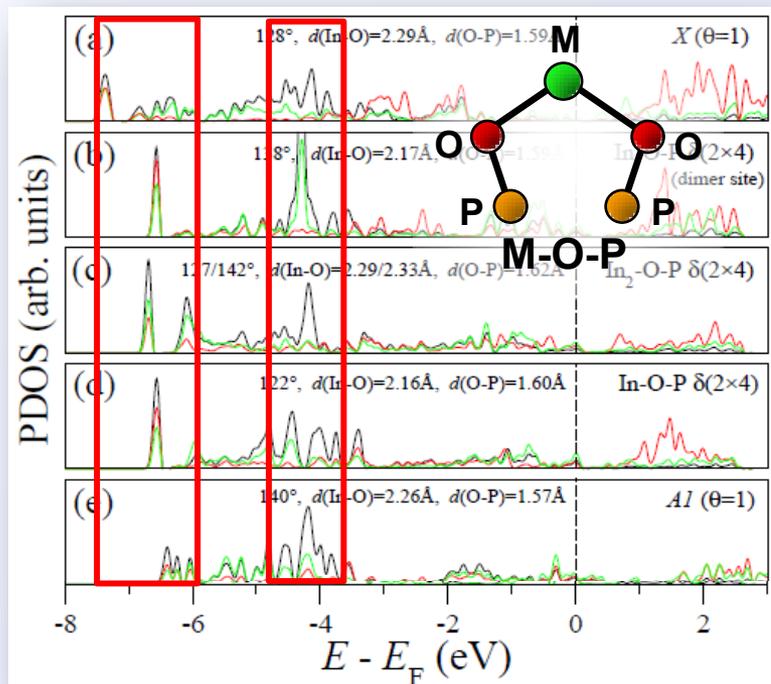
Reactive (M-O-M)



- Certain oxygen topologies are more reactive
 - Dynamics show dissociative adsorption of water on M-O-M

Technical accomplishment: Electronic structure

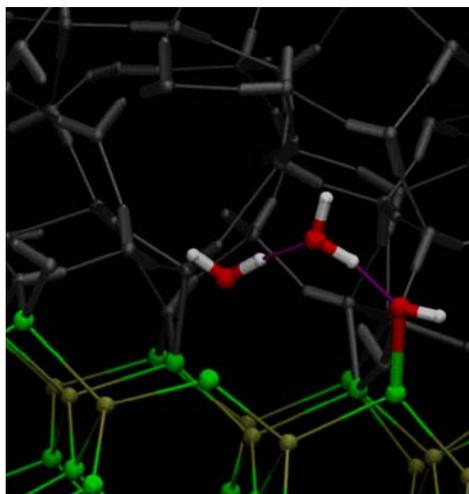
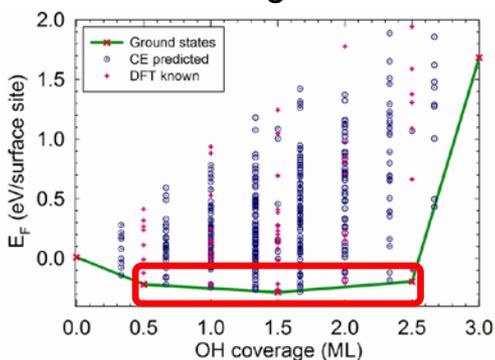
- Different topologies have different sensitivity to chemical environment
 - Valence structure of M-O-P is static, but M-O-M depends strongly on local environment
- M-O-M valence character modulated chemically or by induced strain
- Local models capture surface chemistry
 - Do not need exact structure, only bond topology
 - Can run dynamics on representative topologies



Technical accomplishment: Practical implications

Flat free energy profile for OH-decorated surface:

- ✓ Can shuttle protons to reaction sites via H-bond bridges



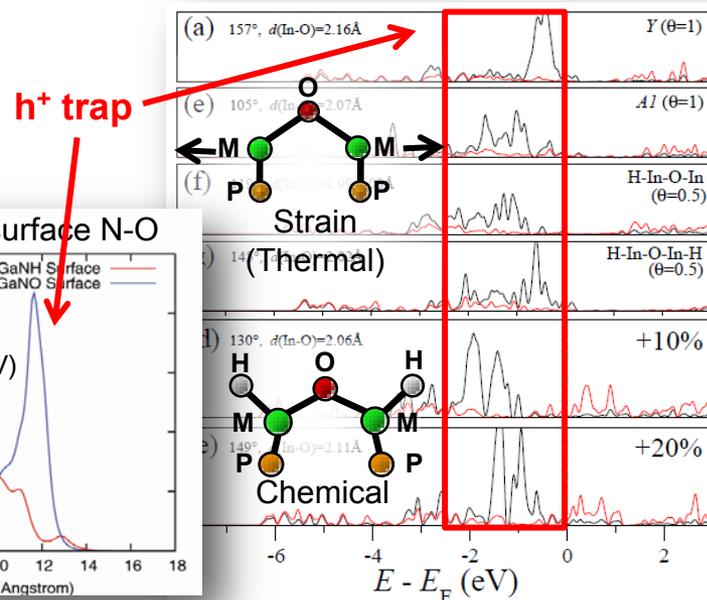
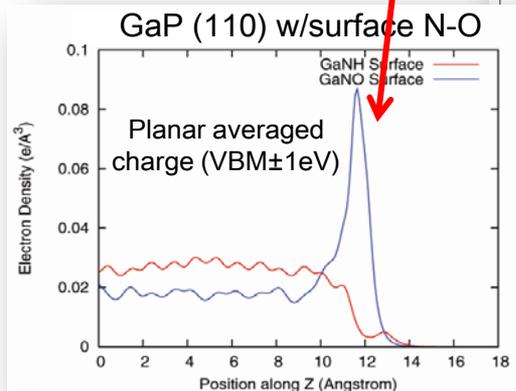
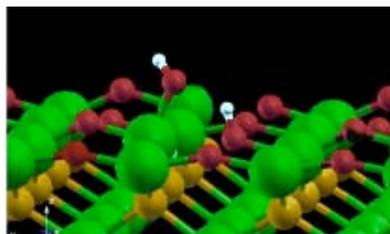
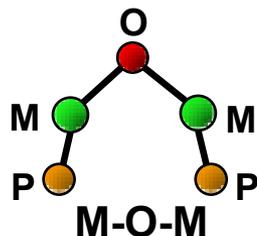
Carrier mobility affected by surface structure

- ✓ Hole trap can be induced mechanically (strain) or chemically (edge bonding)

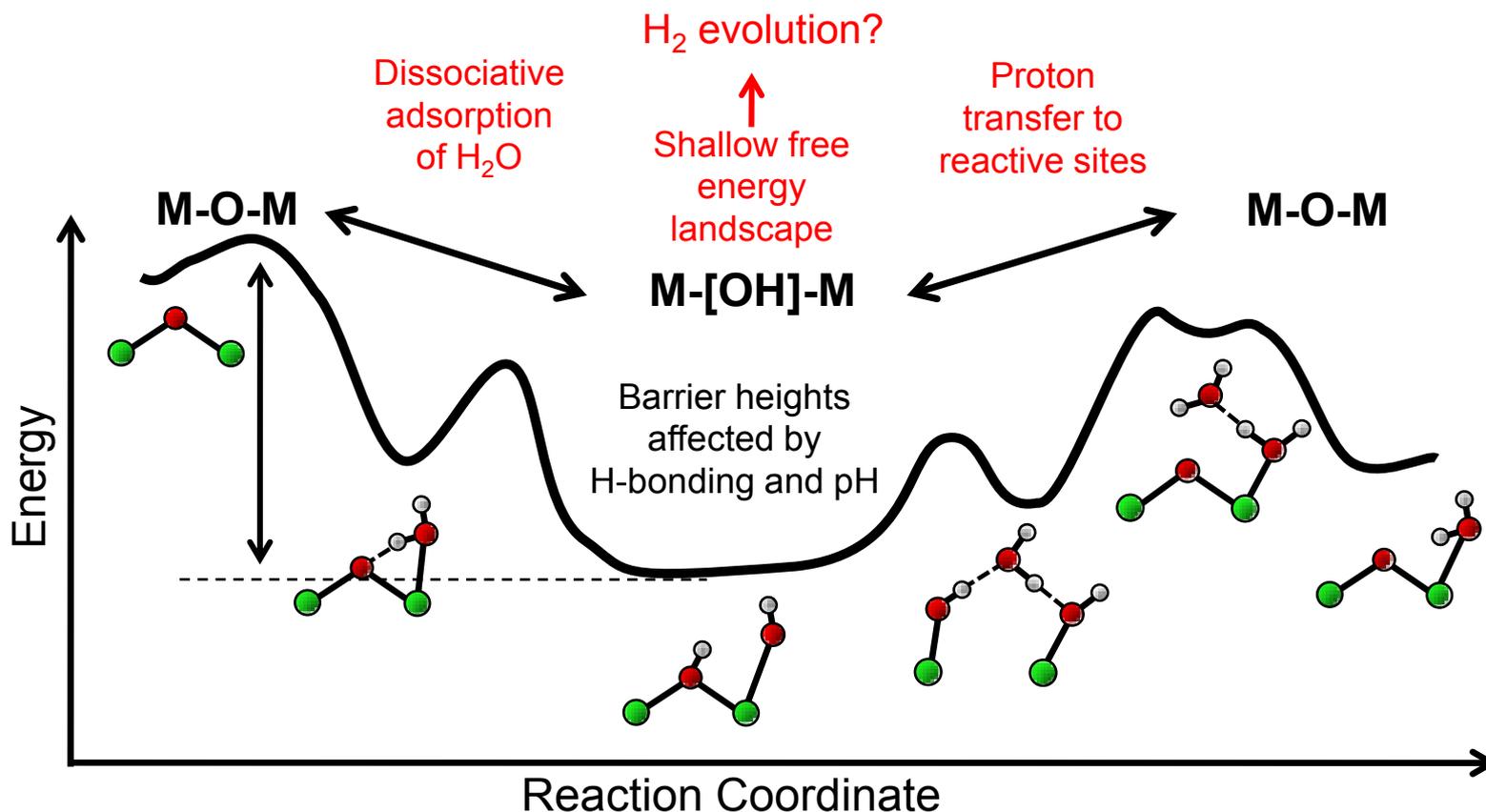
Thermal motion can change electronic structure of M-O-M to branch additional reaction pathways

Oxygen needed for H₂O splitting

- ✓ Connection to known oxide catalysts?



Technical accomplishment: Proposed reaction mechanism



J. Nørskøv: Good catalytic activity and low barrier heights correlate with small energy differences between products, intermediates, and reactants



U.S. DEPARTMENT OF
ENERGY

UNLV
UNIVERSITY OF NEVADA LAS VEGAS

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

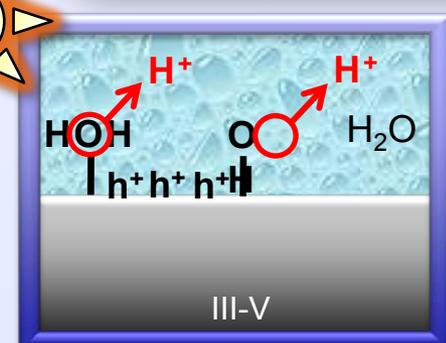
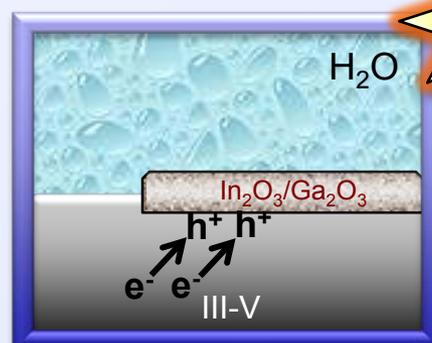
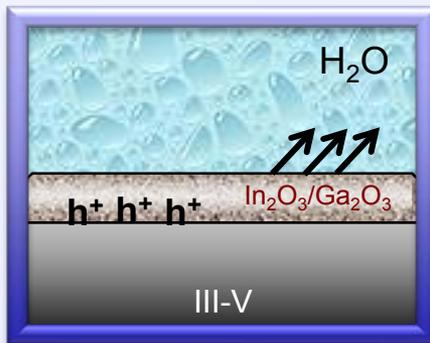
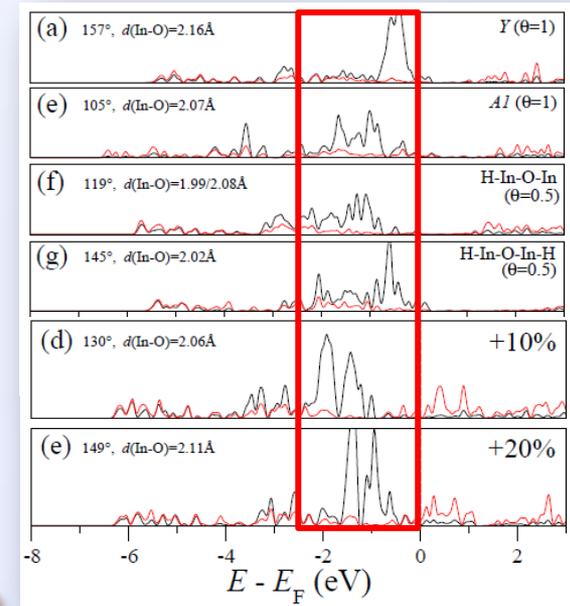
DOE Hydrogen Program Annual Merit Review



Technical accomplishment: Corrosion scenario #1

Hole trapping corrosion scenario

- Holes trapped at III-V/surface-oxide or surface-oxide/water interface
 - Trap associated with M-O-M, so more likely on $\text{In}_2\text{O}_3/\text{Ga}_2\text{O}_3$ than $\text{InPO}_4/\text{GaPO}_4$
 - Emerges upon edge binding or activation of surface modes
- Creates recombination centers
- Poor carrier mobility
- Can peel off surface oxide upon excitation
- Can release protons into solution to relax charge buildup
- Commonality with known water-splitting oxides

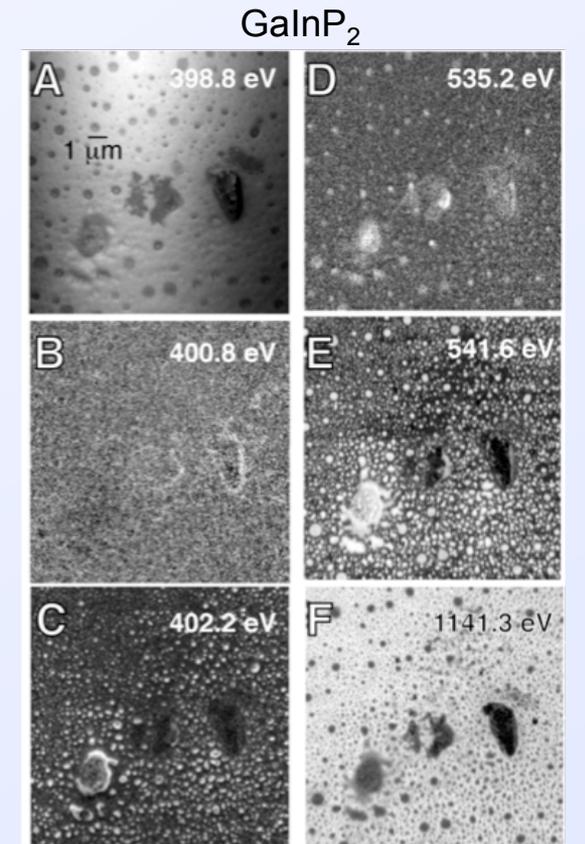
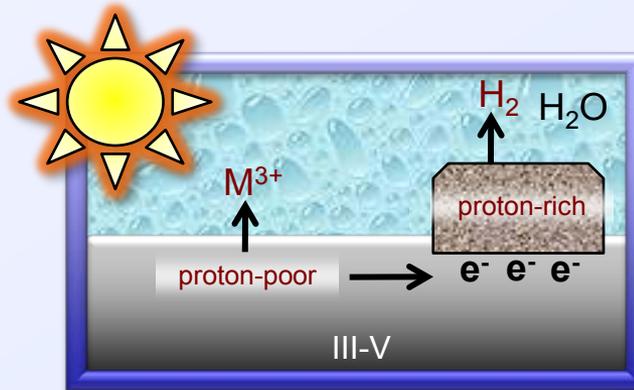


Technical accomplishment: Corrosion scenario #2

Local anode corrosion scenario

- Pitting implies non-uniform composition
 - Oxygen- or hydroxyl-rich region formed at defects or phase boundaries
 - Ordered/disordered phase boundary (e.g., GaInP₂)
 - Impurities
 - Rough surface features
 - Poor oxide interface
- Oxygen-rich region can act as **anode** even under cathodic conditions, creating **short-circuit current** flow
 - Intrinsic *n*-type doping in In₂O₃
 - Contributions from hole accumulation

- **Loss of cathodic protection**

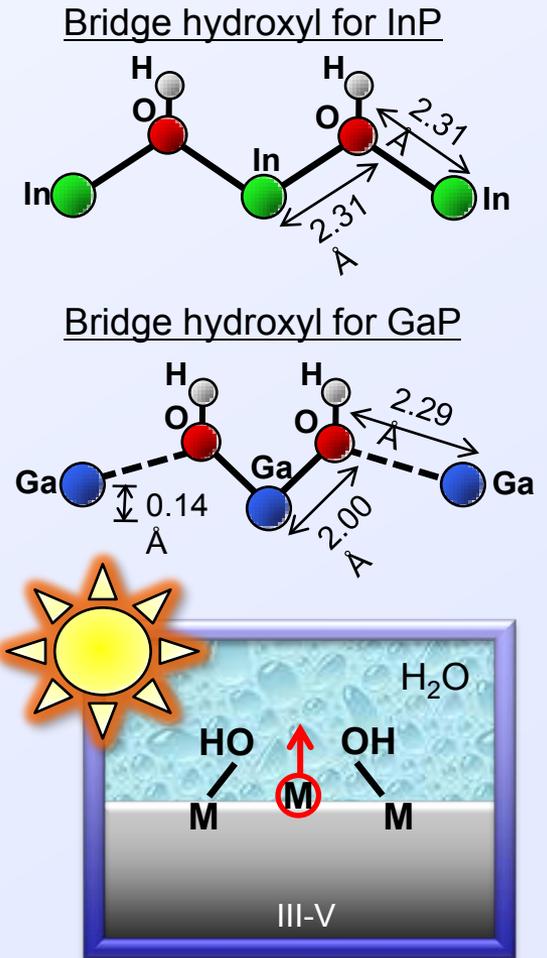
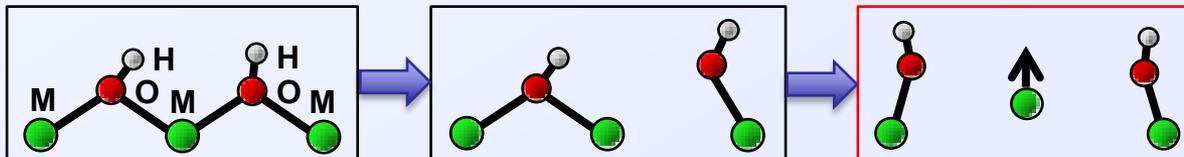
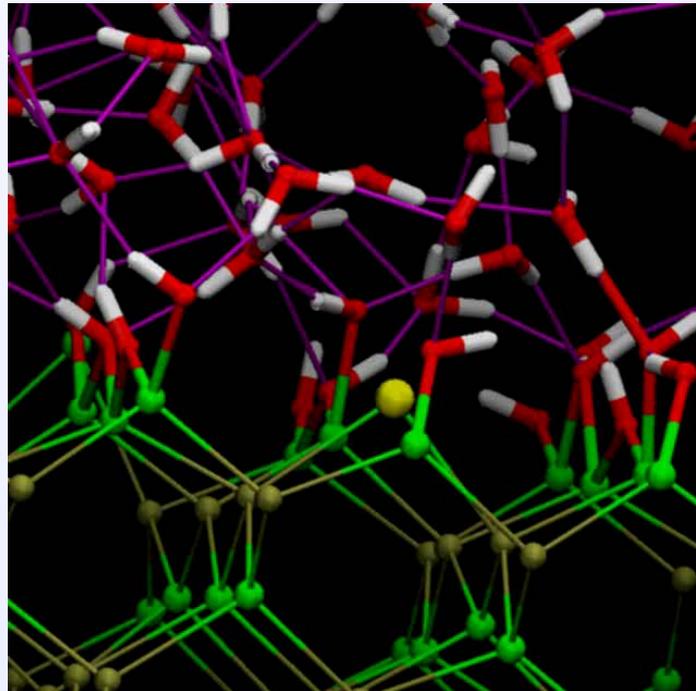


Turner, Deutsch, Wang, Schiros (NREL)

Technical accomplishment: Corrosion scenario #3

Surface metal dissolution corrosion scenario

- Undercoordinated metal atoms dissolve into solution
 - Observed in MD simulations
- Arises from competition between adsorbate binding to new metal site or edges of a M-OH-M bridge



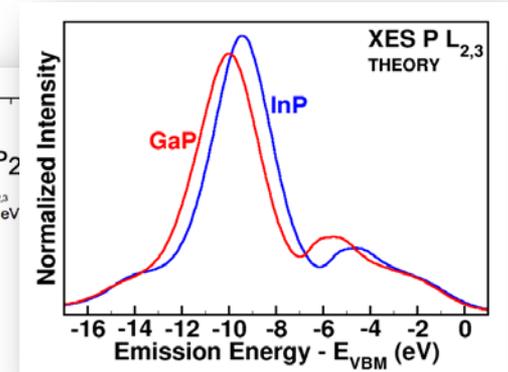
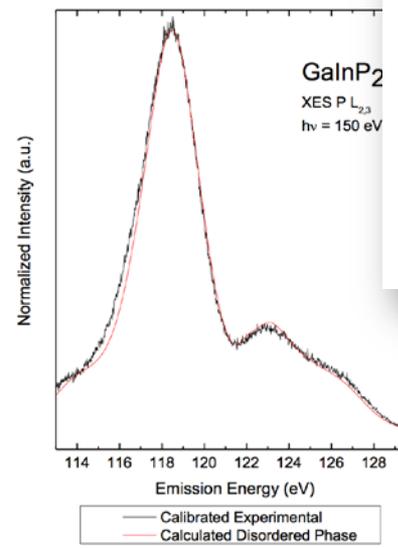
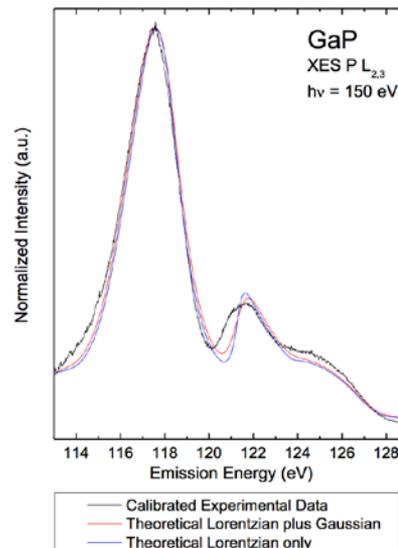
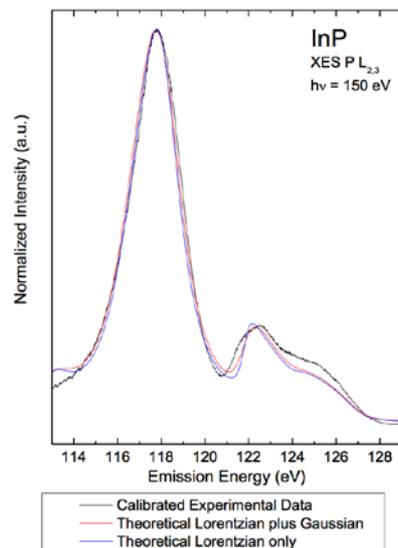
Technical accomplishment: X-ray spectroscopy

- **Theory/experiment collaboration**
 - *Construct model surfaces based on local topologies for comparison of simulated and calculated X-ray spectra*
 - *Permits confirmation of relevant surface states and corrosion pathways*
- **Experiment side:**
 - *Samples provided by T. Deutsch (NREL)*
 - *Detailed characterization performed by C. Heske and K. George (UNLV) using ALS (LBNL)*
 - *Supplemental measurements performed by H. Wang and T. Deutsch (NREL)*
- **Theory side:**
 - *Computation and analysis performed by T. Ogitsu (LLNL)*
 - *Development and support for theoretical ab-initio X-ray absorption/emission spectrum code via Molecular Foundry User Project with D. Prendergast (LBNL)*

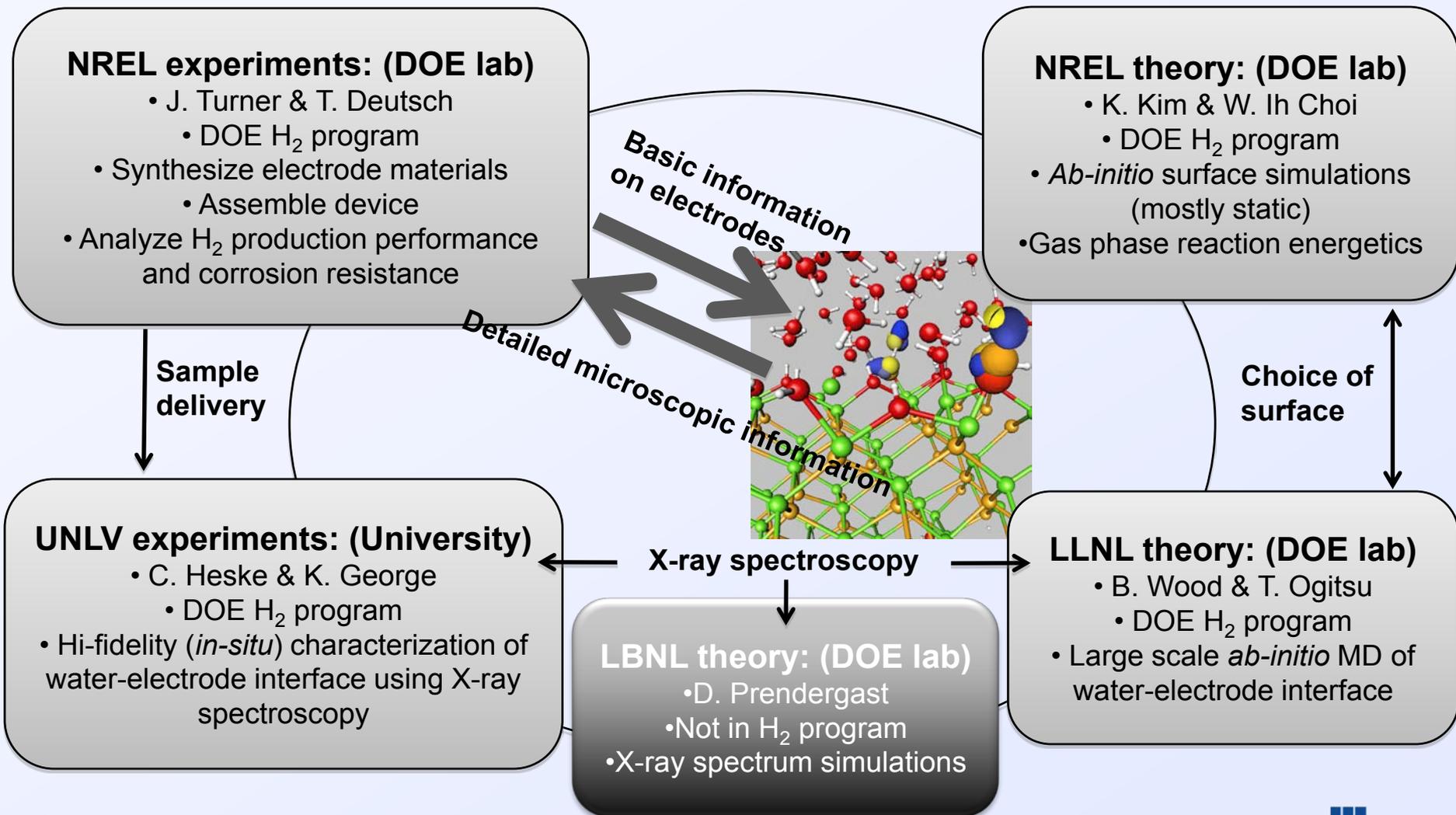


Technical accomplishment: Simulated XES

- Established calculation procedure for P-L_{2,3} edge XES of GaP, InP, GaInP₂
- Experimental and theoretical spectra show excellent agreement
- Characteristics of GaP and InP are experimentally distinguishable
- Theoretical site-dependent spectra can aid experimental interpretation



Collaborations: Theory-experiment feedback cycle



Proposed future work

Milestone	Description	% Completed
1	Modeling of clean, O-decorated, and OH-decorated III-V surfaces and electrode-electrolyte interfaces	90
2	Examine energetics of nitrogen incorporation	70
3	Investigate precursor states for surface photocorrosion processes	80
4	Study mechanisms of dissociative adsorption of water as a first step in photo-induced hydrogen evolution	60
5	Deliver simulated spectra of model surfaces to experimental III-V characterization team at UNLV	30
6	Modeling of surfaces under bias	0
7	Analyze chemical effect of nitrogen surface treatment	0
8	Extend surface and interface simulations to include GaInP ₂ and In/Ga-based oxides	0

Focus on strengthening feedback cycle with experimental collaborators (UNLV & NREL) to provide specific suggestions for device improvement



Summary

- Compiled, reviewed, and shared available information on III-V electrode materials (ongoing)
- Performed quantum molecular dynamics of water-electrode interfaces
 - Evaluated importance of surface oxygen
 - Identified connection between surface structure and reactivity
 - Established validity of local topological model and used it to extract model surfaces for further study
- Group discussion of results led to formulation of three possible corrosion mechanisms
- Began joint theoretical/experimental study on III-V electrode surface (continue through FY11)
 - Calculated X-ray spectra of InP, GaP, and GaInP₂ agree extremely well with experiments

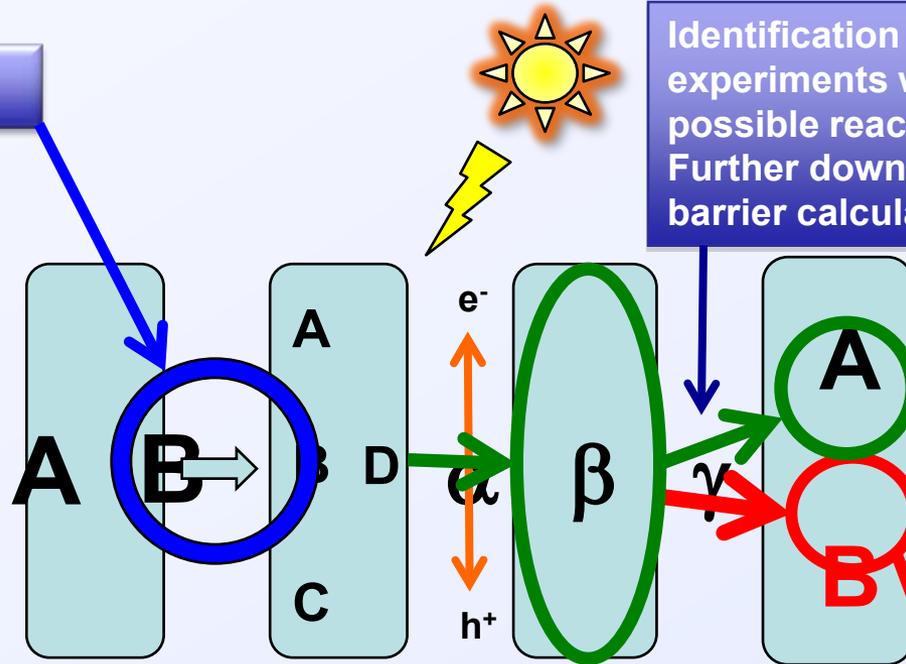


Supplemental materials

Supplementary slide: Combined experimental-theoretical approach to corrosion/hydrogen evolution

Ab-initio method

Identification of intermediates by experiments will constrain the possible reaction pathways
Further down selection by energy barrier calculations



Reactants	Reactants'	Intermediates	Products:
A: InP	A: InP	α : ?	A: H ₂
B: H ₂ O	B: H ₂ O	β : ?	B: In, InO
	C: In-O	γ : ?	
	D: In-OH		

Corrosion!

The intermediates will be characterized by combination of XAS/XES/XPS & *ab-initio* method



U.S. DEPARTMENT OF
ENERGY

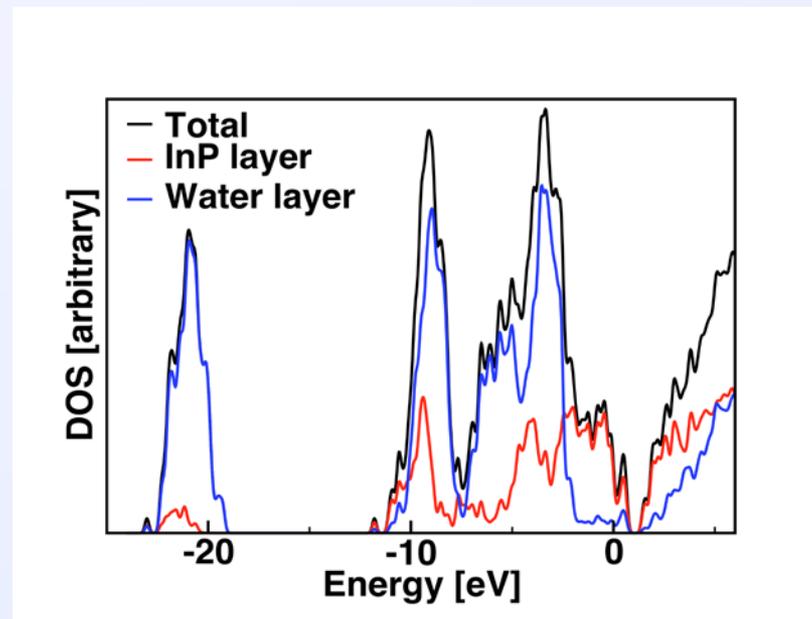
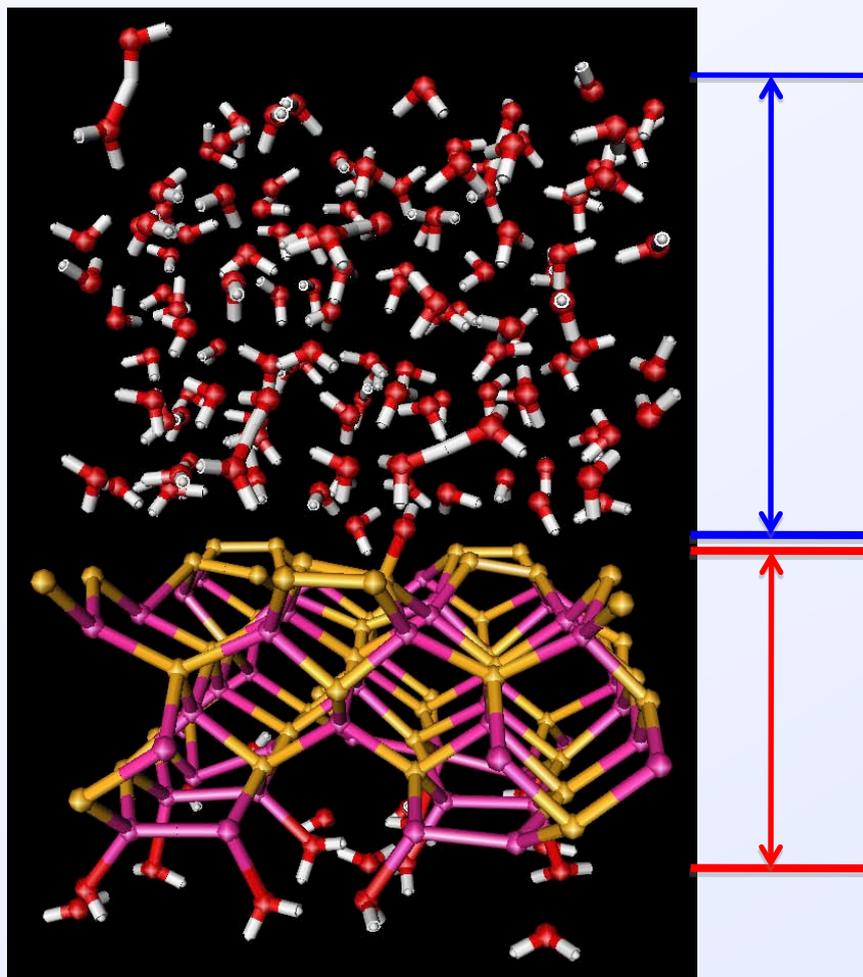
UNLV
UNIVERSITY OF NEVADA LAS VEGAS

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

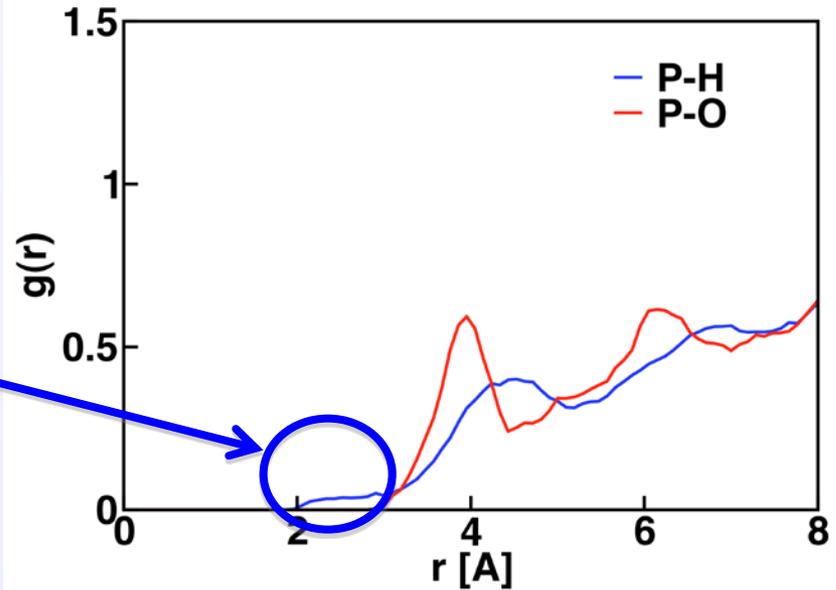
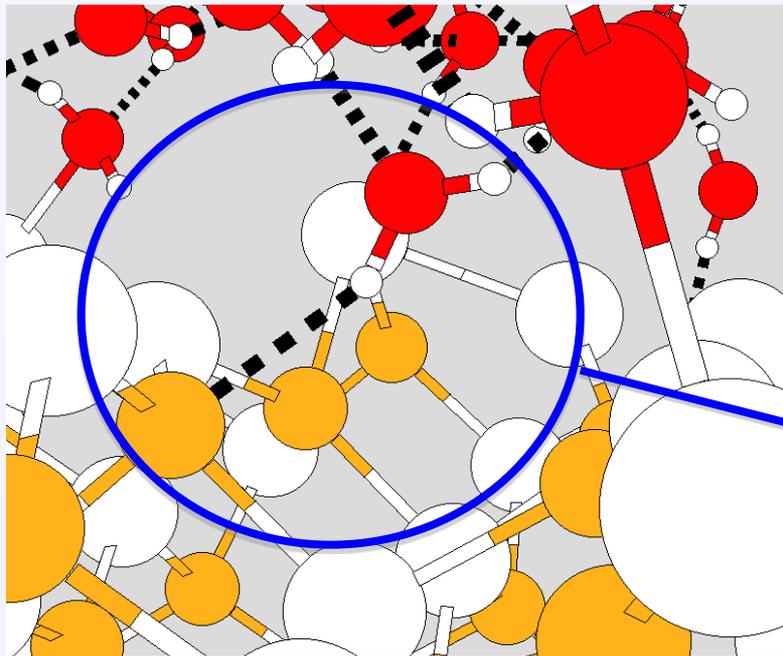
DOE Hydrogen Program Annual Merit Review



Supplementary slide: Interfacial electronic structure

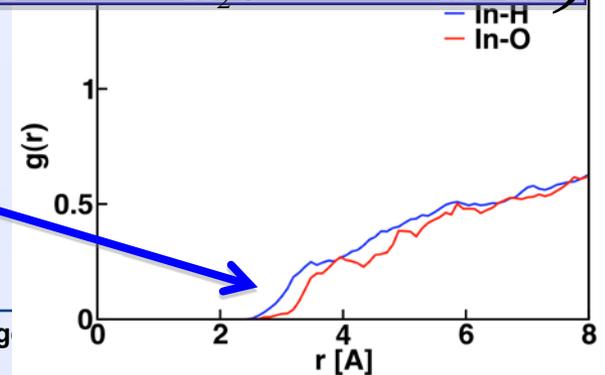


Supplementary slide: Importance of dynamical approach



Size (O vs H) and dynamics $\left(v_{P-P}^{vib} \geq v_{H_2O}^{rot} \geq v_{In-In}^{vib} \right)$

Subsurface indium attracts H₂O (oxygen) less



U.S. DEPARTMENT OF ENERGY

UNLV
UNIVERSITY OF NEVADA LAS VEGAS

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

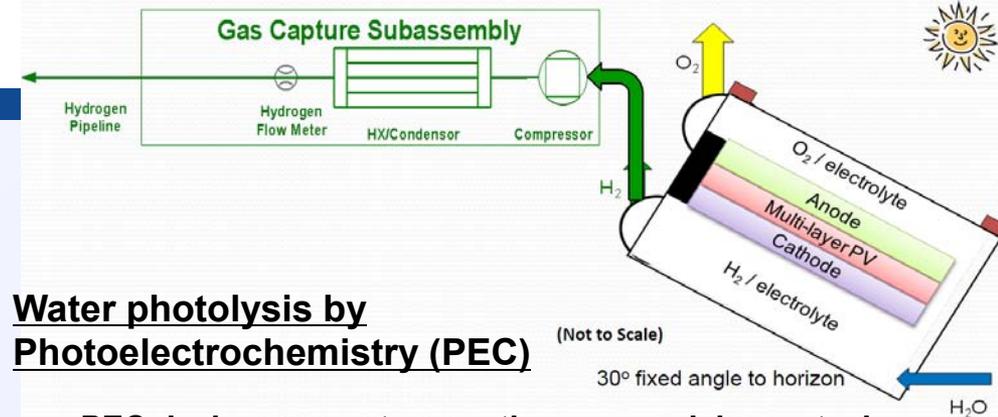
DOE Hydrog

Supplementary slide: PV-electrolysis vs. PEC H₂ Production



Photovoltaic coupled to water electrolyzer

- Water electrolyzers^[1] and PVs^[2] are commercial devices, hence an initial techno-economic analysis was constructed by coupling known costs for each.
- Cost of electrolytic H₂ is dominated by electricity.^[1]
- For a 1000 kg H₂ / day facility, ~53 MWhr/day are needed. In a sunny climate, an 11 MW PV installation provides this, on average, over a year.
- 4.5 ¢/kWh electricity yields a cost of \$4.09/kg H₂.^[1]
- Electricity from large-scale industrial PV (500+ kW) costs 16.6 ¢/kWh in a sunny climate (Nevada).^[2]
- Five times as many electrolyzers are needed if PVs are used instead of coal, as electrolyzers must be sized to fit peak electricity production (11 MW).
- This yields estimated total costs of \$17.49/kg H₂.
- A cloudy climate yields approx. 2X cost \$35/kg H₂.



Water photolysis by Photoelectrochemistry (PEC)

- PEC devices are not currently commercial, so a techno-economic analysis was conducted to estimate \$ / kg H₂.^[3]
- Four different reactor types were evaluated, along with the balance of plant required to produce 1000 kg H₂ / day.
 - Type 1: single compartment colloidal suspension.
 - Type 2: dual compartment colloidal suspension.
 - Type 3: planar PEC array (pictured above).
 - Type 4: planar PEC array with ~ 10X concentration.
- For each reactor type, hypothetical material performances were estimated based on the current state and the trajectory of PEC materials research: e.g. 10 % efficiency, 10 year lifetime, \$153/m² cost.
- The baseline assumptions yielded sunny climate estimated costs of: \$1.63/kg H₂ (Type 1), \$3.19/kg H₂ (Type 2), \$10.36/kg H₂ (Type 3), and \$4.05/kg H₂ (Type 4).

Conclusion: H₂ production by PV-electrolysis is currently less expensive than PEC, however PEC can potentially reach DOE cost targets of \$9-\$15/kg H₂ sooner with the development of improved materials.

1. "Electrolysis: Information and Opportunities for Electric Power Utilities", DOE-NREL Technical Report, NREL/TP-581-40605, Sep 2006.
2. www.solarbuzz.com (February 18, 2011)

3. B.D. James, G.N. Baum, J. Perez, K.N. Baum, "Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production", DOE Report (2009) Contract # GS-10F-009J.



U.S. DEPARTMENT OF
ENERGY

UNLV
UNIVERSITY OF NEVADA LAS VEGAS

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

