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

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Presenter: Brandon C. Wood & Tadashi Ogitsu
Lawrence Livermore National Laboratory
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Project ID# PD058

Work performed under the auspices of the U.S. Dept. of Energy by LLNL under Contract DE-AC52-07NA27344.

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:

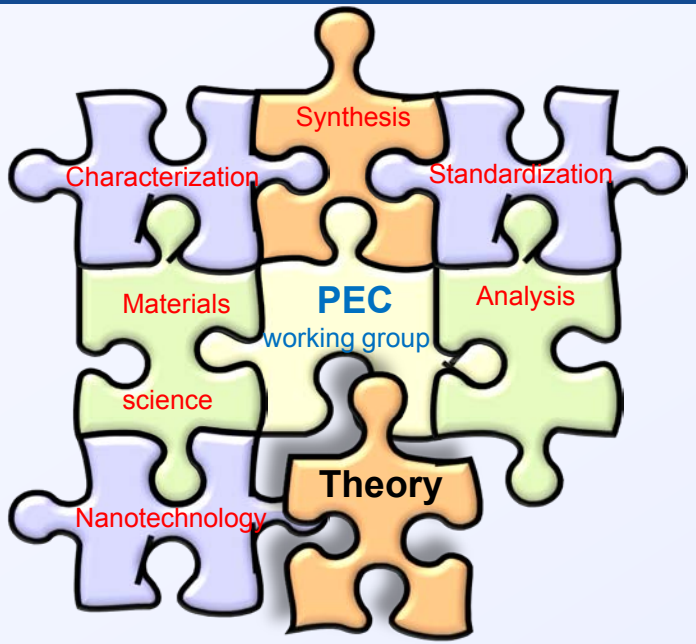
Deutsch/Wang/Turner/Kim (NREL)
Heske (UNLV)

- Unfunded partners:

Prendergast (LBNL)
Otani (AIST Japan)

Project lead: T. Ogitsu, LLNL

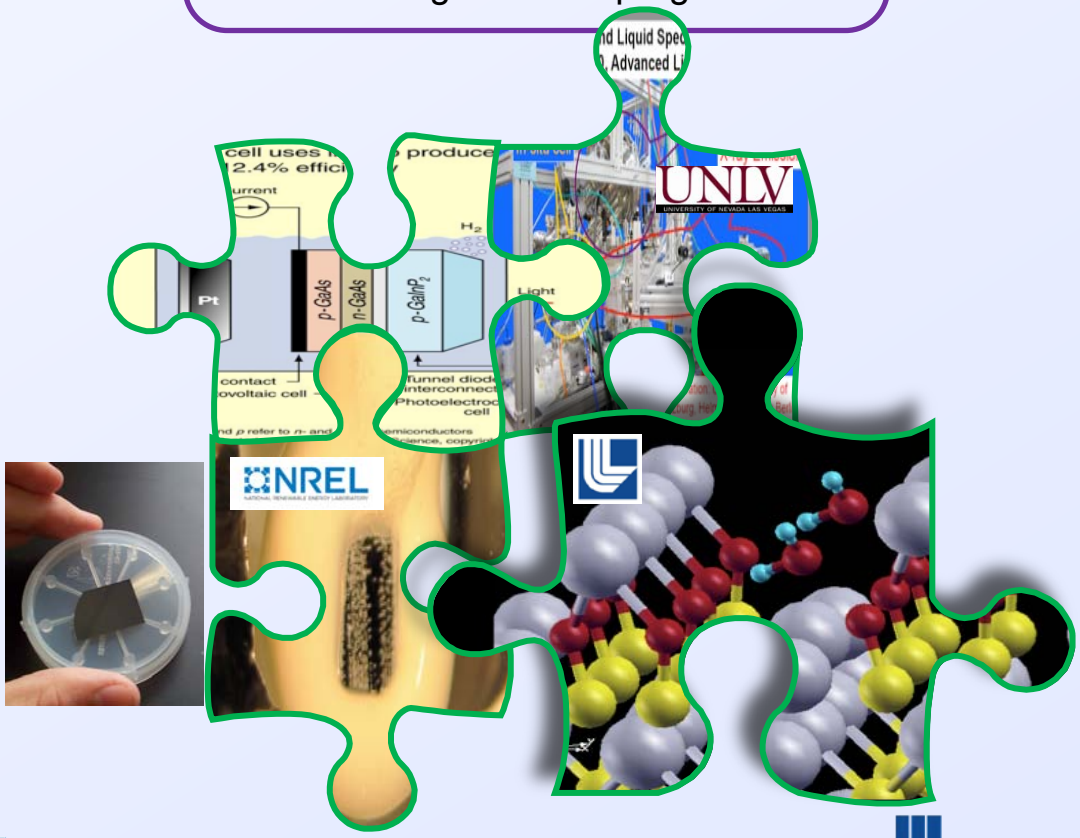
III-V Surface Validation Team



Theory and simulation

PEC Working Group:

Evaluating working directions
Sharing and building-up knowledge
Accelerating research progress



III-V Surface Validation

DOE Targets:
>1000h @STH > 8% (2013)
$2 - 4/kg H_2 projected PEC cost
(beating >$10/kg H_2 for PV-electrolysis)

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 H_2 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)*

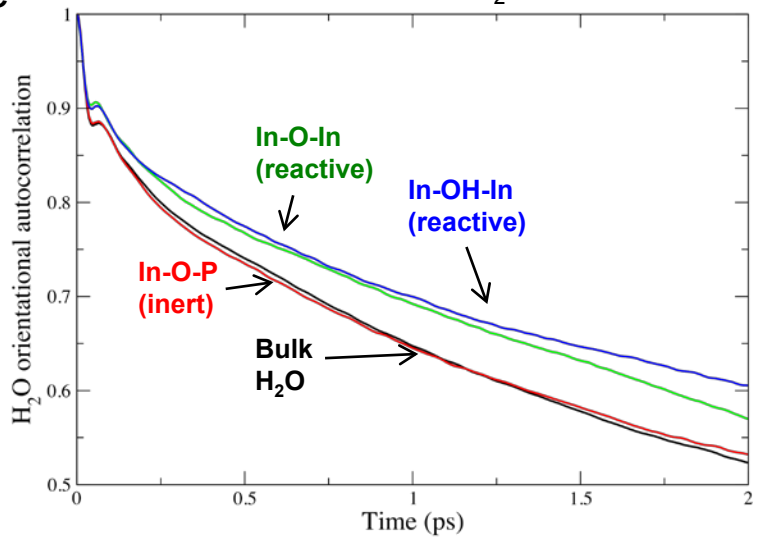
Milestones and Deliverables

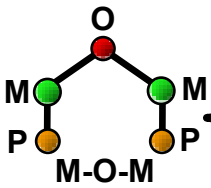
Milestone	Description	% Completed
1	Modeling of clean, O-decorated, and OH-decorated III-V surfaces and electrode-electrolyte interfaces	90
2	Implementation of tools for modeling of surfaces under bias	100
3	Examine energetics of nitrogen incorporation	70
4	Investigate precursor states for surface photocorrosion 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

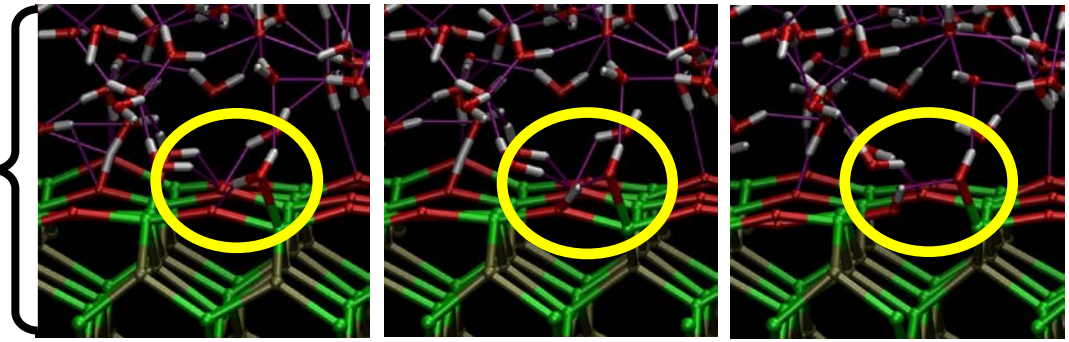
Review: Structure and reactivity of InP(001)-H_2O interface

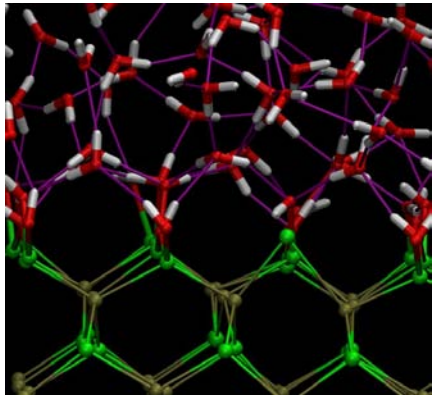
- *Ab-initio* investigation of InP(001) surface & interface
  - Clean surface is chemically inert
- Experiment + theory show importance of surface oxygen/hydroxyl
  - Oxygen topology connected to reactivity
- Dynamics: dissociative adsorption of H_2O on In-O-In
- Hydrogen bonding is important for surface structure
  - Unusually strong water-water bonding at reactive interface
  - Facilitates hydrogen diffusion along surface and first adsorption layer

Time autocorrelation of H_2O orientation









Water structure: InP(001) w/OH

Overview of new technical accomplishments

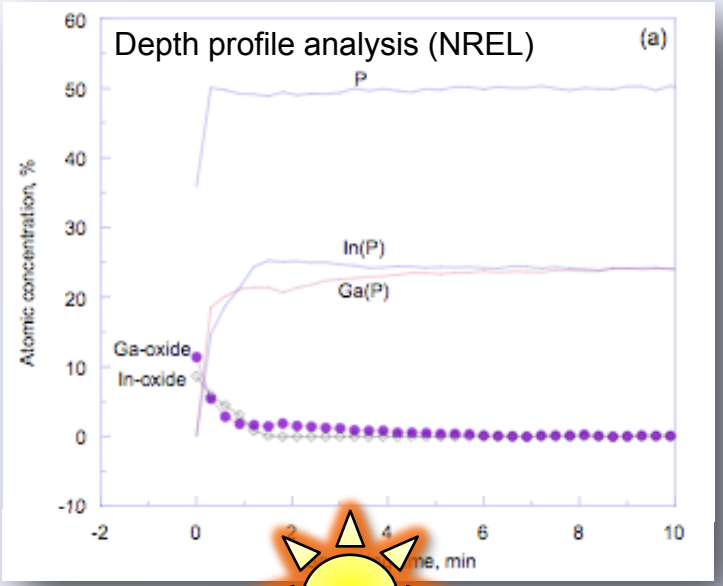
Project has met all target milestones

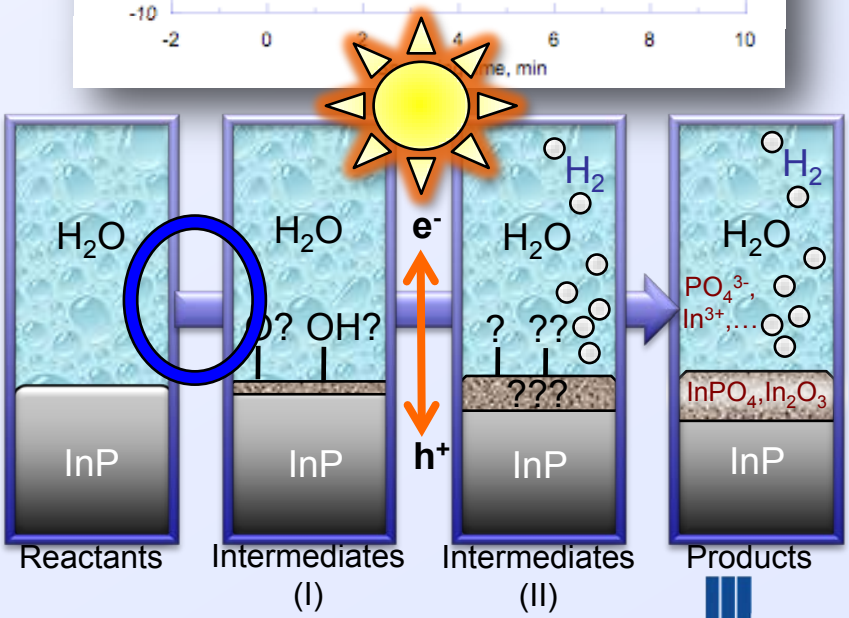
- Performed literature search to understand science of III-V oxides (idea of oxygen relevance dates to 1980s)
- Theory + characterization: oxygen is relevant
- Shifted focus to understanding **precursor oxygen-rich states** of GaP, InP, and $GaInP_2$

LLNL Theory Team focus:

1. *Structure of surface and bulk oxides*
2. *Relationship of surface structure to electronic structure of oxide surfaces*
3. *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)

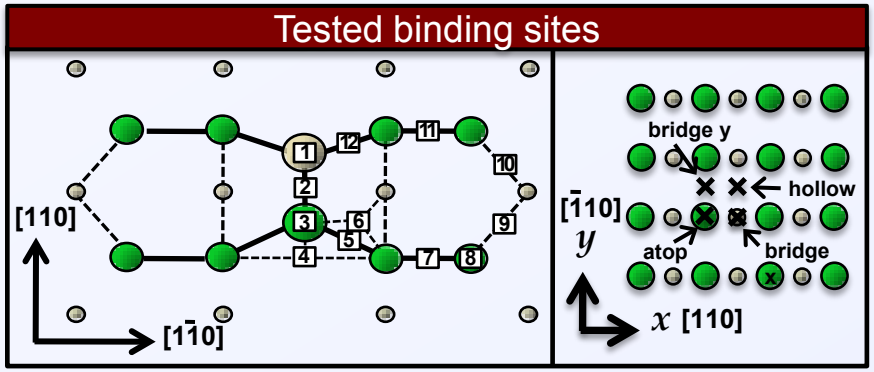




Technical Accomplishment: Database of PEC Research (in progress)

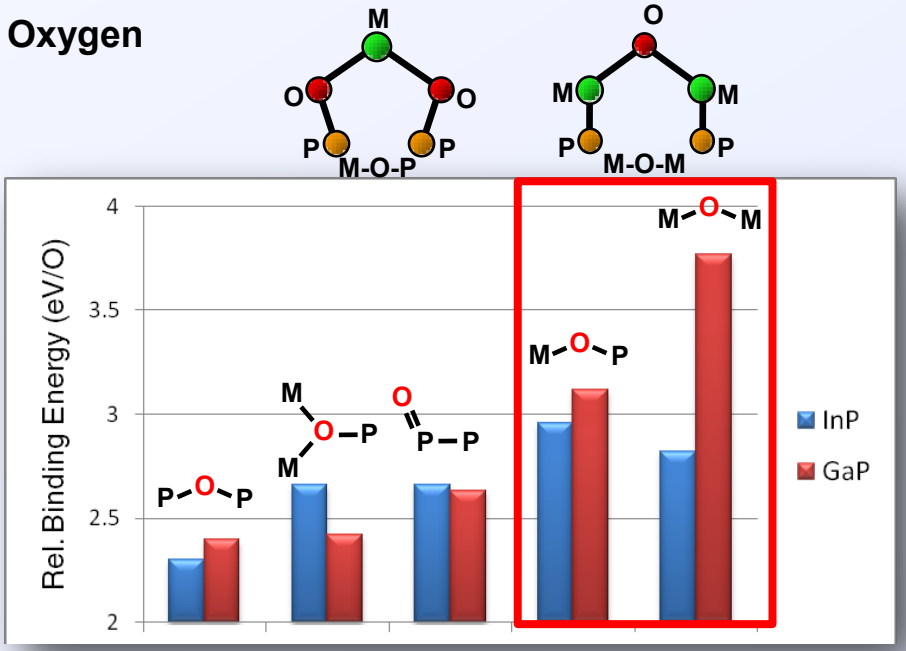
- Approximately 700 papers (1960-present) have been collected, indexed, and stored as of March 2011
- Information on relevant papers is shared among WG members using online collaboration tools
- Completed detailed review on surface and interfacial properties of $GaInP_2$ (89 papers total), shared with 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

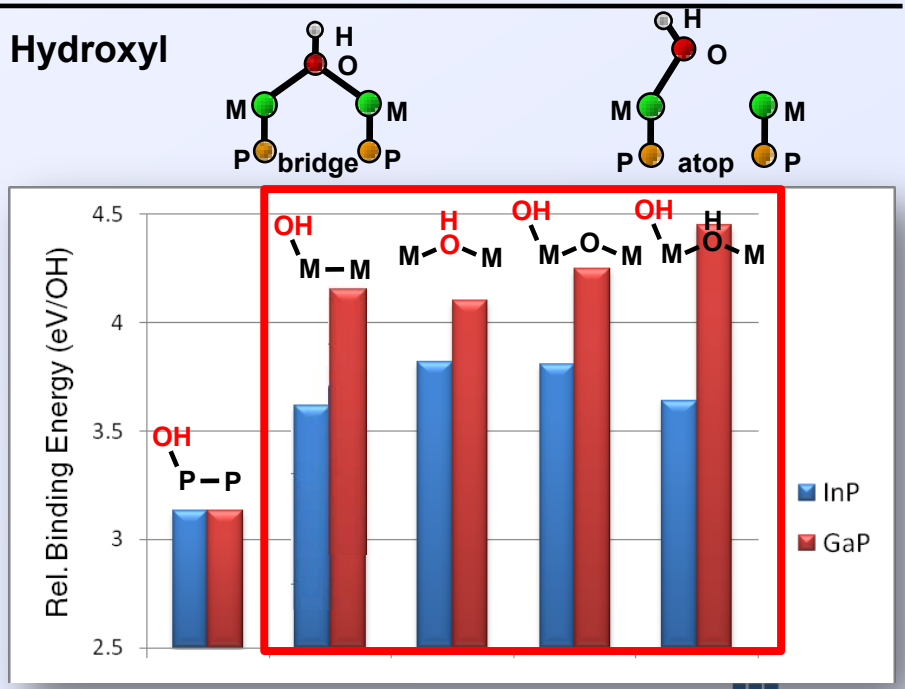


- Wide study of oxygen binding on GaP, InP
- Identified common local structural motifs
  - Oxide: M-O-P, M-O-M, P=O
  - Hydroxide: M-[OH]-M, P-OH, M-OH
- Features resemble motifs in bulk oxides
  - Connects local oxygen binding to bulk oxide nucleation

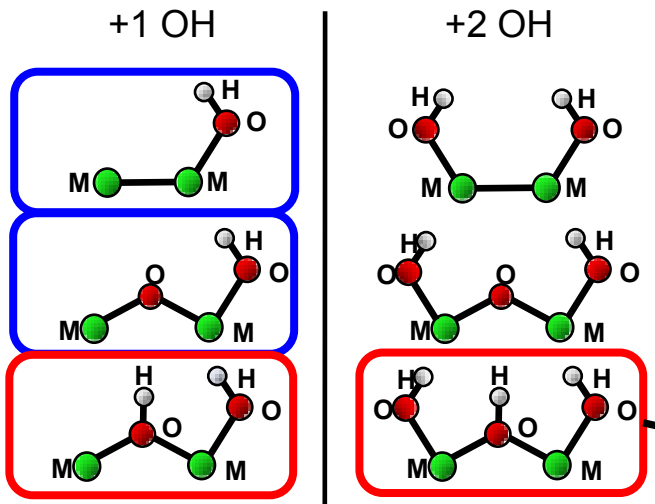
Oxygen



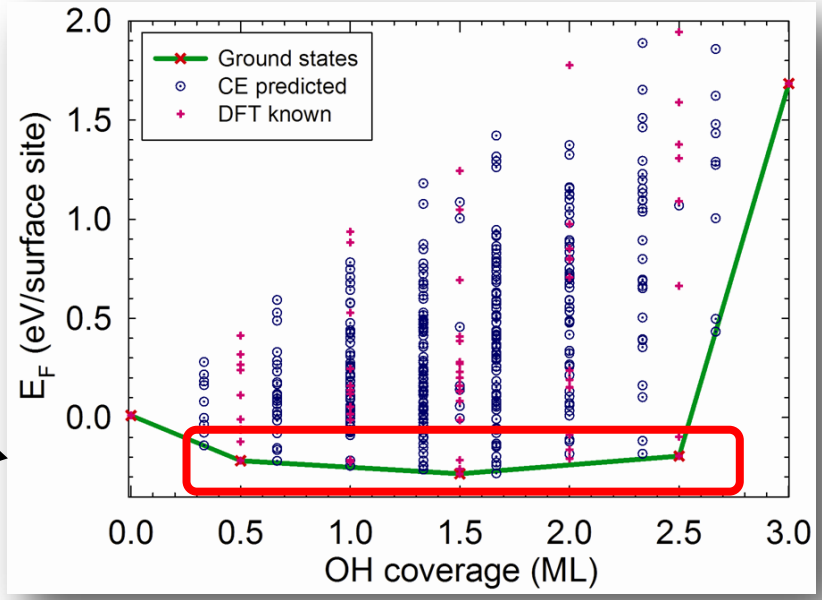
Hydroxyl



Technical accomplishment: Surface structure



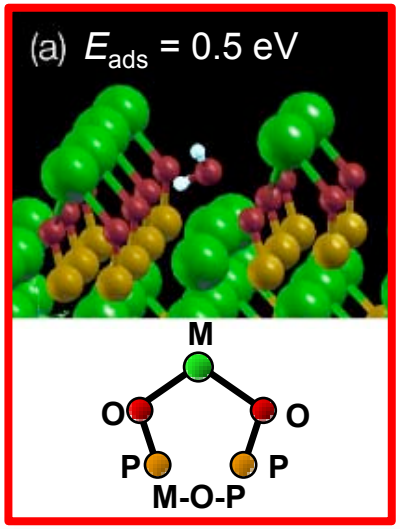
Cluster Expansion Method explores OH surface coverages (unfunded collaboration with Wolverton/Chen (Northwestern U.)



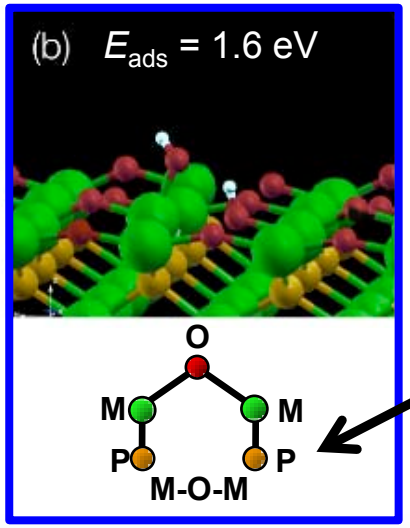
- OH binding shows strong site correlation in presence of surface dimer or oxygen
  - Binding energy of first atop OH is independent of host topology but second is not
- Cluster expansion of atop OH shows surface energy has little coverage dependence
  - System is not governed by octet rule

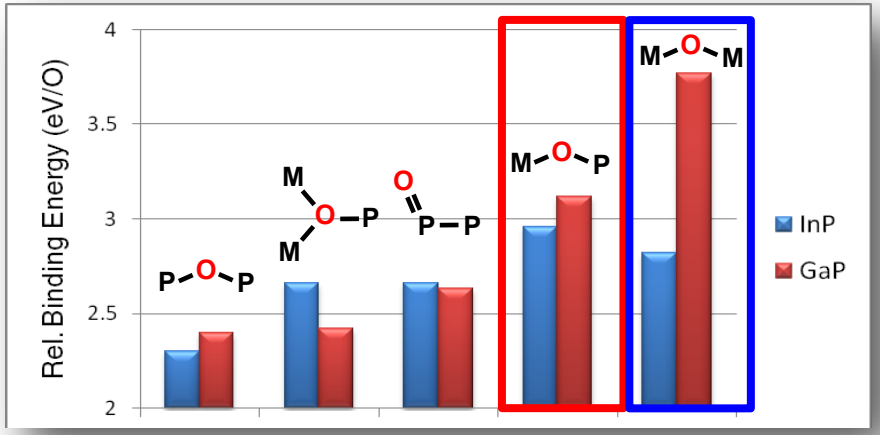
Technical accomplishment: Electronic structure

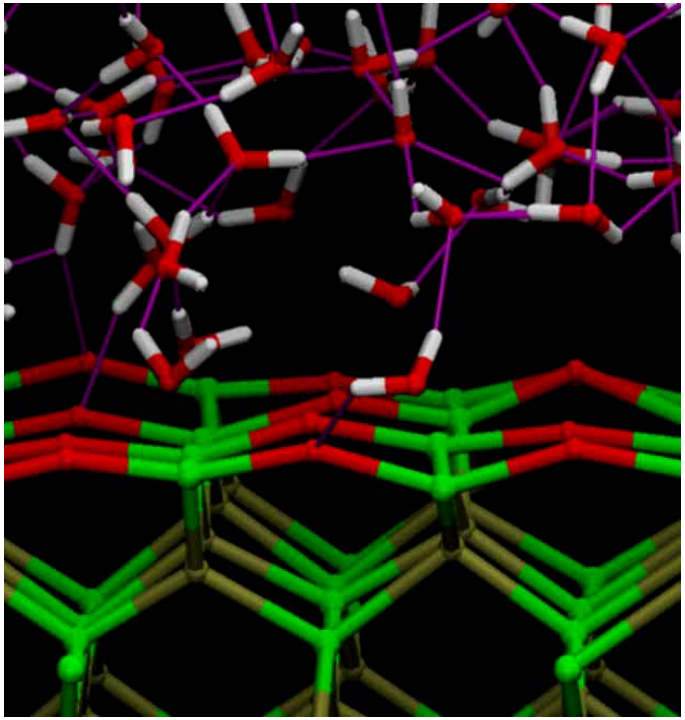
Inert (M-O-P)



Reactive (M-O-M)



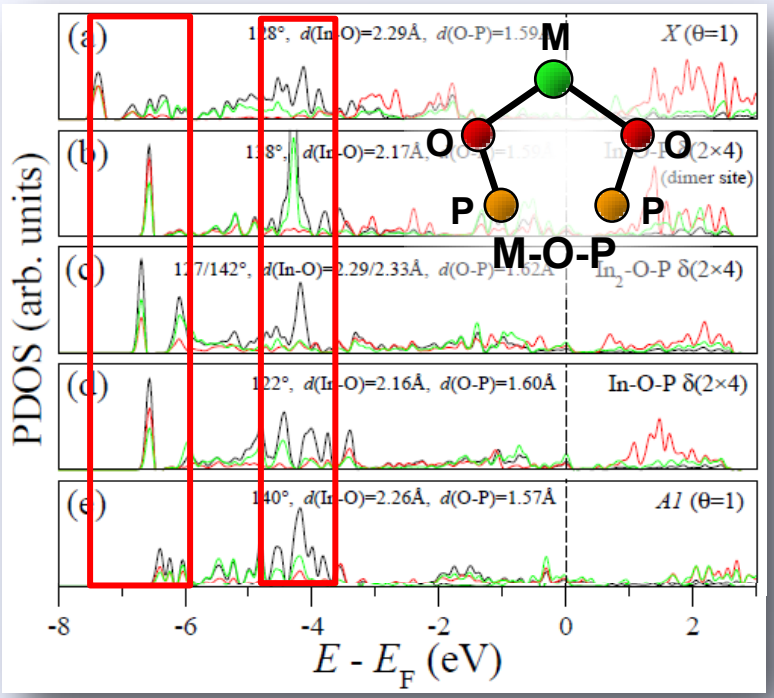


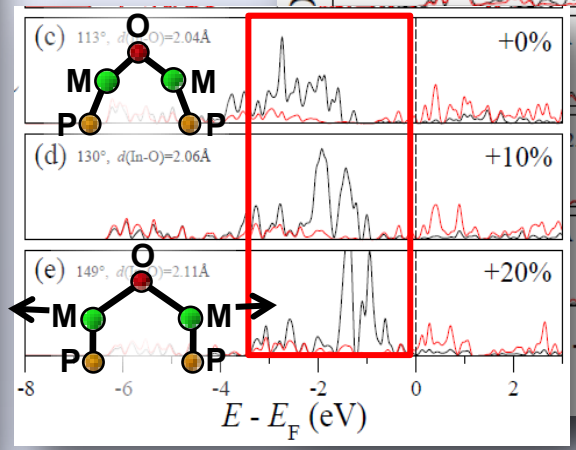


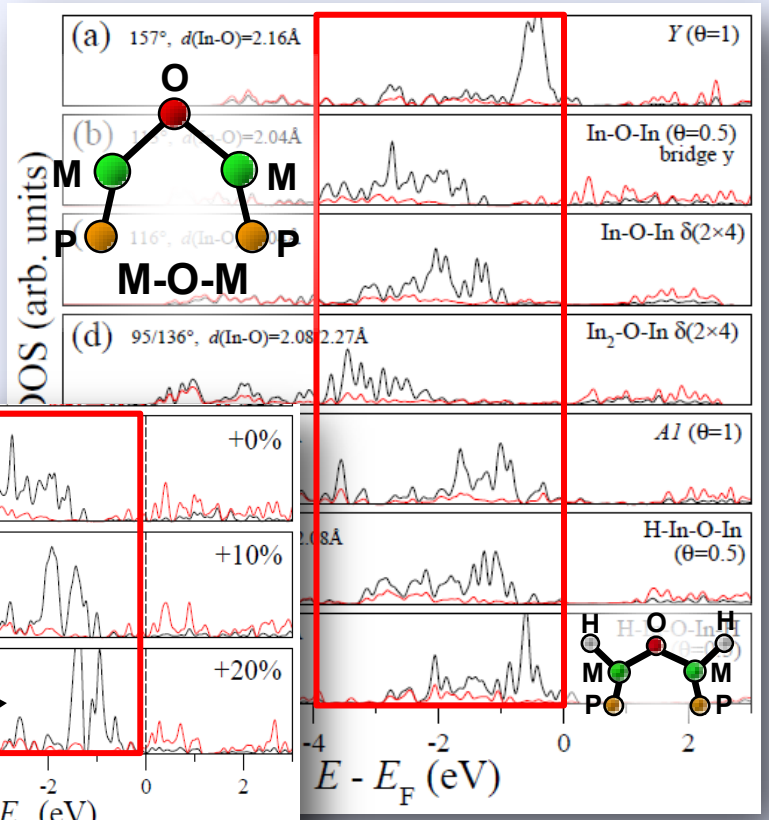
- Certain oxygen topologies are more reactive
  - Dynamics show dissociative adsorption of water on M-O-M

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



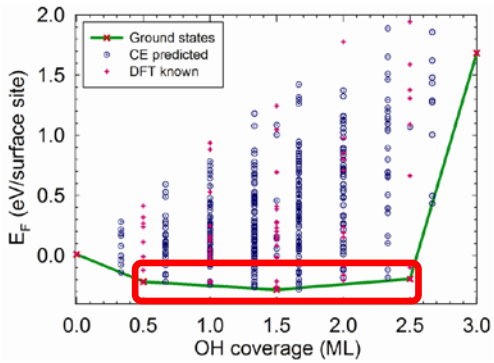


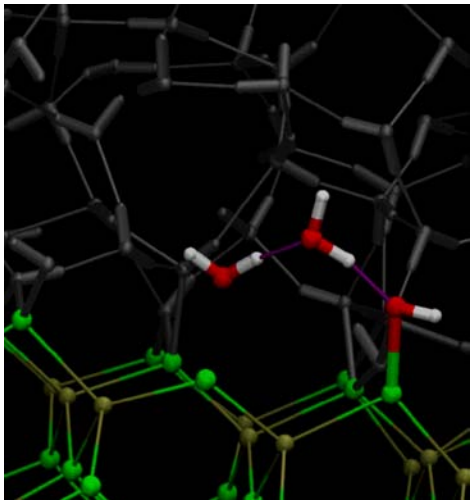


Technical accomplishment: Practical implications

Flat free energy profile for OH-decorated surface:

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

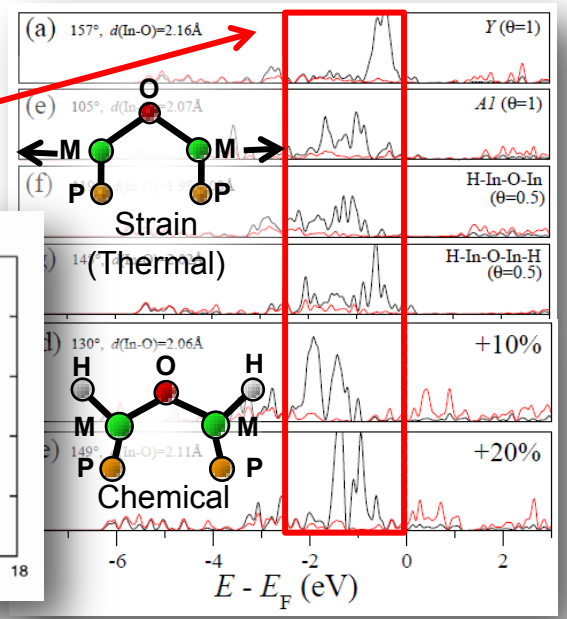




Carrier mobility affected by surface structure

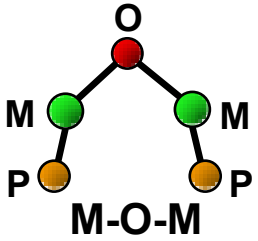
- ✓ Hole trap can be induced mechanically (strain) or chemically (edge bonding)

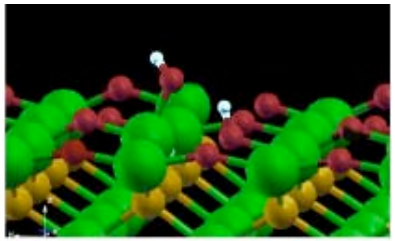
Thermal motion can change electronic structure of M-O-M to branch additional reaction pathways

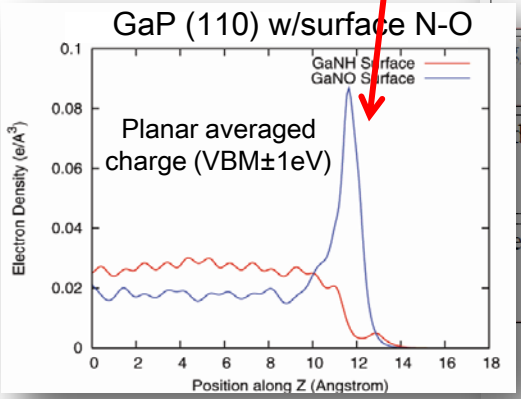


Oxygen needed for H_2O splitting

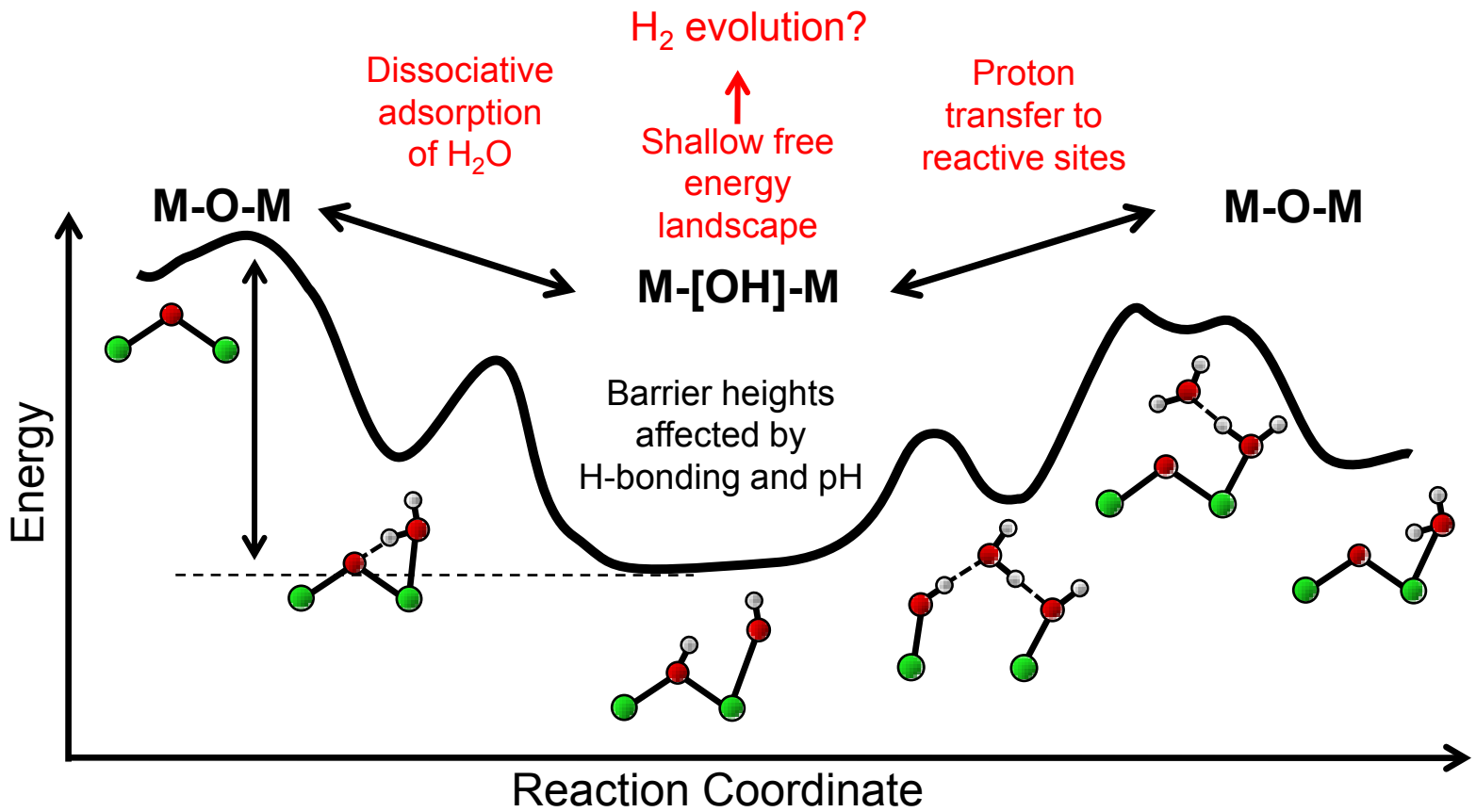
- ✓ Connection to known oxide catalysts?







Technical accomplishment: Proposed reaction mechanism

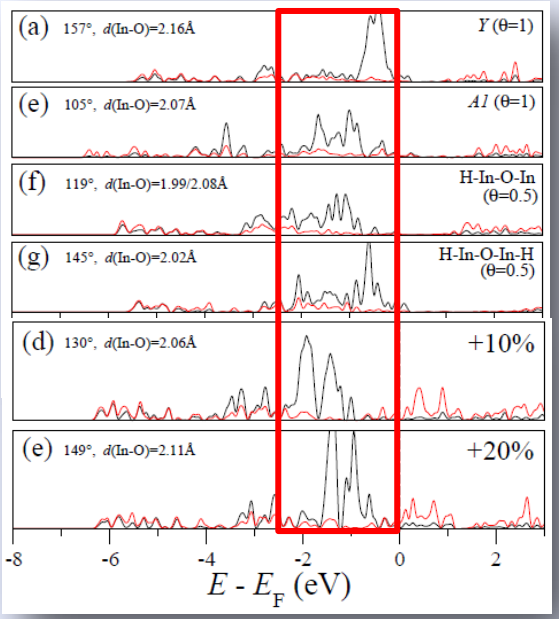


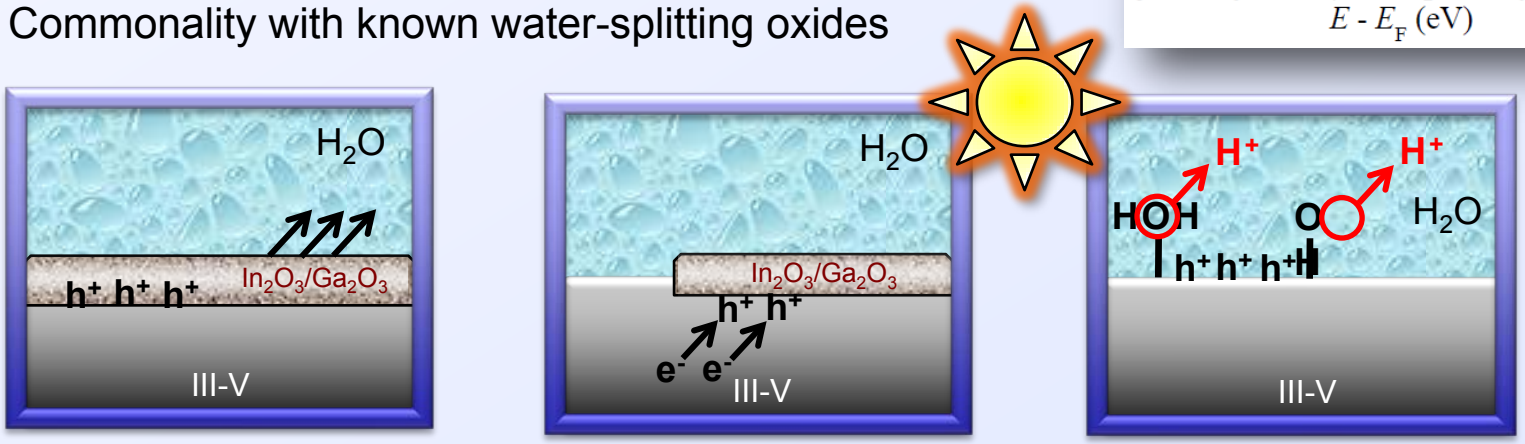
J. Nørskøv: Good catalytic activity and low barrier heights correlate with small energy differences between products, intermediates, and reactants

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 In_2O_3/Ga_2O_3 than $InPO_4/GaPO_4$
  - 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

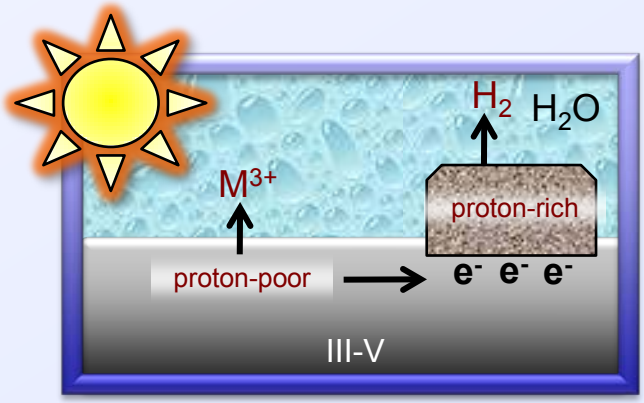




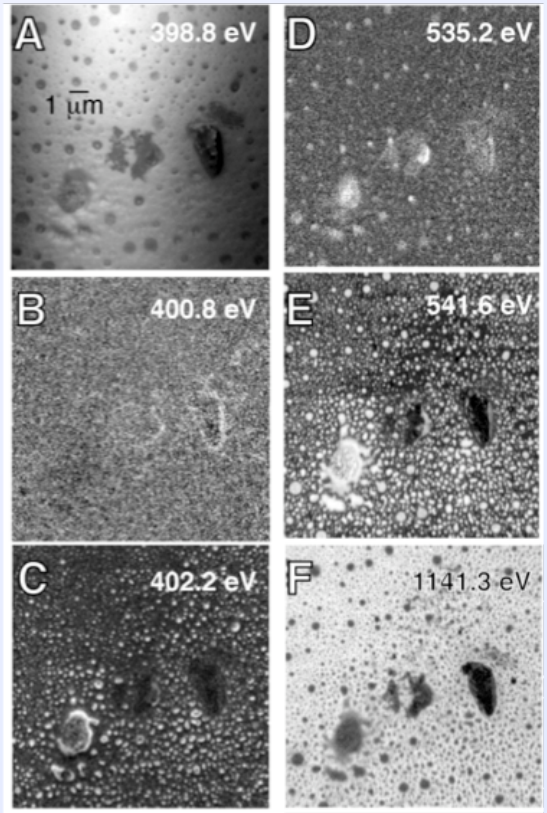
Technical accomplishment: Corrosion scenario #2

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., $GaInP_2$)
    - 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 In_2O_3
  - Contributions from hole accumulation
- **Loss of cathodic protection**



$GaInP_2$

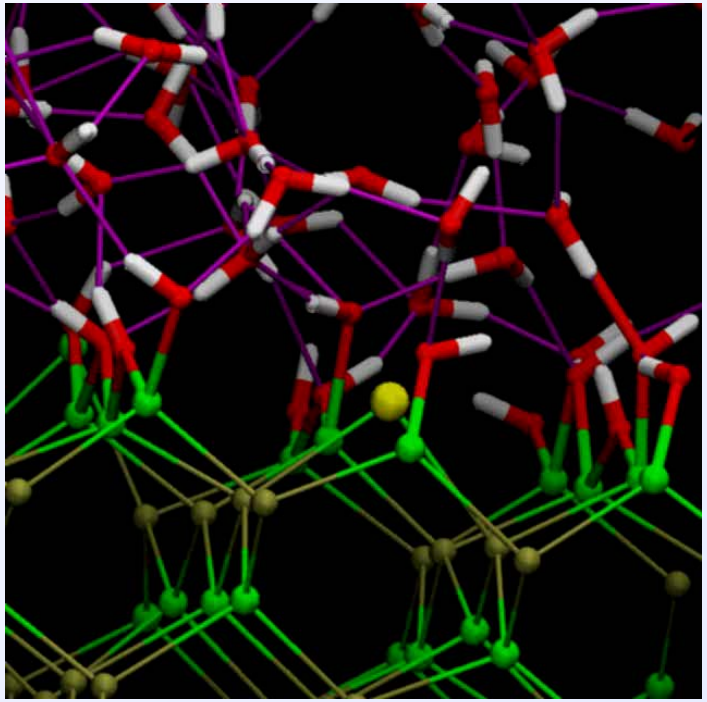


Turner, Deutsch, Wang, Schiros (NREL)

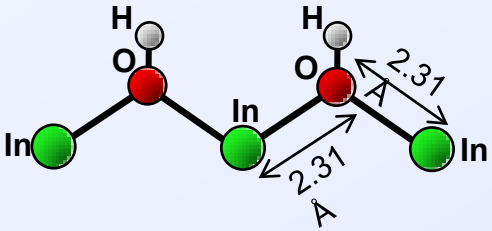
Technical accomplishment: Corrosion scenario #3

Surface metal dissolution corrosion scenario

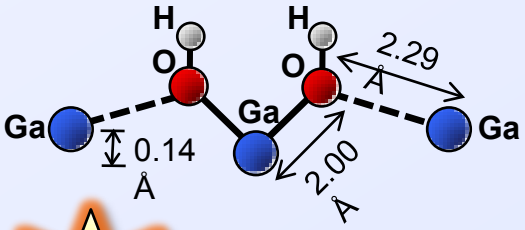
- Undercoordinated metal atoms dissolve into solution
  - Observed in MD simulations
- Arises from competition between adsorbate binding to new metal site or edges of a M-OH-M bridge

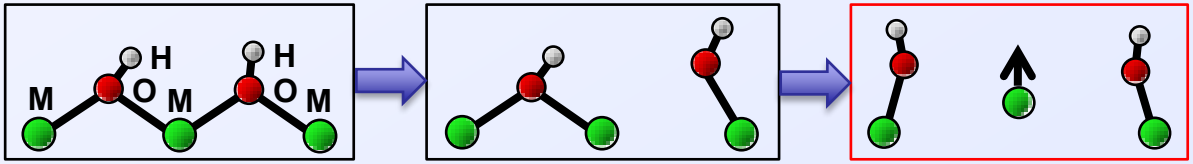


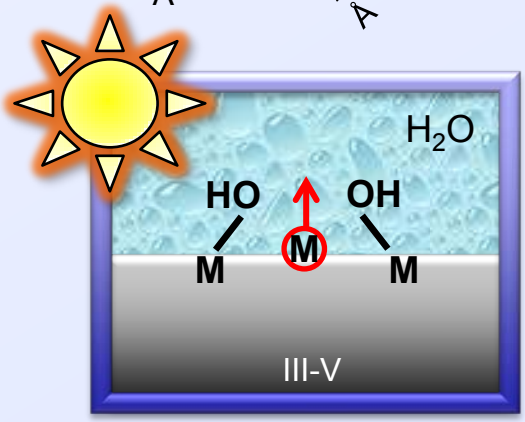
Bridge hydroxyl for InP



Bridge hydroxyl for GaP





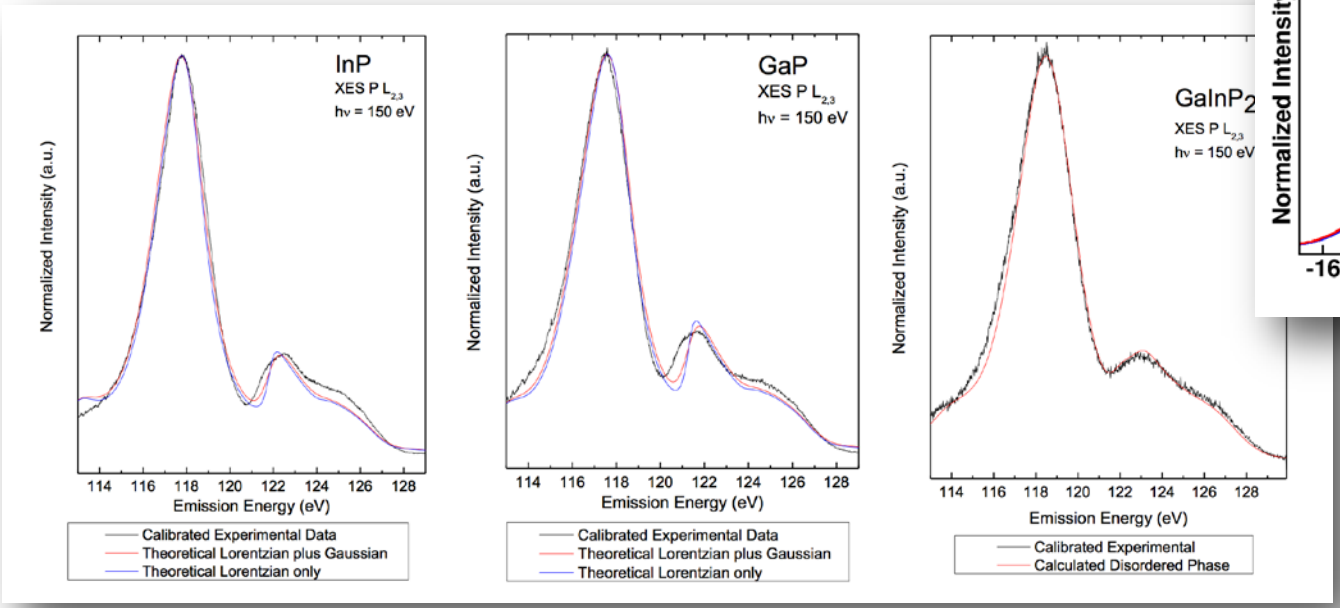


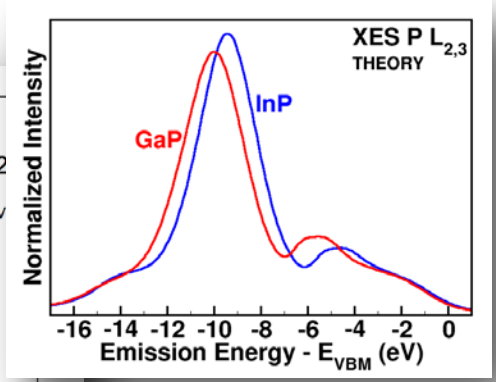
Technical accomplishment: X-ray spectroscopy

- **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-L2,3 edge XES of GaP, InP, $GaInP_2$
- Experimental and theoretical spectra show excellent agreement
- Characteristics of GaP and InP are experimentally distinguishable
- Theoretical site-dependent spectra can aid experimental interpretation





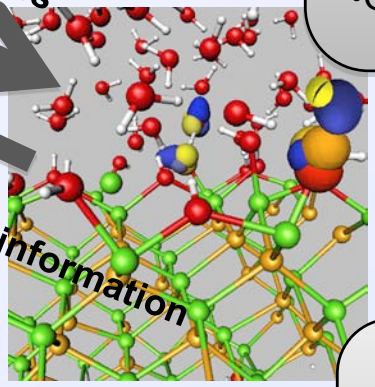
Collaborations: Theory-experiment feedback cycle

NREL experiments: (DOE lab)
- J. Turner & T. Deutsch
- DOE H_2 program
- Synthesize electrode materials
- Assemble device
- Analyze H_2 production performance and corrosion resistance

NREL theory: (DOE lab)
- K. Kim & W. Ih Choi
- DOE H_2 program
- *Ab-initio* surface simulations (mostly static)
- Gas phase reaction energetics

Basic information on electrodes

Detailed microscopic information



Sample delivery

Choice of surface

UNLV experiments: (University)
- C. Heske & K. George
- DOE H_2 program
- Hi-fidelity (*in-situ*) characterization of water-electrode interface using X-ray spectroscopy

X-ray spectroscopy

LLNL theory: (DOE lab)
- B. Wood & T. Ogitsu
- DOE H_2 program
- Large scale *ab-initio* MD of water-electrode interface

LBNL theory: (DOE lab)
- D. Prendergast
- Not in H_2 program
- X-ray spectrum simulations

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

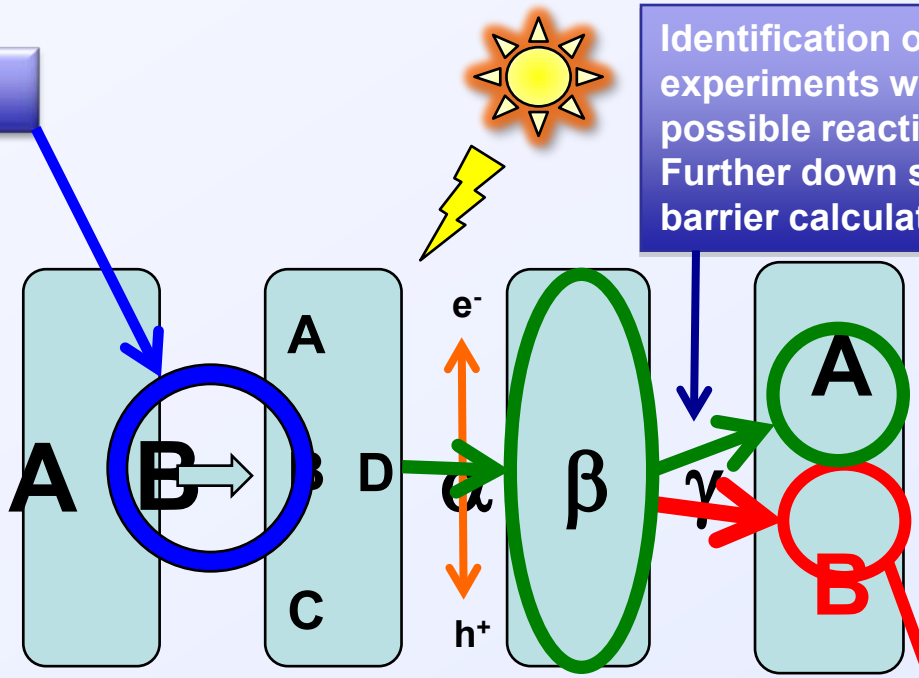
- Compiled, reviewed, and shared available information on III-V electrode materials (ongoing)
- Performed quantum molecular dynamics of water-electrode interfaces
  - Evaluated importance of surface oxygen
  - Identified connection between surface structure and reactivity
  - Established validity of 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 $GaInP_2$ 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

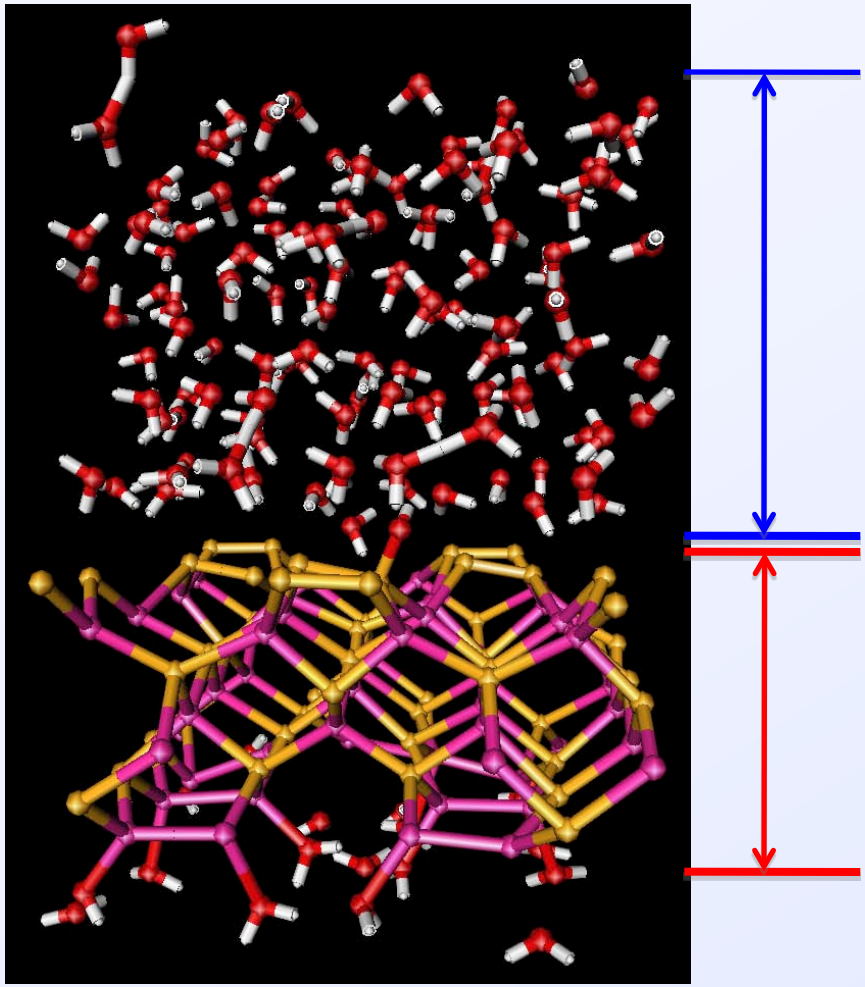


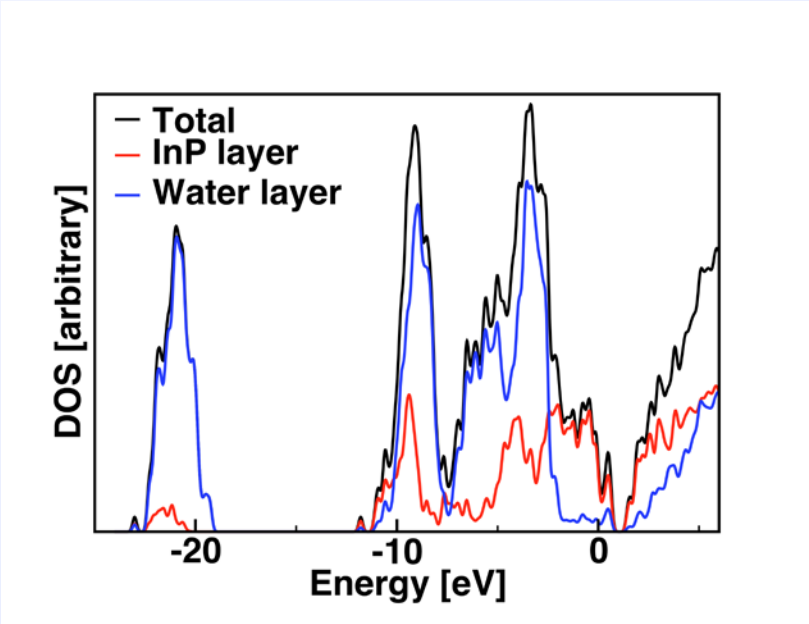
Reactants	Reactants'	Intermediates	Products:
A: InP	A: InP	α: ?	A: H_2
B: H_2O	B: H_2O	β: ?	B: In, InO
	C: In-O	γ: ?	
	D: In-OH		

Corrosion!

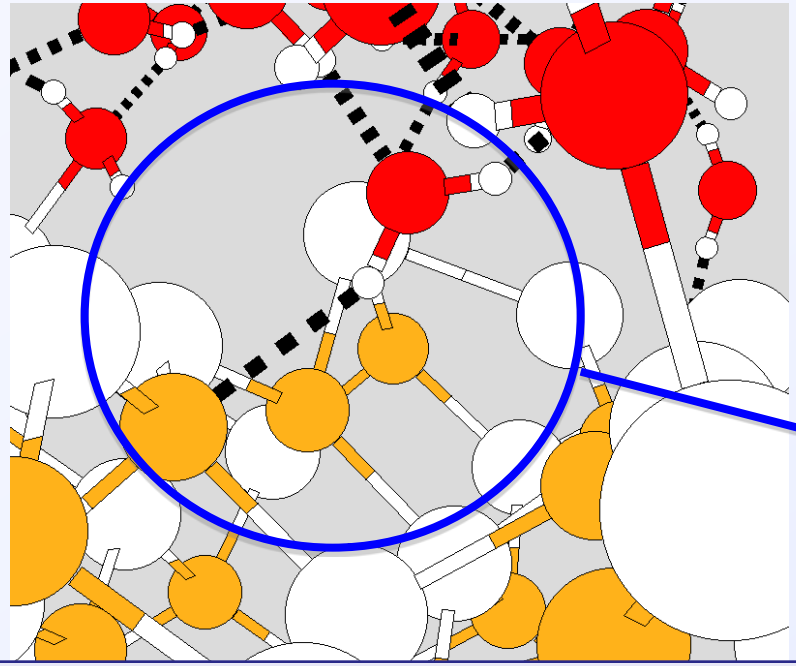
The intermediates will be characterized by combination of XAS/XES/XPS & *ab-initio* method

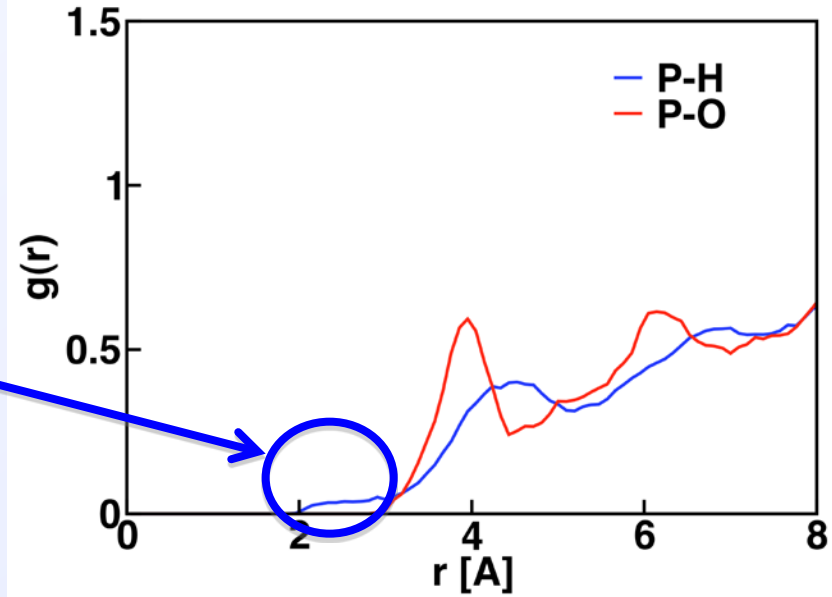
Supplementary slide: Interfacial electronic structure





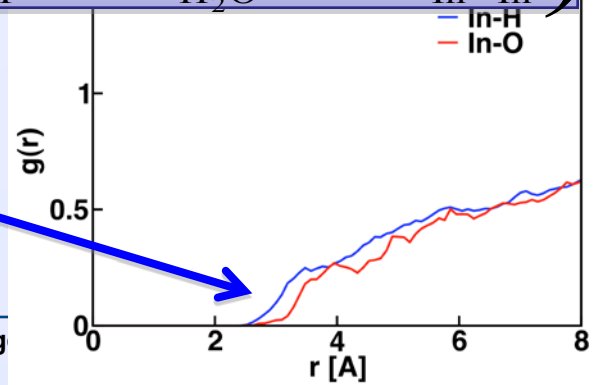
Supplementary slide: Importance of dynamical approach



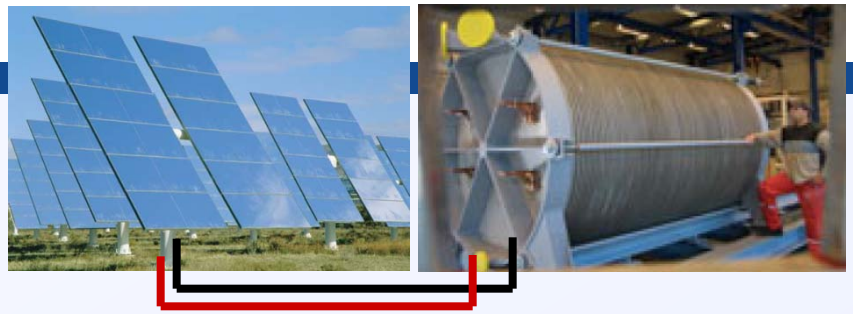


Size (O vs H) and dynamics $\left(\nu^{vib}_{\mathrm{P-P}} \geq \nu^{\mathrm{rot}}_{\mathrm{H_2O}} \geq \nu^{vib}_{\mathrm{In-In}}\right)$

Subsurface indium attracts H_2O (oxygen) less

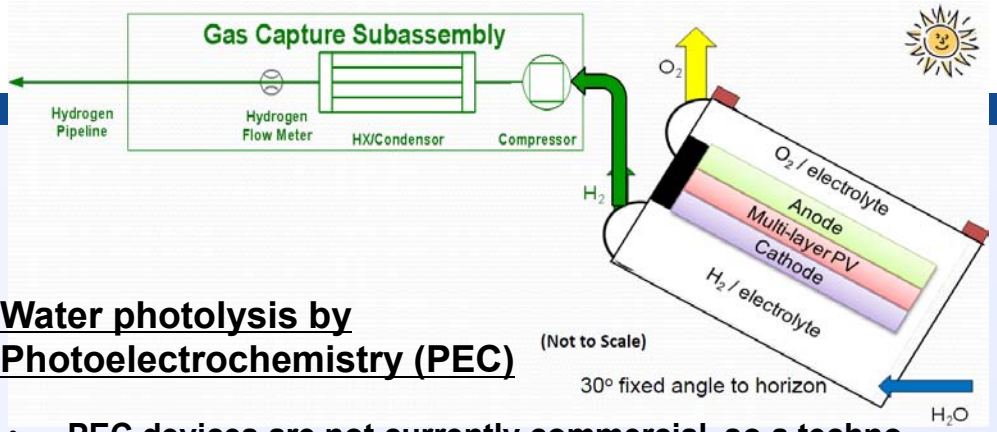


Supplementary slide: PV-electrolysis vs. PEC H_2 Production



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 H_2 is dominated by electricity.[1]
- For a 1000 kg H_2 / 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 H_2. [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 H_2.
- A cloudy climate yields approx. 2X cost \$35/kg H_2.



Water photolysis by Photoelectrochemistry (PEC)

- PEC devices are not currently commercial, so a techno-economic analysis was conducted to estimate \$ / kg H_2.[3]
- Four different reactor types were evaluated, along with the balance of plant required to produce 1000 kg H_2 / 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/m^2 cost.
- The baseline assumptions yielded sunny climate estimated costs of: \$1.63/kg H_2 (Type 1), \$3.19/kg H_2 (Type 2), \$10.36/kg H_2 (Type 3), and \$4.05/kg H_2 (Type 4).

Conclusion: H_2 production by PV-electrolysis is currently less expensive than PEC, however PEC can potentially reach DOE cost targets of \$9-\$15/kg H_2 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.