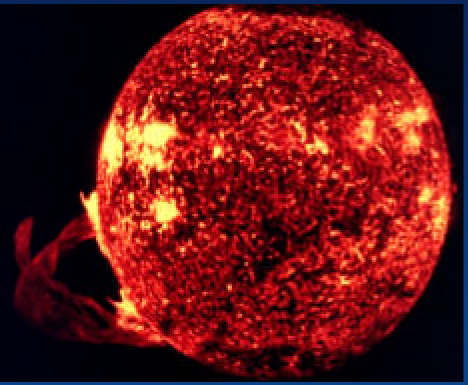
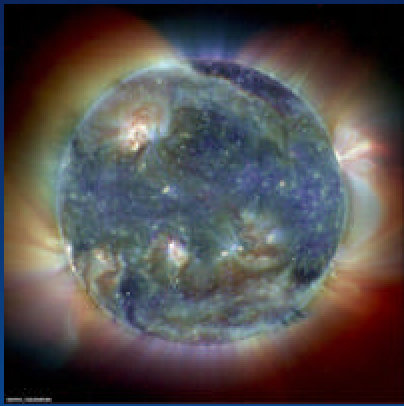
Direct Photoelectrochemical Production of Hydrogen



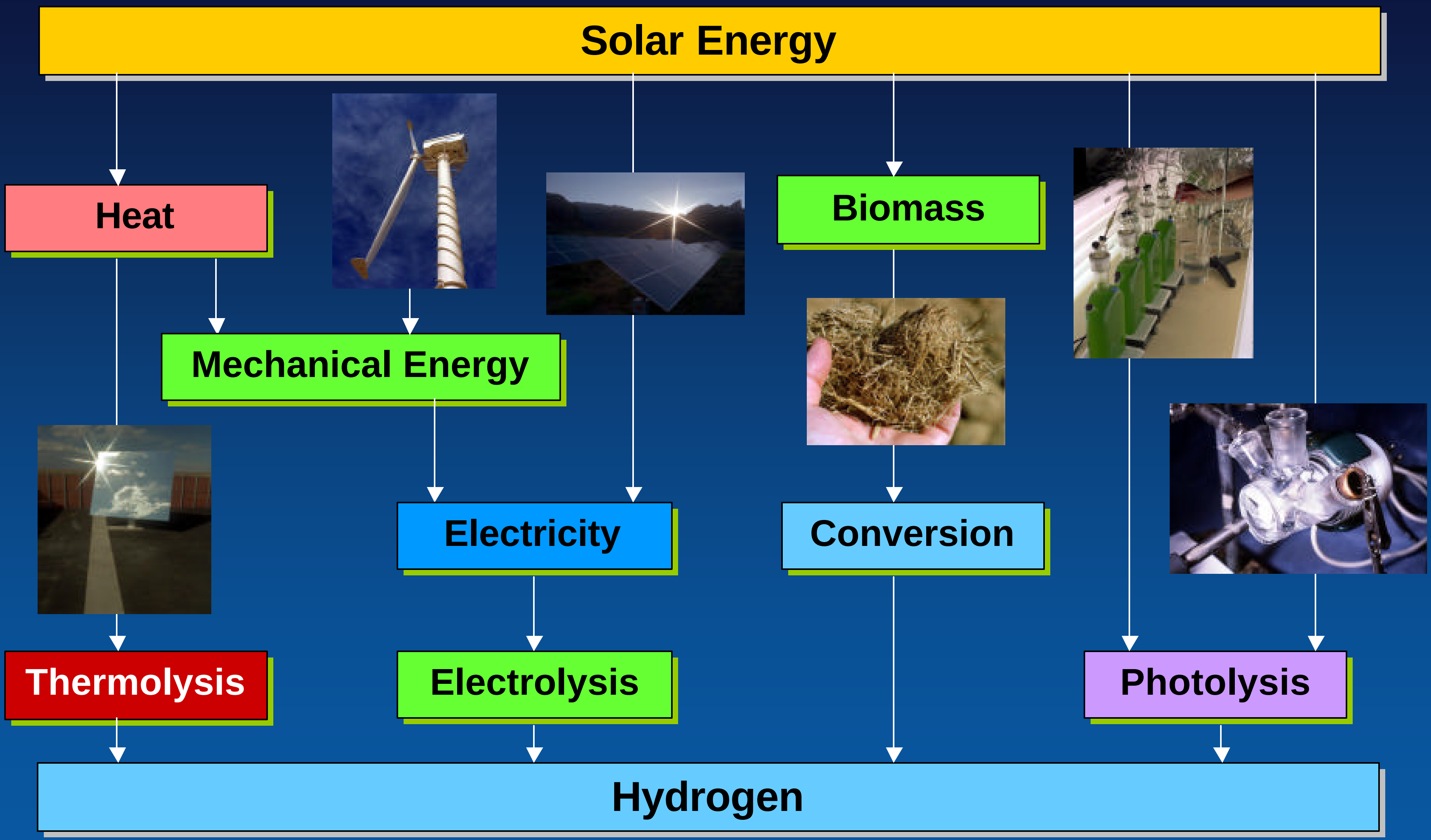
Solar-Hydrogen Workshop

November 9, 2004



John A. Turner
National Renewable Energy Laboratory
John_Turner@nrel.gov   303-275-4270

Sustainable Paths to Hydrogen



Hydrogen From Visible Light and Water

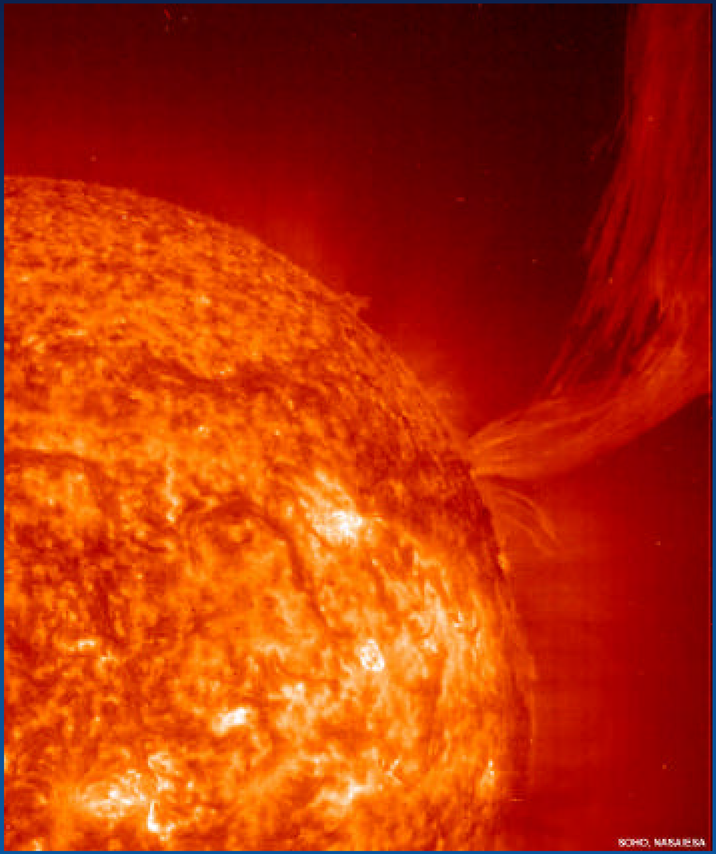
- Visible light has enough energy to split water (H_2O) into hydrogen (H_2) and oxygen (O_2).
  - *Fortunately water is transparent and does not absorb this energy.*
- The combination of a light harvesting system and a water splitting system is necessary to be able to use sunlight to split water.
- Photoelectrochemical processes along with certain algae can use this light to produce hydrogen from water.

$$2H_2O \rightarrow 2H_2 + O_2$$

Visible
Light

Direct Conversion Systems

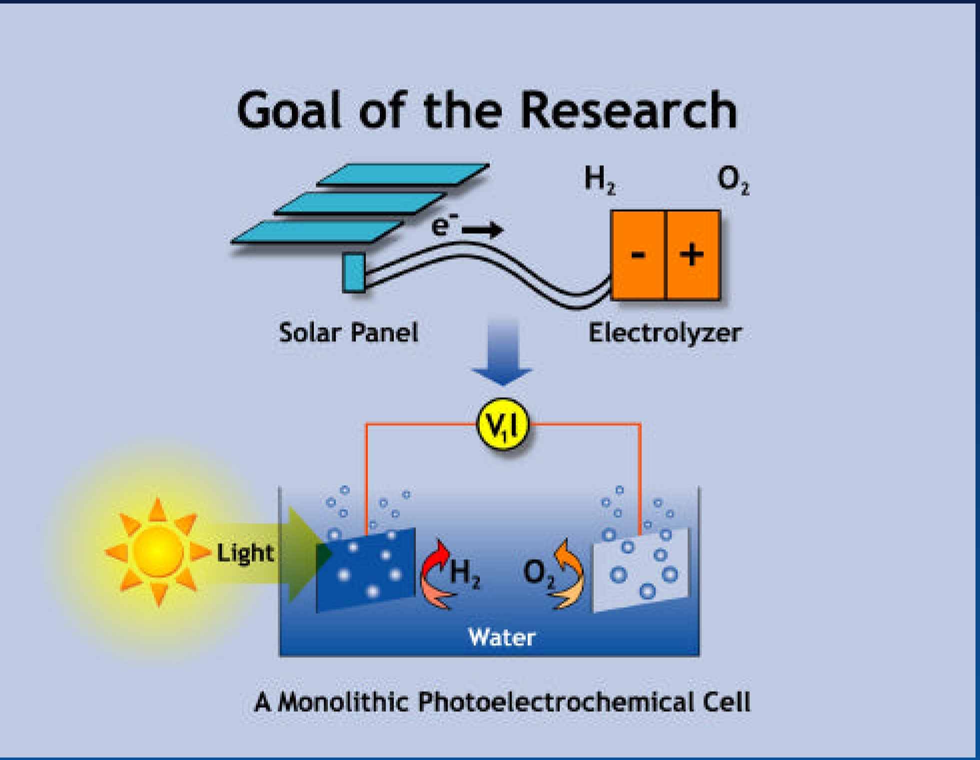
Combination of a Light Harvesting System and a Water Splitting System



- Semiconductor photoelectrolysis
- Photobiological Systems
- Homogeneous water splitting
- Heterogeneous water splitting
- Thermal cycles

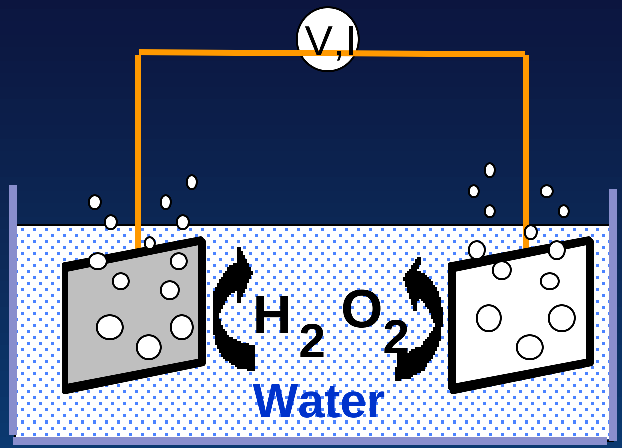
(Sunlight and Water to Hydrogen with No External Electron Flow)

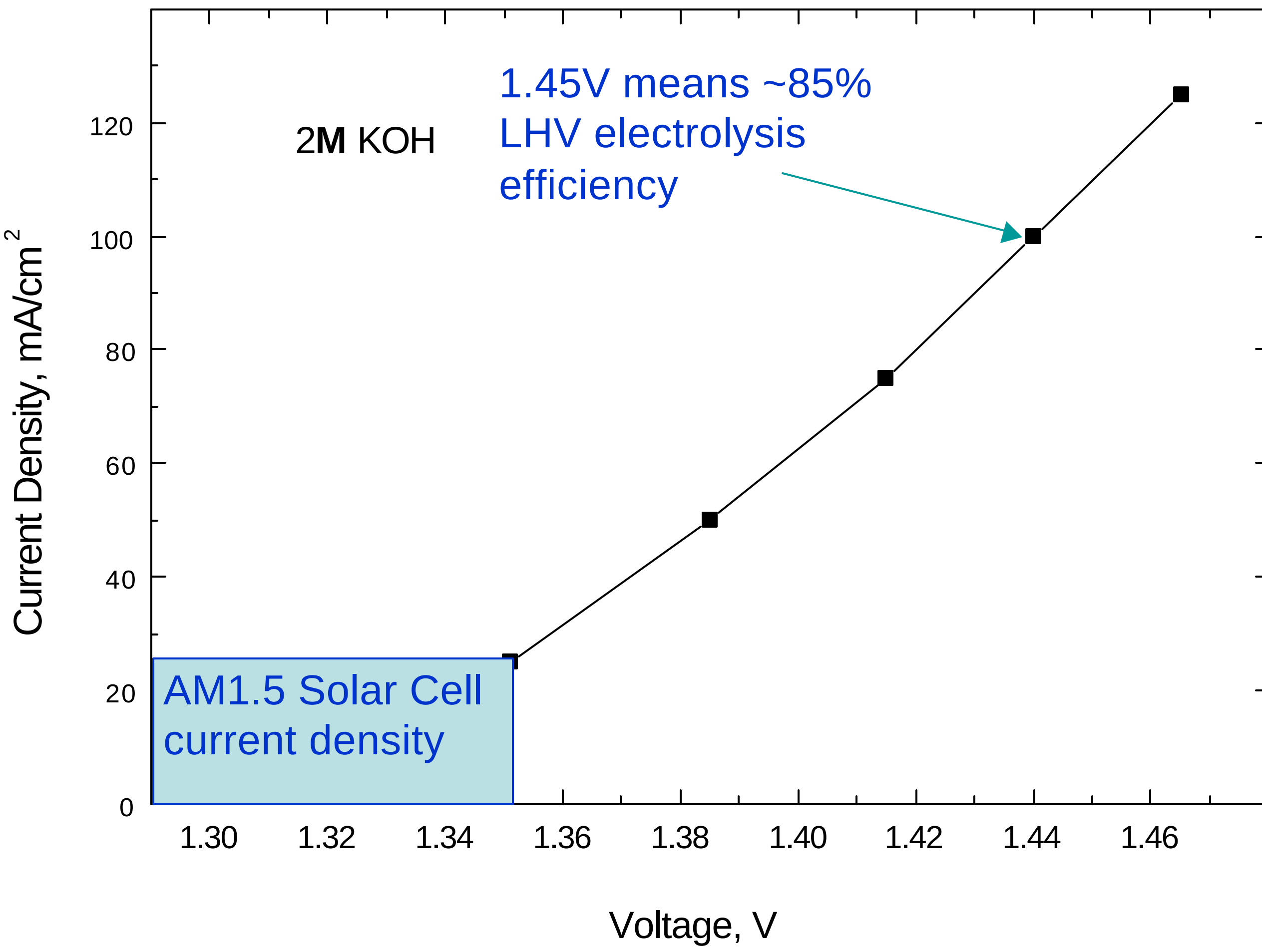
Photoelectrochemical-Based Direct Conversion Systems



- Combines a photovoltaic system (light harvesting) and an electrolyzer (water splitting) into a single monolithic device.
  - Electrolysis area approximates that of the solar cell - the current density is reduced.
- Balance of system costs reduced.
  - Capital cost of electrolyzer eliminated
- Semiconductor processing reduced.
- Efficiency can be 30% higher than separated system.

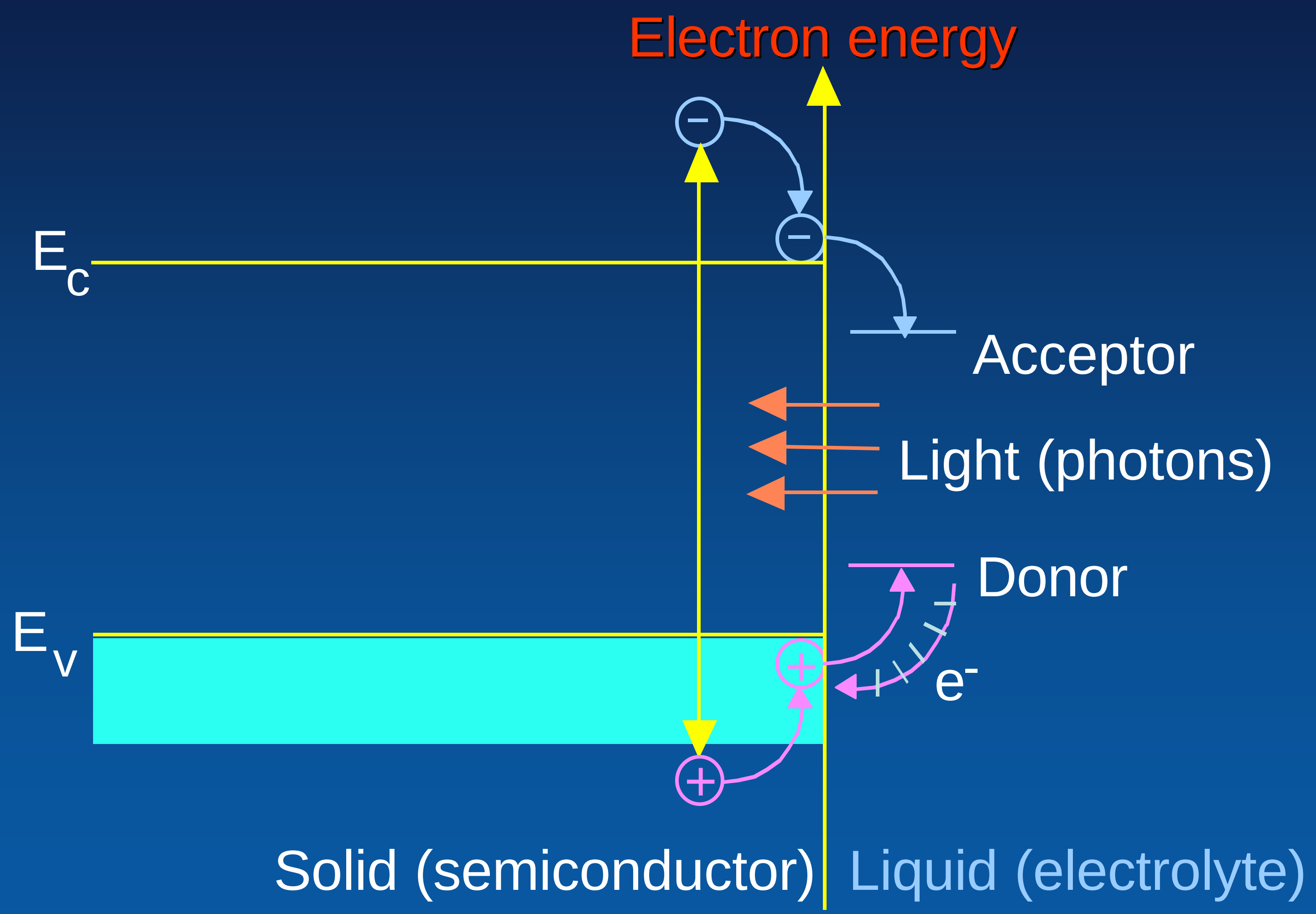
Current Density vs. Voltage for 2 Pt Electrodes of Equal Area.



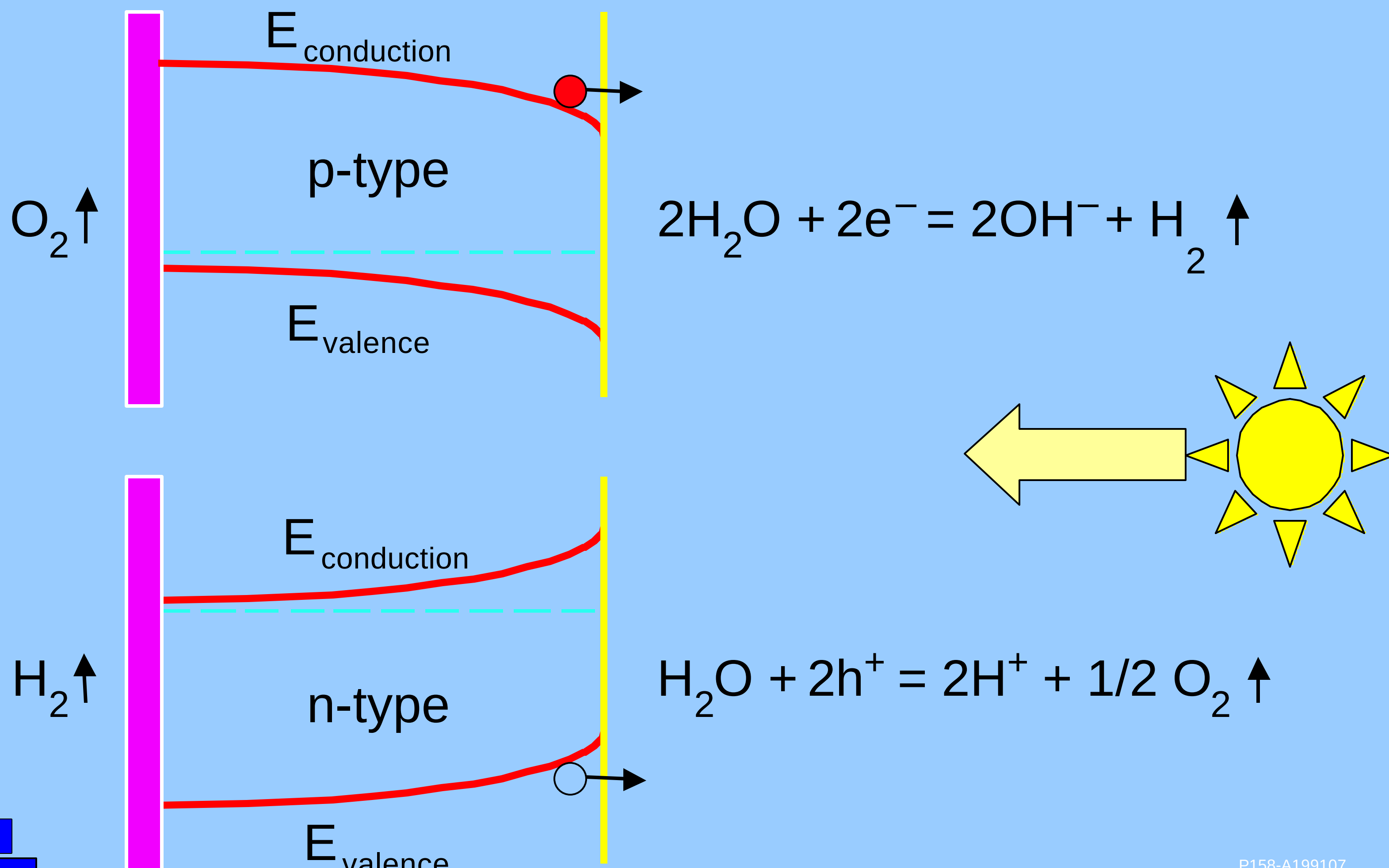


O. Khaselev, A. Bansal and J. A. Turner, *International Journal of Hydrogen Energy*, **26**, p 127-132 (2001).

Chemical Reactions at a Semiconductor Electrolyte Interphase



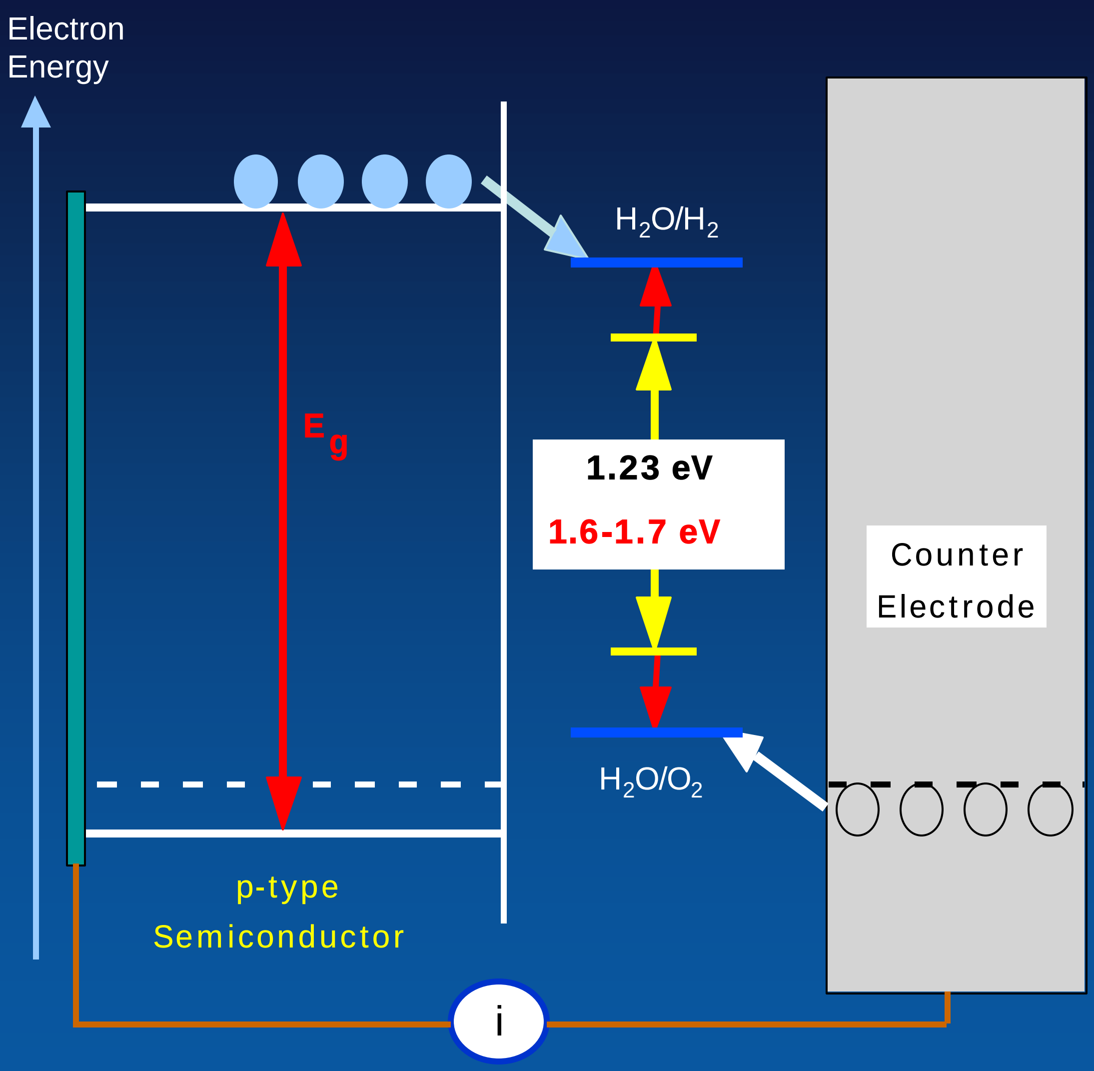
Band Edges of p- and n-Type Semiconductors Immersed in Aqueous Electrolytes to Form Liquid Junctions



P158-A199107

Technical Challenges *(the big three)*

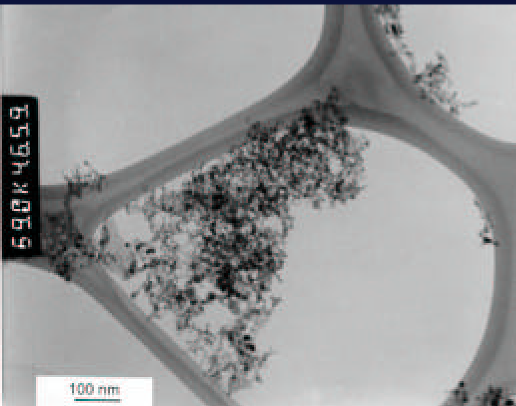
Material Characteristics for Photoelectrochemical Hydrogen Production



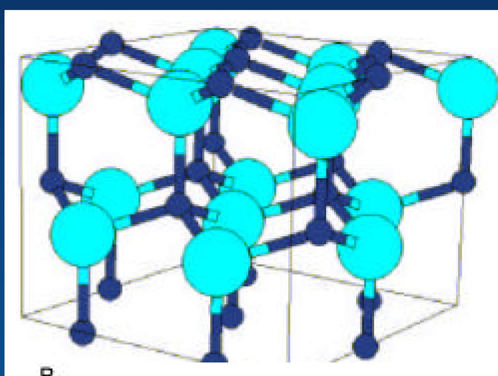
- **Material Durability –** semiconductor must be stable in aqueous solution
- **Efficiency –** the band gap (E_g) must be at least 1.6-1.7 eV, but not over 2.2 eV
- **Energetics –** the band edges must straddle H_2O redox potentials (Grand Challenge)

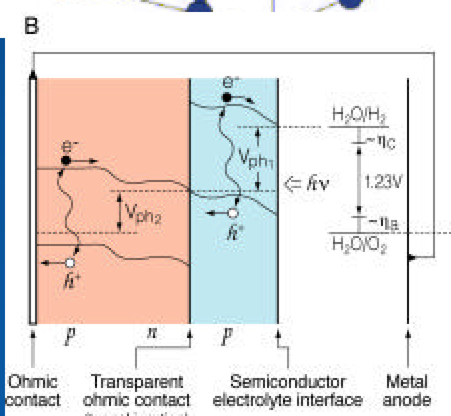
All must be satisfied simultaneously

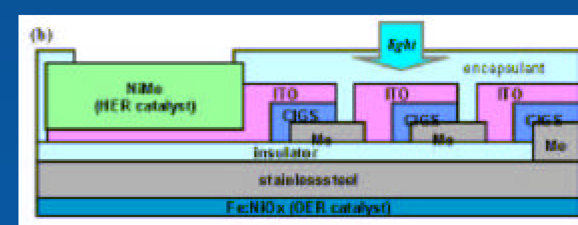
Current Areas of Effort



- Metal oxides (mixed and single).
  - Most studied area
  - Largest possibility of materials
  - Greatest stability, lowest efficiency to date
- Novel and new materials
  - Typically from the PV industry
  - PV materials are not always directly applicable to PEC systems, so some modifications needed
- Advanced structures/hybrid designs
  - Tandem cells, triple junctions, p-n combinations.
  - Specialty designs
- Characterization Tools
- Catalysts







Tuesday, October 19, 2004

Hydrogen Research Projects Selected for $75 Million in DOE Awards

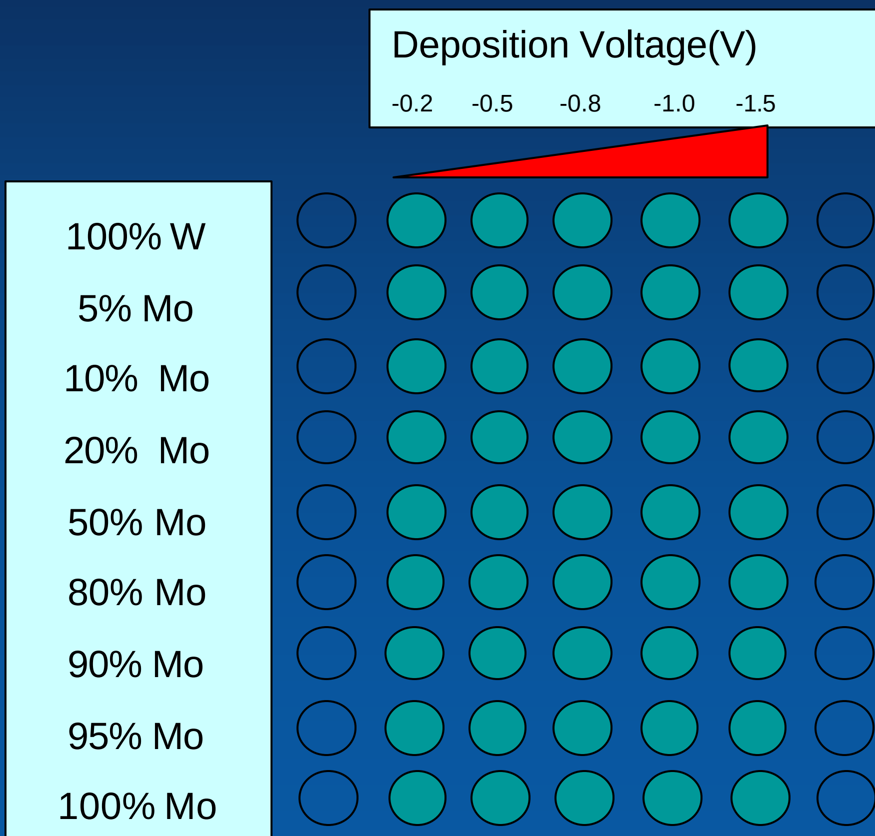
Solar Electrochemical Water Splitting (Photoelectrochemical)

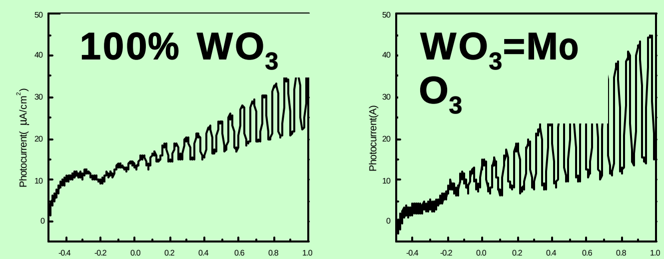
Team Lead	Additional Team Members	Total DOE Amount
GE Global Research (Niskayuna, NY	Caltech	$3,000,042
University of California-Santa Barbara (Santa Barbara, CA)	GE Global Research, National Renewable Energy Laboratory (NREL)	$894,000
MVSystems Inc. (Golden, CO)	University of Hawaii, Intematix Corporation, Southwest Research Institute, Duquesne University, NREL, University of California - Santa Barbara	$3,271,630
Midwest Optoelectronics (Toledo, OH)	University of Toledo, NREL, United Solar Ovonic Corporation	$2,921,501

High-Throughput Discovery of New and Optimized Metal Oxide Photocatalysts

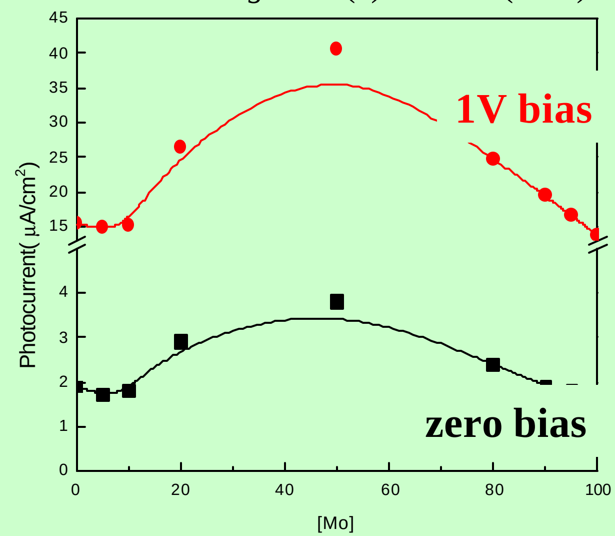
Eric W. McFarland (PI), Tom Jaramillo, Sung-Hyeon Baeck, Alan Kleinman
Dept. of Chemical Engineering, University of California, Santa Barbara

Tungsten-Molybdenum Mixed Oxides





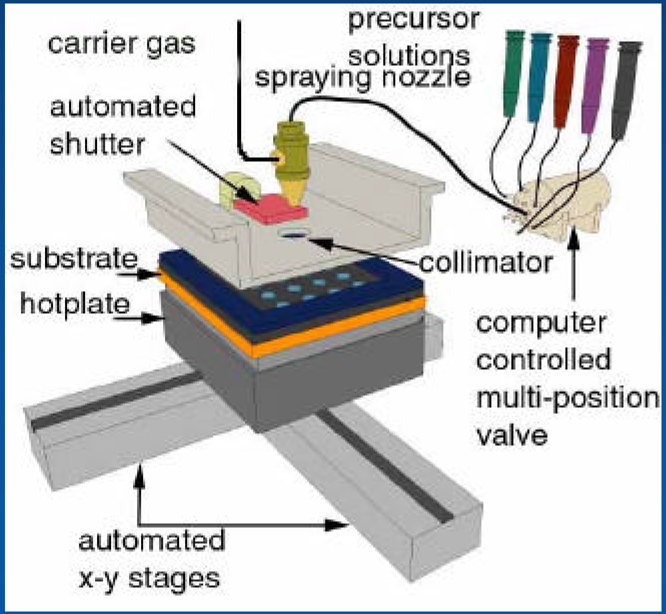
Korean J. Chem. Engin. 19 (4) 593-596 (2002).



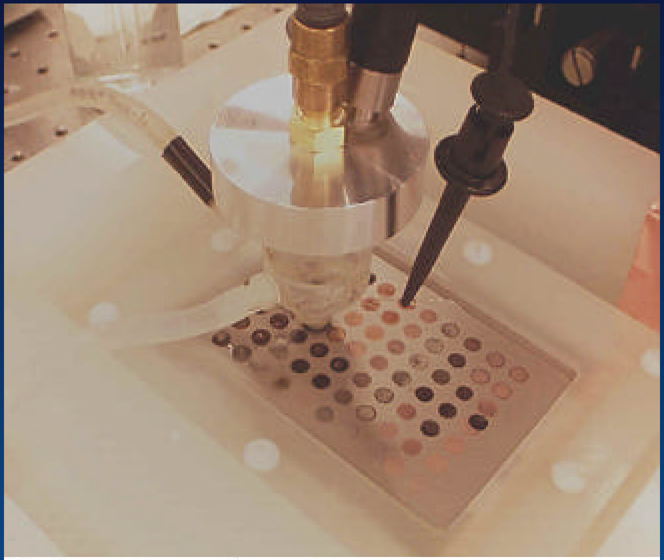
Synthesis of Mixed Metal Oxides

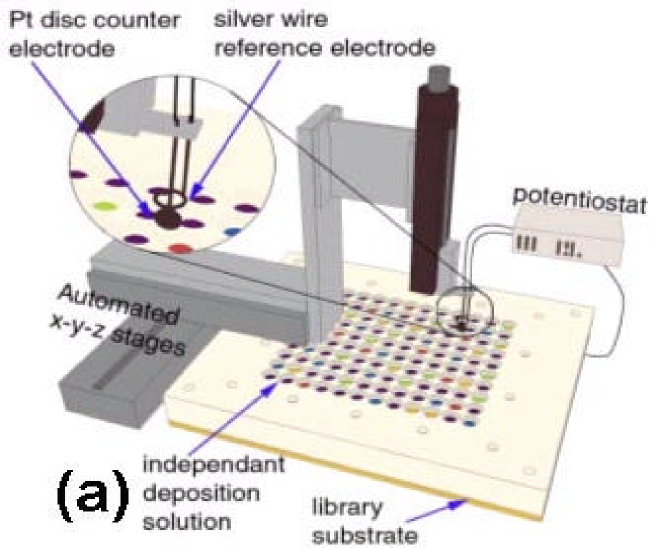
Approach

- Solid-State Synthesis
- Physical Vapor Deposition
- **Electrosynthesis**
- **Spray Pyrolysis**



Automated Electrodeposition of Thin Films





Generalized Electrosynthesis Chemistries

Eric W. McFarland - UCSB

Metal deposition/Oxidation

$M^+ \rightarrow M \rightarrow MO$

1. Metal Electrodeposition

$M^{n+} + n\,e^- \rightarrow M^o$ (Cathodic)

2. Anodization/Anneal

$M^o + H_2O \rightarrow MO + 2\,H^+ + 2\,e^-$

$M^o + O_2 \rightarrow MO$

Electrochemical Deposition

- Voltage, Current Density
- Electrolyte, Electrode, Dopants
- Time, Temperature, pH, Concentration

Metal Oxide Deposition

Aqueous: $M^+ \rightarrow MOH \rightarrow MO$

1. MO Deposition

electrode: $2\,H_2O + 2\,e^- \rightarrow H_2 + 2(OH^-)_{sur}$

$[M^{n+}(\text{ligand})] + n(OH^-)_{sur} \rightarrow M(OH)_n$

ligands (acidic) = peroxide

(basic) = lactate, citrate, ethylene glycol, acetate

2. Dehydration/Anneal

$M(OH)_n \rightarrow MO_{n/2} + {}^{n}/_{2}\,H_2O$

Non-Aqueous: $M^+ + O_2 \rightarrow MO$

1. Direct MO Deposition

$xM^{n+} + {}^{y}/_{2}O_2 + ne- \rightarrow M_xO_y$

In DMSO etc

Electrodeposition of Metal oxide from Metal Peroxo Electrolyte (WO_3, MoO_3, TiO_2, ZrO_2, Nb_2O_5)

Eric W. McFarland - UCSB

Metal (W, Mo) or Metal Chloride (Ti, Nb,Zr)

+ Hydrogen Peroxide (H_2O_2)

↓

Decomposition of excess H_2O_2 by Pt black

↓

Dilute with mixture of DI Water and i-Propanol

↓

Cathodic Metal oxide deposition from Metal-peroxo

electrode: $2\ H_2O + 2\ e^- \rightarrow H_2 + 2(OH^-)_{sur}$

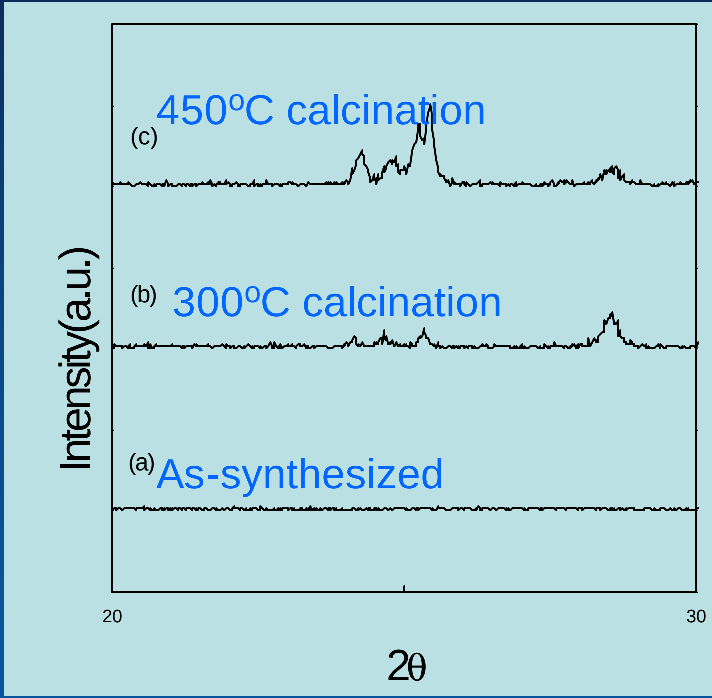
$[M^{n+}(\text{Peroxide})] + n(OH^-)_{sur} \rightarrow M(OH)_n$

↓

Calcination at elevated T

↓

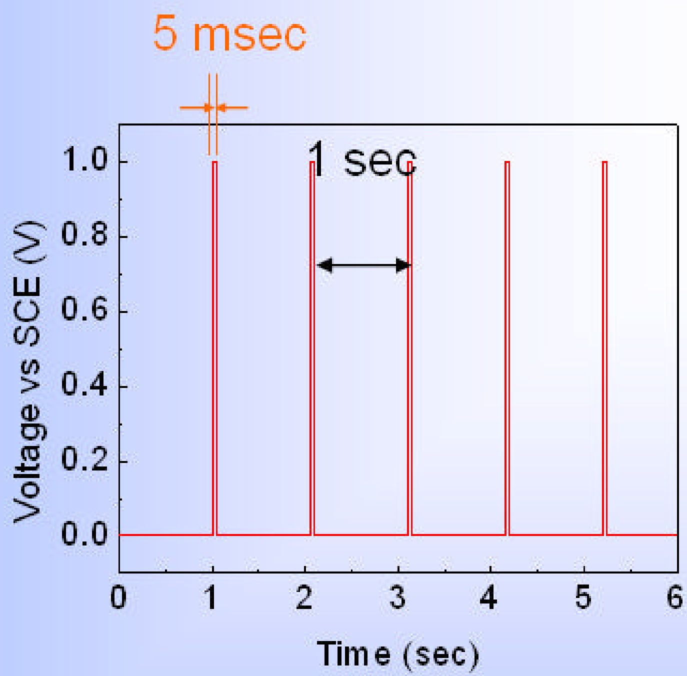
MeO_x

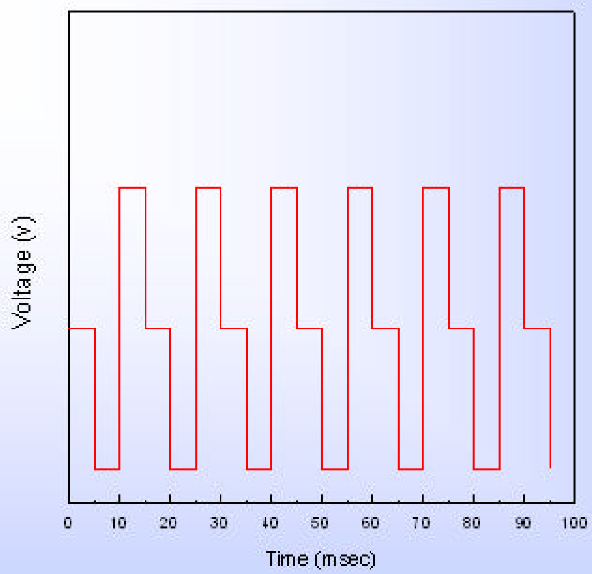


➢ Pulse Electrodeposition

Eric W. McFarland - UCSB

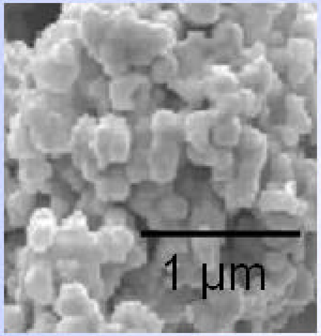
1. Formation of isolated nuclei
2. Growth to larger particles
3. Coalescence of larger particles
4. Formation of a linked network
5. Formation of a continuous deposit



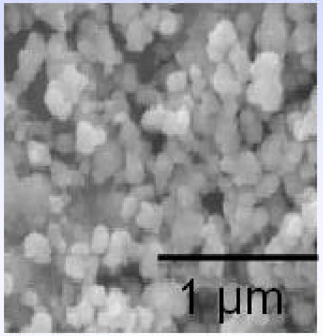


❖ Pulse Parameters : Pulse time, Pulse V, Off time (toff), Total deposition time

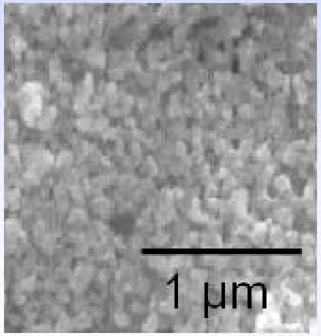
Electrodeposition of nanocrystalline WO_3 by pulsed deposition



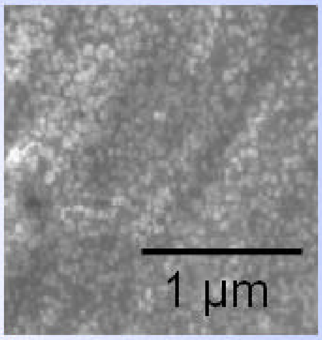
T_{pulse} =500msec



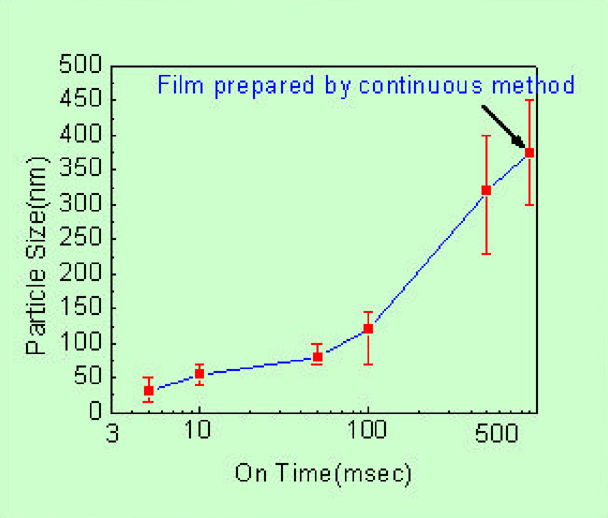
T_{pulse} =100msec

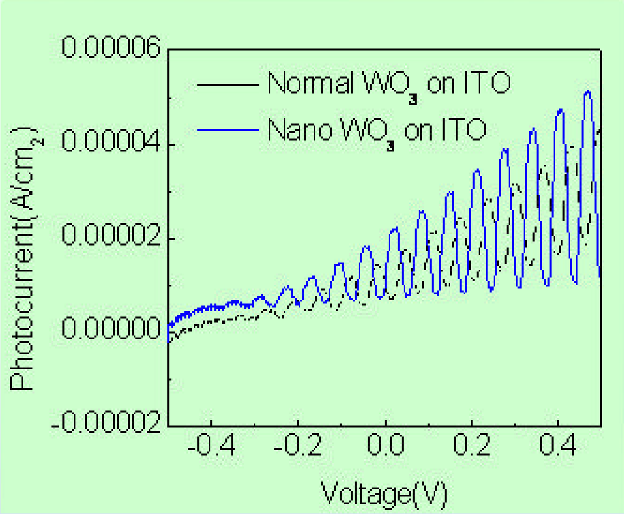


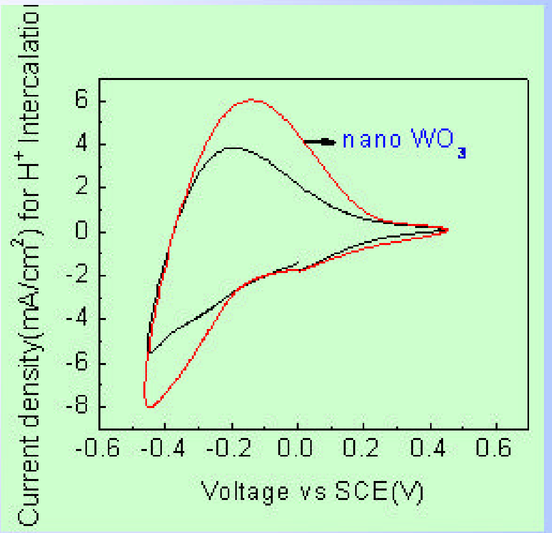
T_{pulse} =50msec



T_{pulse} =5msec



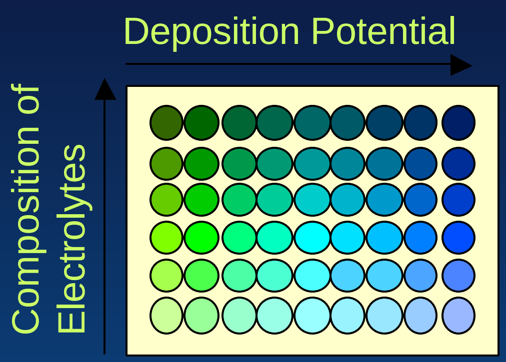




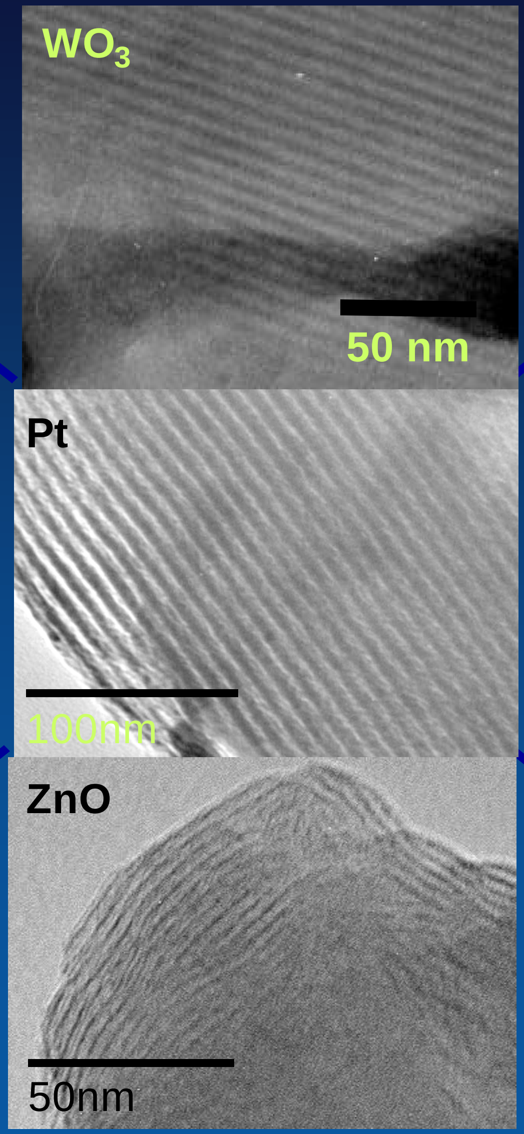
- S.H.Baeck, T. Jaramillo, G.D.Stucky, and E.W.McFarland, ***Nano Letters***, 2(8), 831(2002).

Combinatorial Approach for Producing and Modifying Mesoporous Films

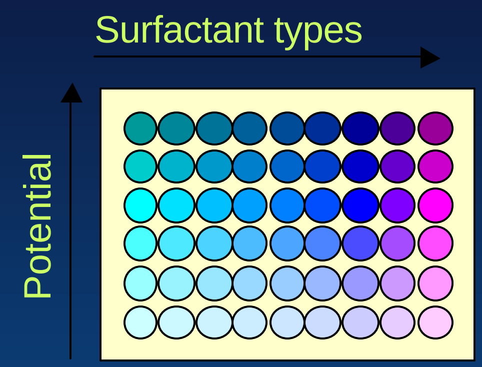
Processing a variety of materials as porous films



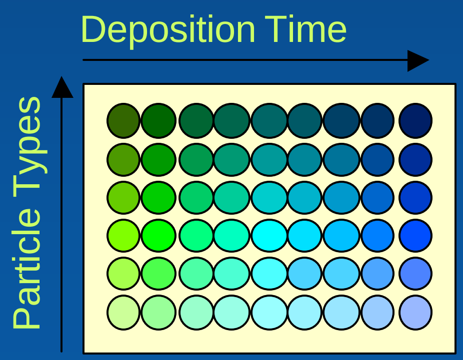
(i.e. Pt, Au, ZnO, WO_3)



Controlling pore sizes and porous structure

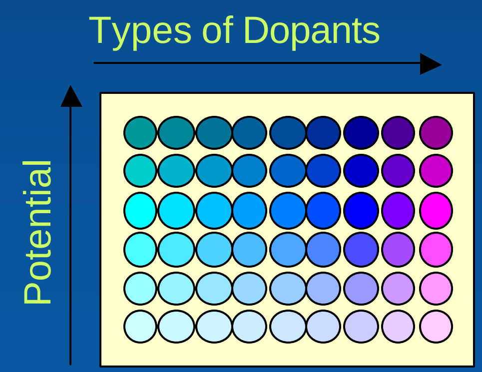


Modifying surfaces of the porous Films with metal and metal oxide particles



Mesoporous TiO_2 Substrate

Incorporating dopants or forming solid solutions in the wall structure



S.H.Baeck, K.-S. Choi, T. Jaramillo, G.D.Stucky, and E.W.McFarland, ***Advanced Materials***, 15(15), 1669(2003).

SRI International

Neophotonics Compositions Produced (Partial List)

Compositions Produced:

Amorphous Glass Materials

SiO_2, PSG, BPSG, GPSG

Elemental Metals

Fe, Ag, Ni, Co, Pt

Oxides

TiO_2, ZnO, VO_2, V_2O_3 , V_2O_5 , MnO, Mn_2O_3, Mn_3O_4, MoO_3, NbO_2, Nb_2O_5, Y_2O_3, SnO, SnO_2, SiO_2, Al_2O_3 , Fe_2O_3, Fe_3O_4

Complex oxides

$LiMn_2O_4$, $Li_2Mn_4O_9$, $Li_4Mn_5O_{12}$, $LiCoO_2$, $LiNiO_2$
$LiNi_{0.8}Co_{0.2}O_2$, $LiMn_{2-y}Al_yO_4$, $LiMn_{2-y}Co_yO_4$
$Li_4Ti_5O_{12}$, Y_2MoO_6, $Ag_2V_4O_{11}$, $BaMgAl_{10}O_{17}$:Eu

Carbon and Carbides

C, SiC, NbC, V_8C_7

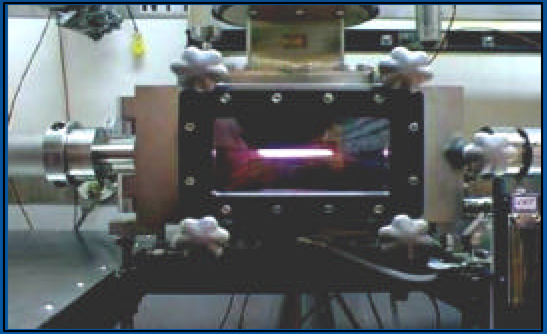
Nitrides

Si_3N_4

Phosphates

$LiFePO_4$

NPM™ NanoParticle Discovery System

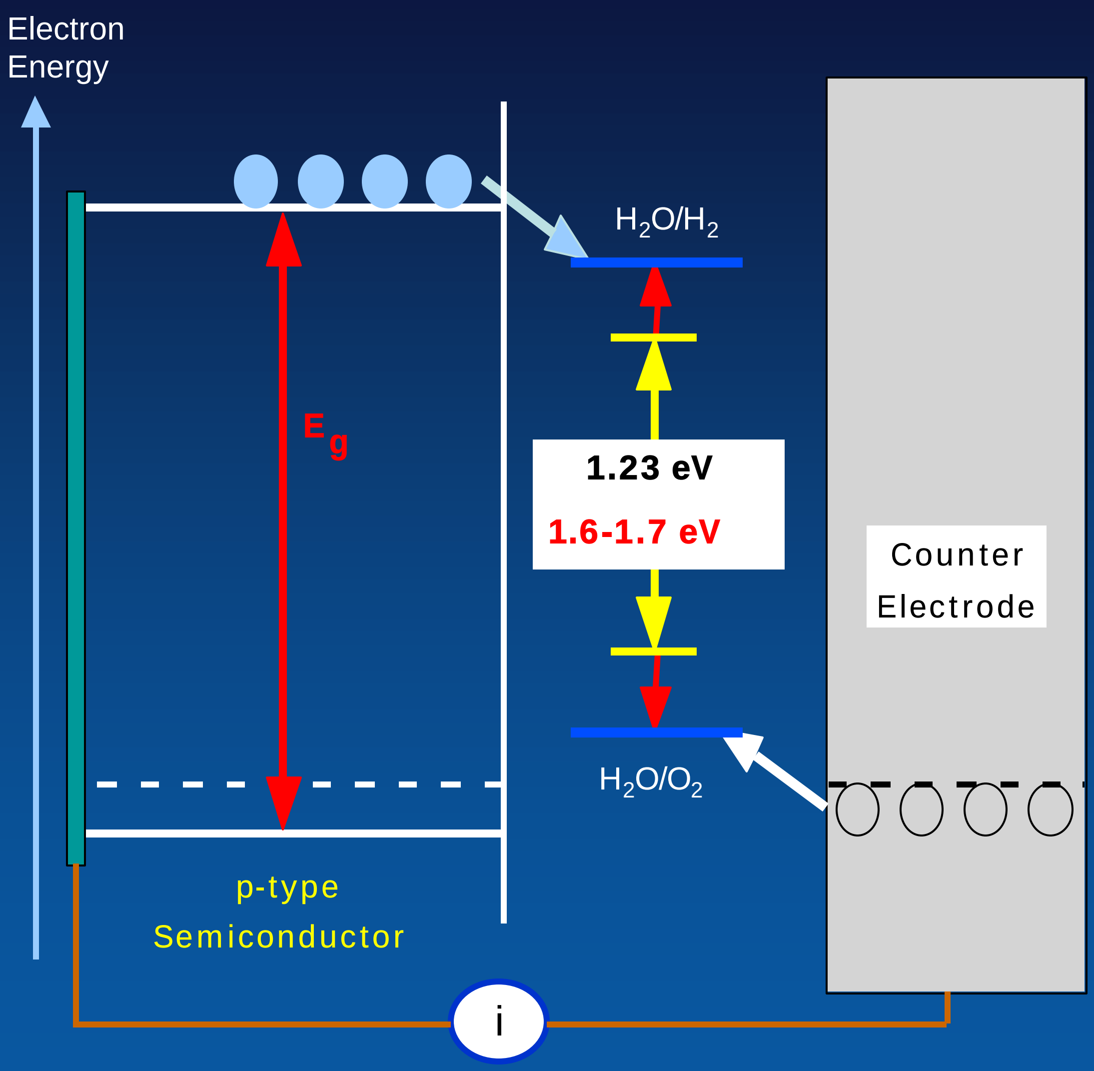


Close-up: NanoParticle Laser Reaction Chamber

C9000 Volume Production Module

Technical Challenges *(the big three)*

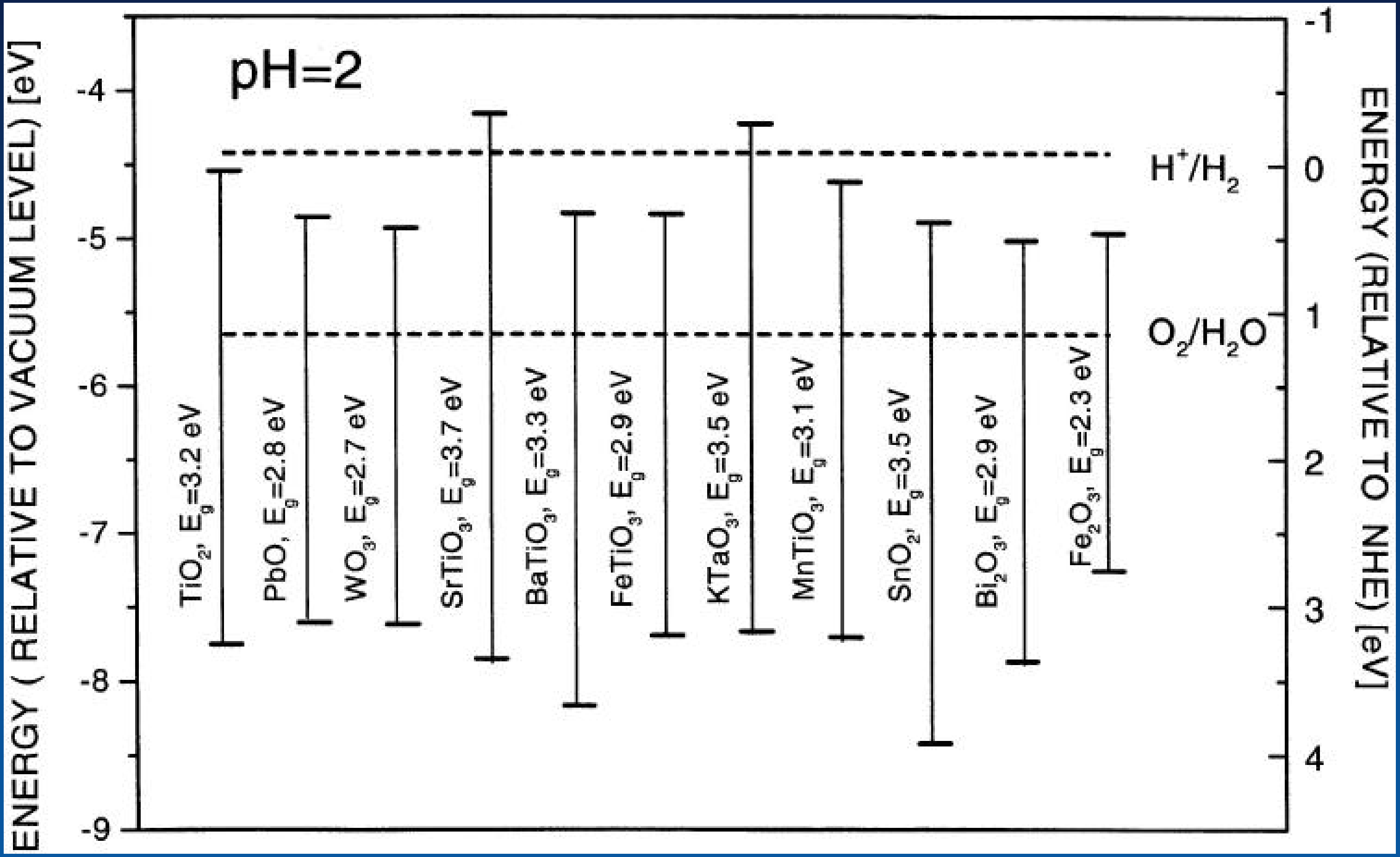
Material Characteristics for Photoelectrochemical Hydrogen Production



- **Material Durability** – semiconductor must be stable in aqueous solution
- **Efficiency** – the band gap (E_g) must be at least 1.6-1.7 eV, but not over 2.2 eV
- **Energetics** – the band edges must straddle H_2O redox potentials (Grand Challenge)

All must be satisfied simultaneously

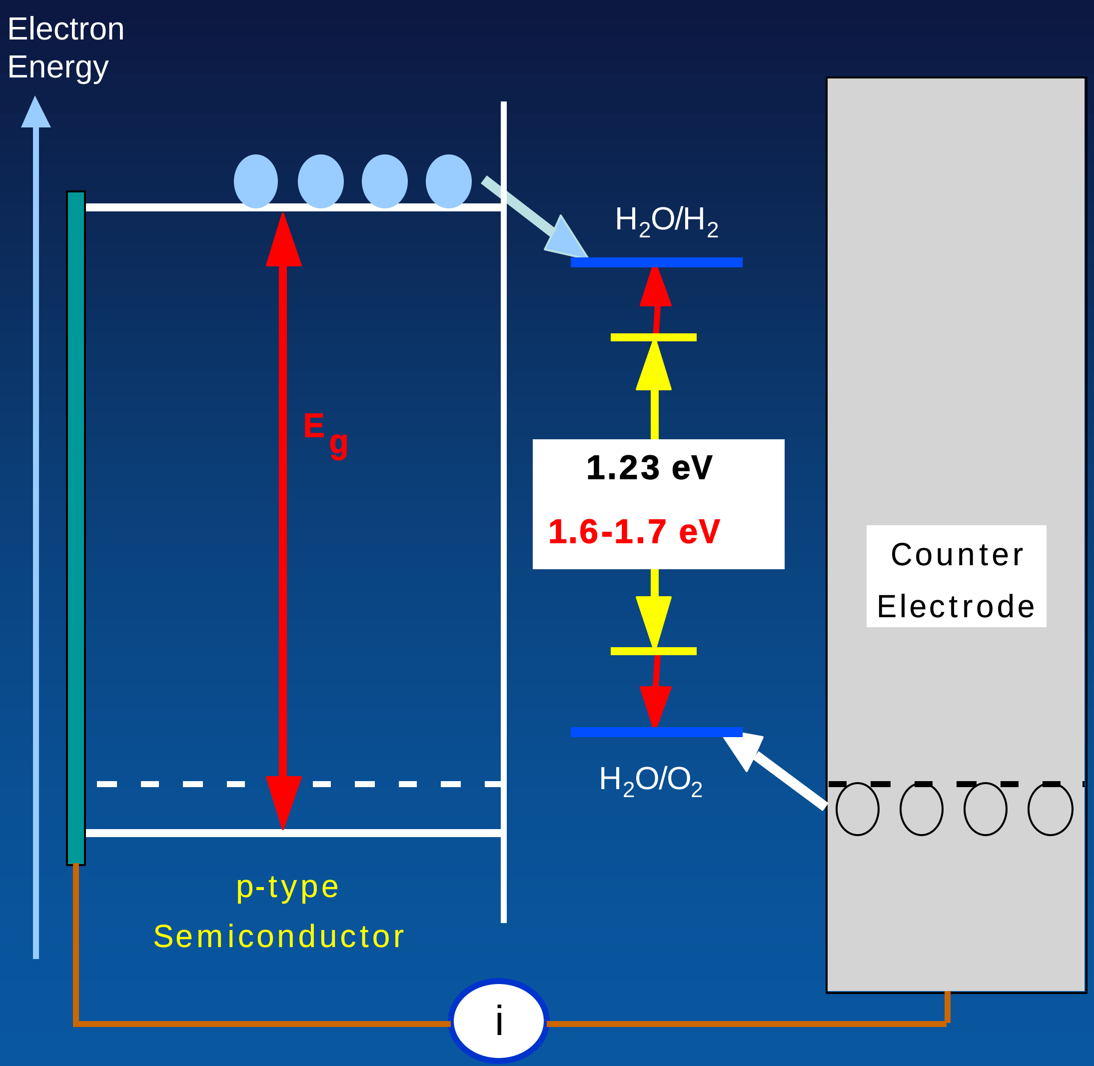
Bandedge Energetic Considerations



T. Bak, J. Nowotny, M. Rekas, C.C. Sorrell, International Journal of Hydrogen Energy **27** (2002) 991– 1022

Technical Challenges *(the big three)*

Material Characteristics for Photoelectrochemical Hydrogen Production



- **Material Durability –** semiconductor must be stable in aqueous solution
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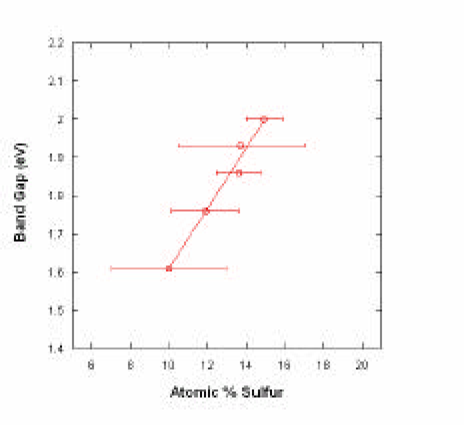
- **Energetics –** the band edges must straddle H_2O redox potentials (Grand Challenge)

All must be satisfied <u>simultaneously</u>

High Efficiency Semiconductor Materials

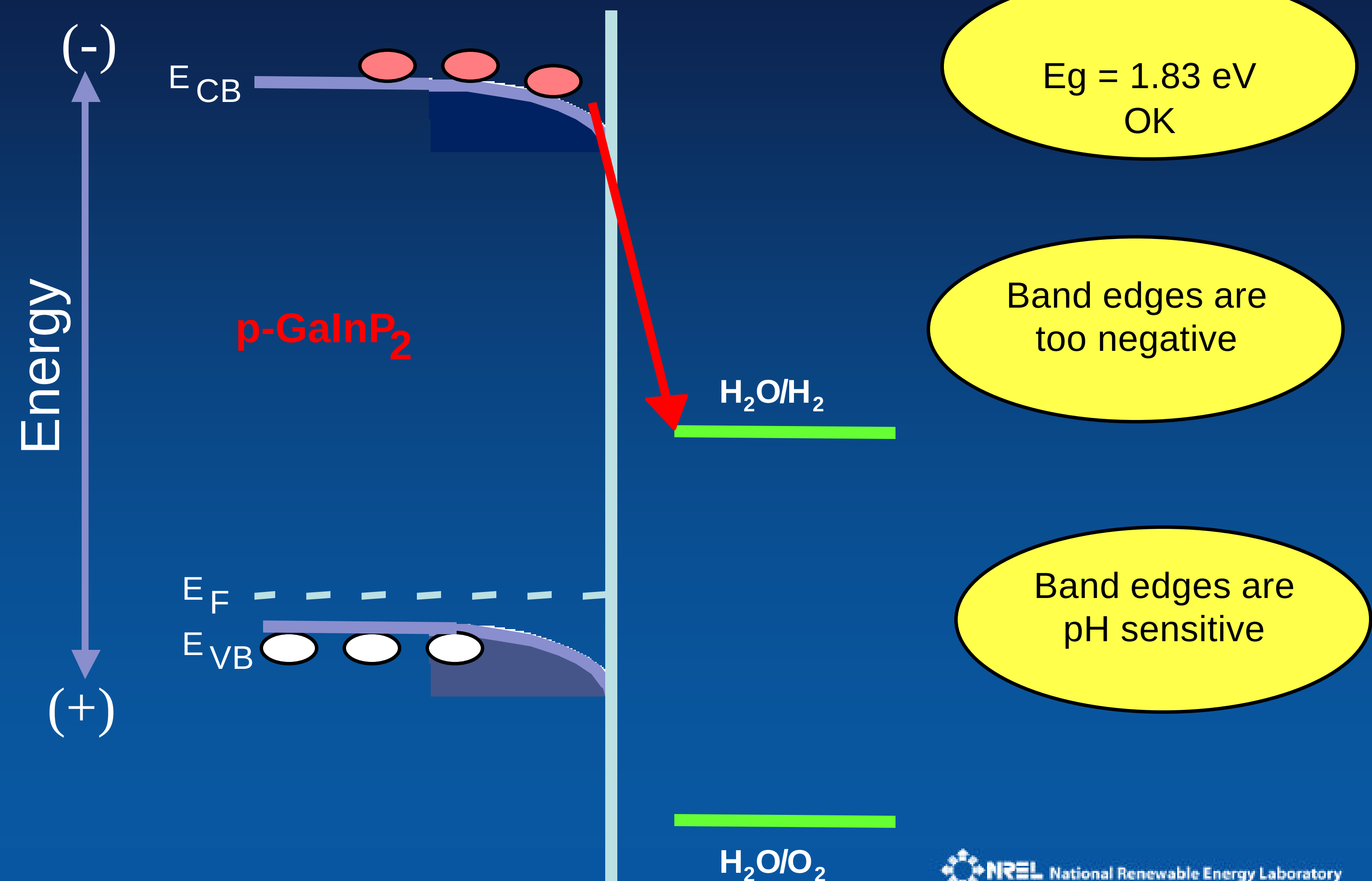
- III-V materials have the highest PV efficiency of any semiconductor material.
  - Largest range of available bandgaps
  - ….but
    - Unstable in aqueous solution (exception nitrides)
    - Band-edge mismatch (exception nitrides).

- I-III-VI materials offer low-cost manufacturing.
  - Synthesis procedures for desired bandgap unknown.
  - ….but
    - Unstable in aqueous solution?
    - Band-edge mismatch?

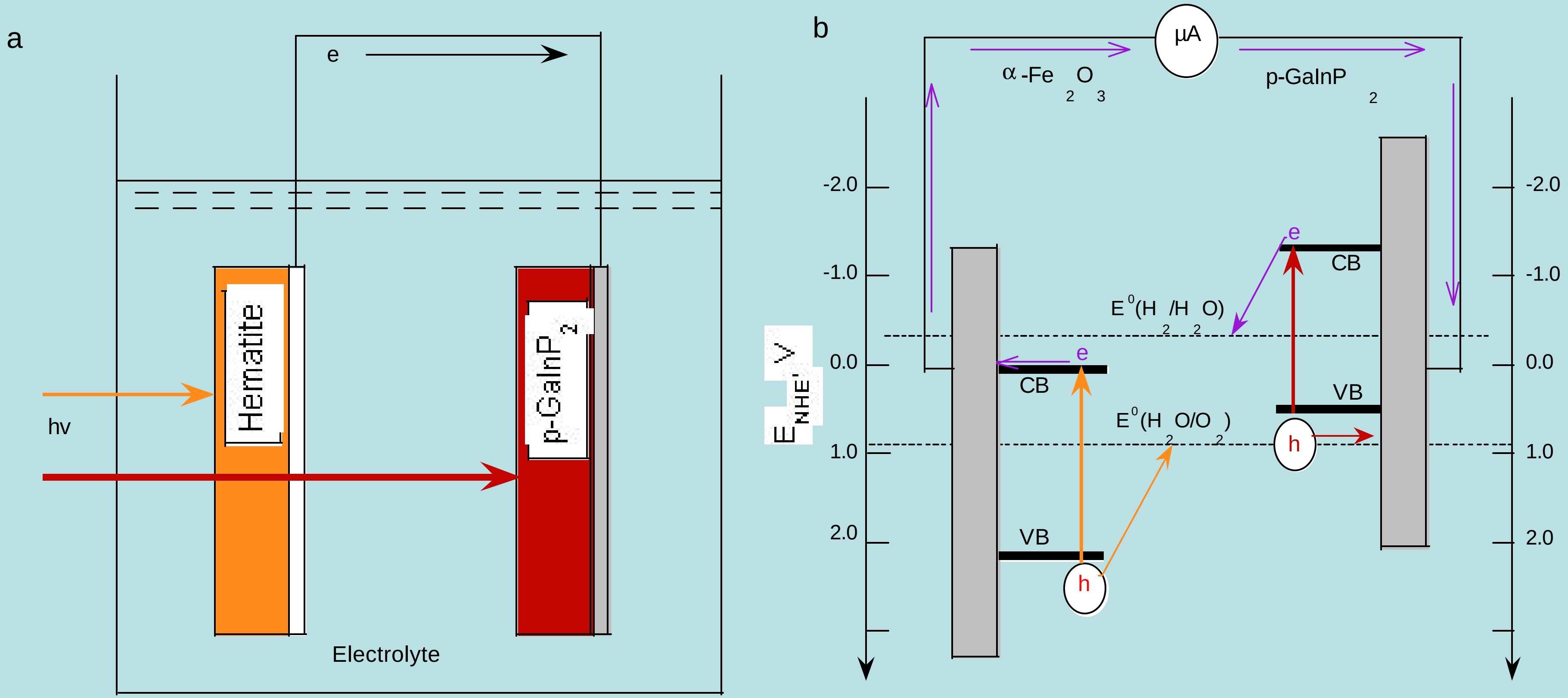


Gallium Indium Phosphide/Electrolyte System

Used to gain a fundamental understanding of semiconductor/electrolyte junctions



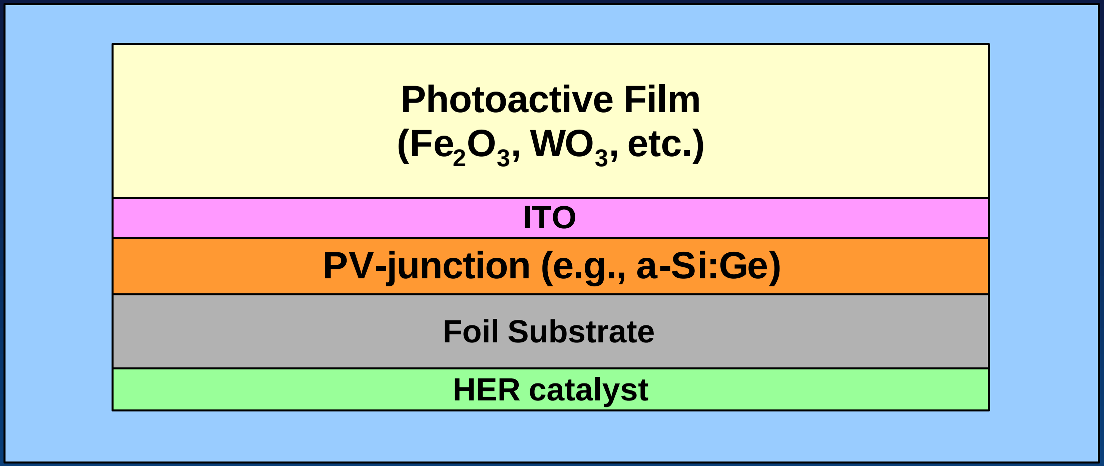
Dual Photoelectrode Approach for Bandedge Mismatch and Stability Issues



Lower cost Fe_2O_3 electrode is a possibility, but while the system splits water, the efficiency is very low.

Hawaii PEC Work: Hybrid Photoelectrode

Monolithic Hybrid Multijunction Photoelectrode



- Photoactive film acts as ‘top junction’ of multi-junction photoelectrode
- PV junction provides voltage ‘boost’ to drive OER & HER
- Current & optical ‘matching’ critical part of design
- Robust designs possible for corrosion resistance & long life
- Efficiency dependent on photocurrent levels of PEC interface
  - ***NEED GOOD PHOTOACTIVE TOP PEC FILMS***

Electrodeposition of Metal oxide from Metal Peroxo Electrolyte
(WO_3, MoO_3, TiO_2, ZrO_2, Nb_2O_5)

Eric W. McFarland - UCSB

Metal (W, Mo) or Metal Chloride (Ti, Nb,Zr)

+ Hydrogen Peroxide (H_2O_2)

↓

Decomposition of excess H_2O_2 by Pt black

↓

Dilute with mixture of DI Water and i-Propanol

↓

Cathodic Metal oxide deposition from Metal-peroxo

electrode: $2\ H_2O + 2\ e^- \rightarrow H_2 + 2(OH^-)_{sur}$

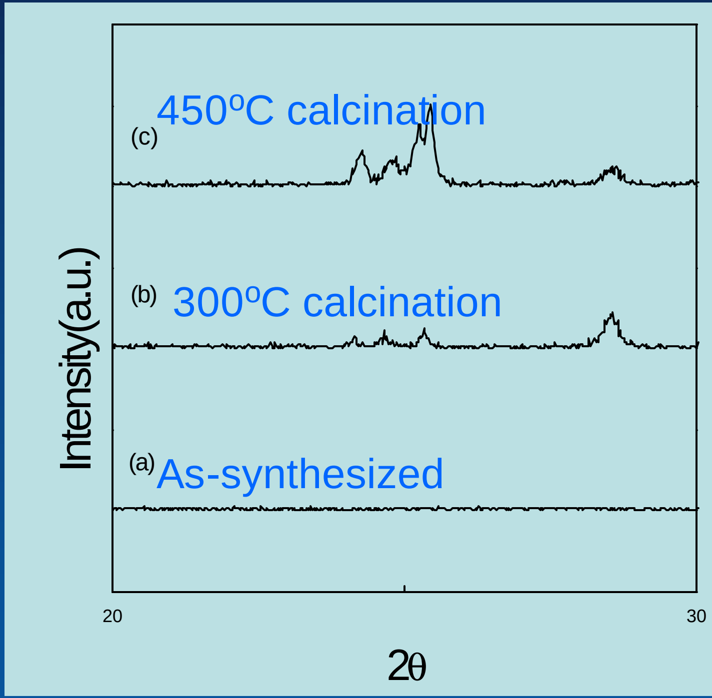
$[M^{n+}(\text{Peroxide})] + n(OH^-)_{sur} \rightarrow M(OH)_n$

↓

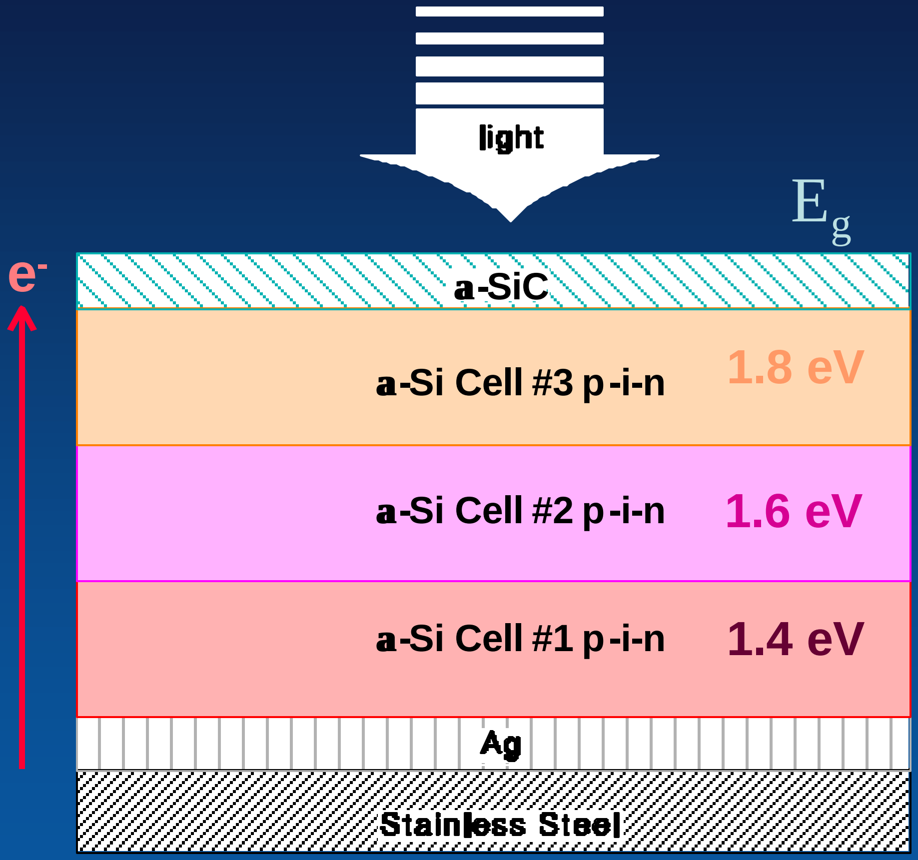
Calcination at elevated T

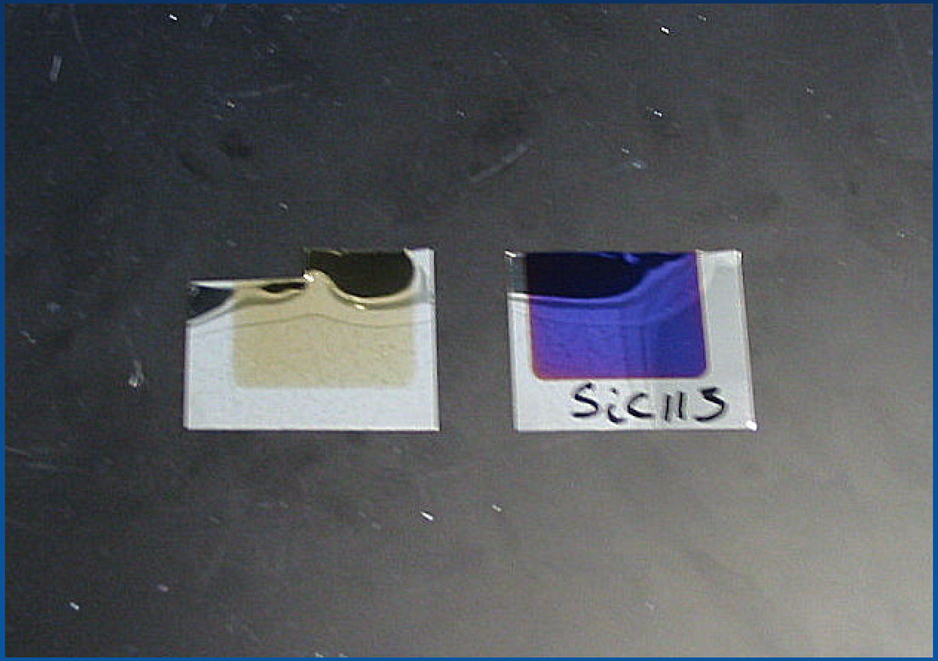
↓

MeO_x

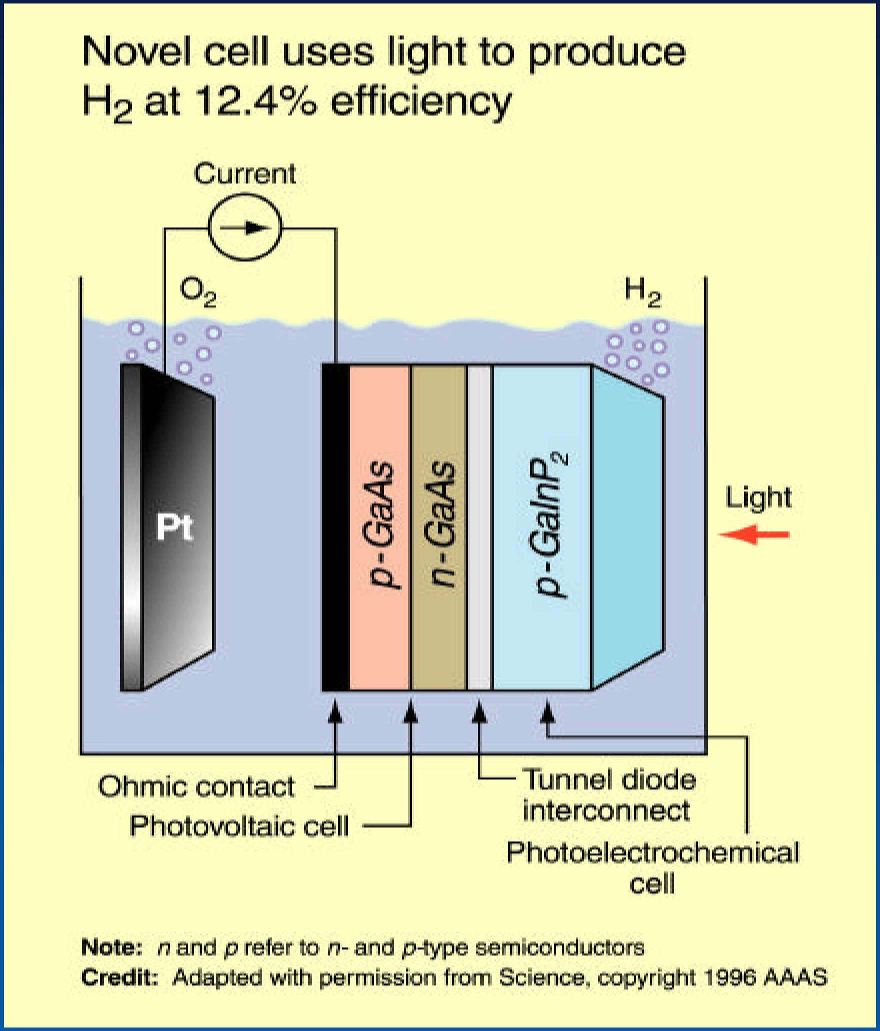


ECD Amorphous Silicon Triple Cell (reverse design for water splitting)





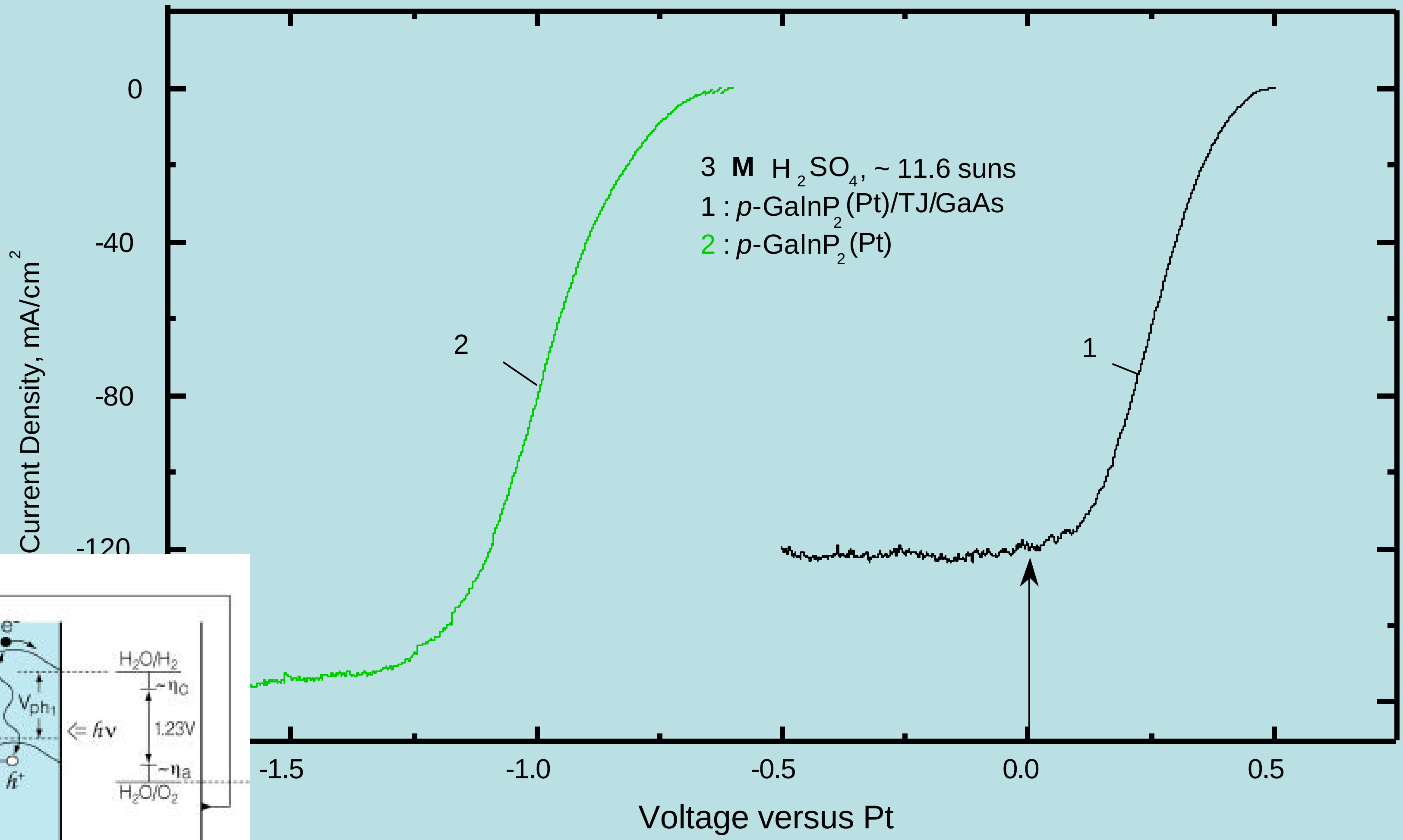
PV/PEC Photoelectrolysis Device <u>Science</u>, April 17 1998.

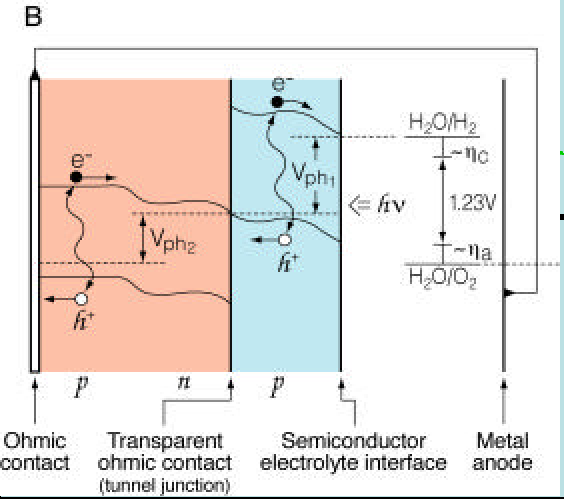


- ✓Direct water electrolysis.
- ✓Unique tandem (PV/PEC) design.
- ✓12.4% Solar-to-hydrogen

Experimental Cell

Comparison of *p*-$GaInP_2$ and PEC/PV device

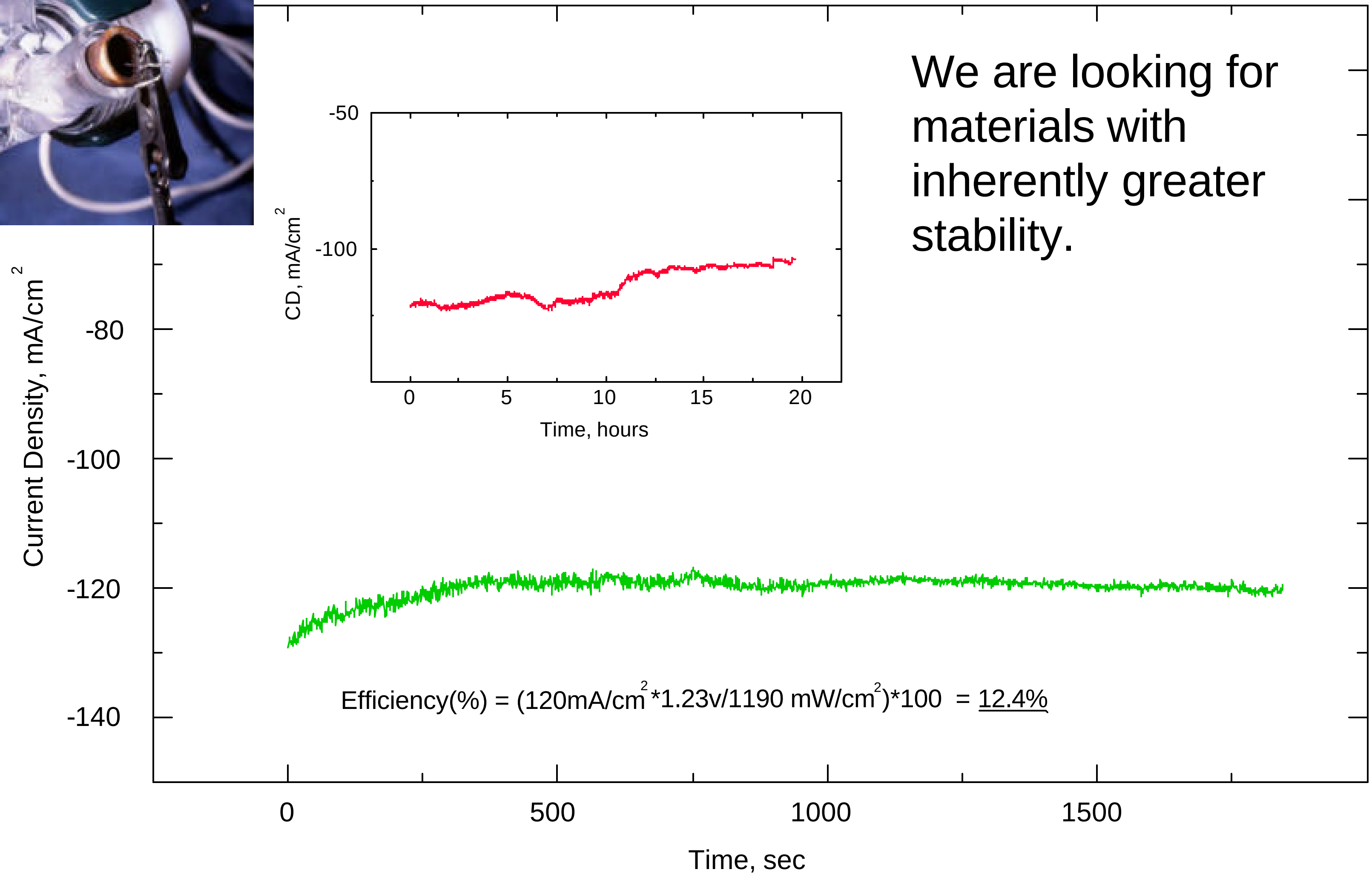




The GaAs integrated PV cell compensates for the energetic mismatch – but expensive

Photocurrent time profile for PEC/PV Water-Splitting device, showing current decay due to corrosion.

O. Khaselev and J. A. Turner, Science, **280**, pg 425 (1998).



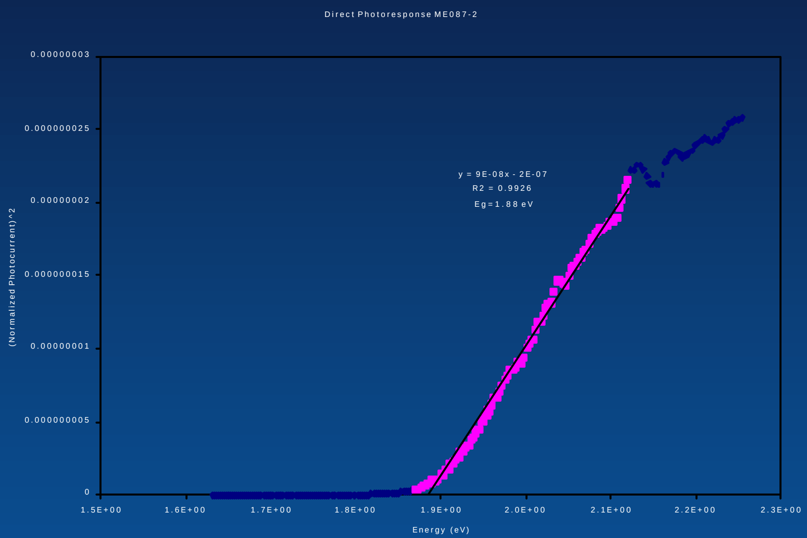
We are looking for materials with inherently greater stability.

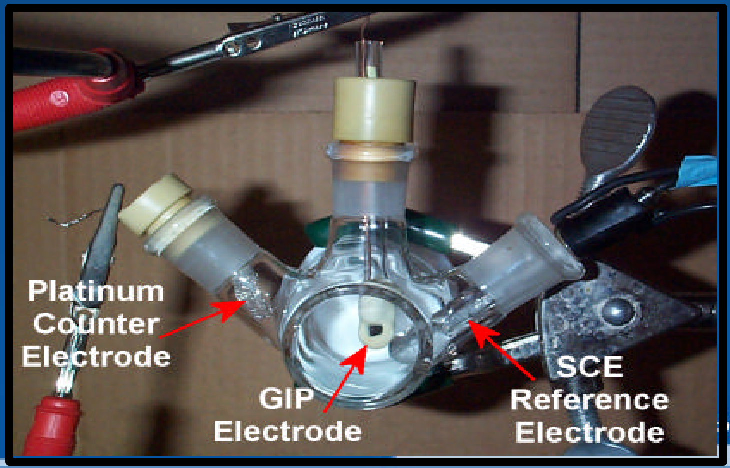
Other material possibilities include…..

Preliminary Investigation of $GaP_xN_{(1-x)}$ for PEC Water Splitting Systems

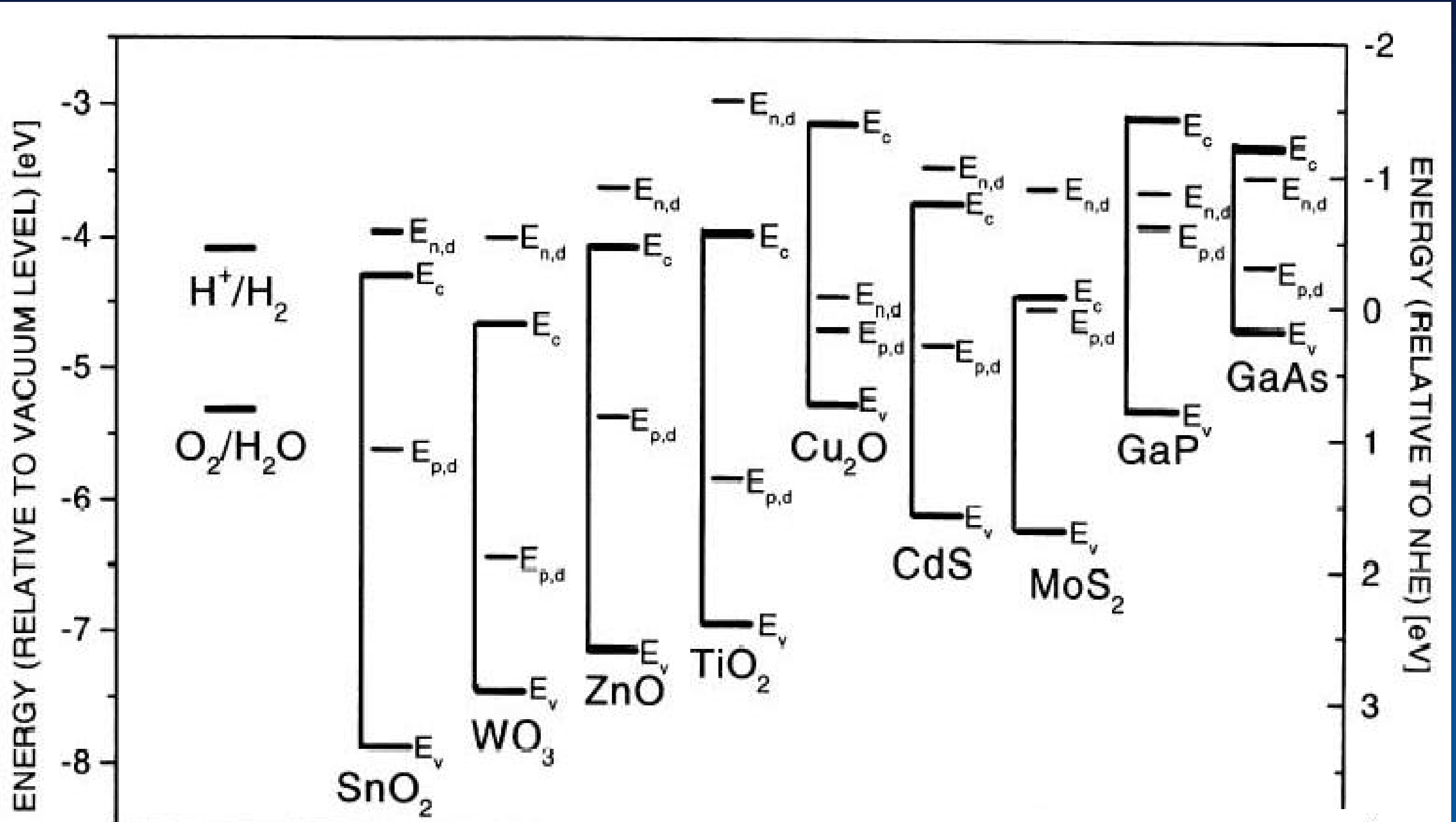
with Professor Carl Koval *University of Colorado at Boulder*

Electrode	% Nitrogen	Meas. Direct E_g
ME477-3	1.6	2.07
ME477-4	1.6	2.06
ME460-3	2.1	2.01
ME460-4	2.1	2.01
ME463-3	2.6	2
ME463-4	2.6	2
ME461-3	3.5	1.96
ME461-4	3.5	1.96





No theory can predict a material with adequate absorbance (bandgap/surface states), conductivity, bandedge locations, stability. Eric W. McFarland - UCSB



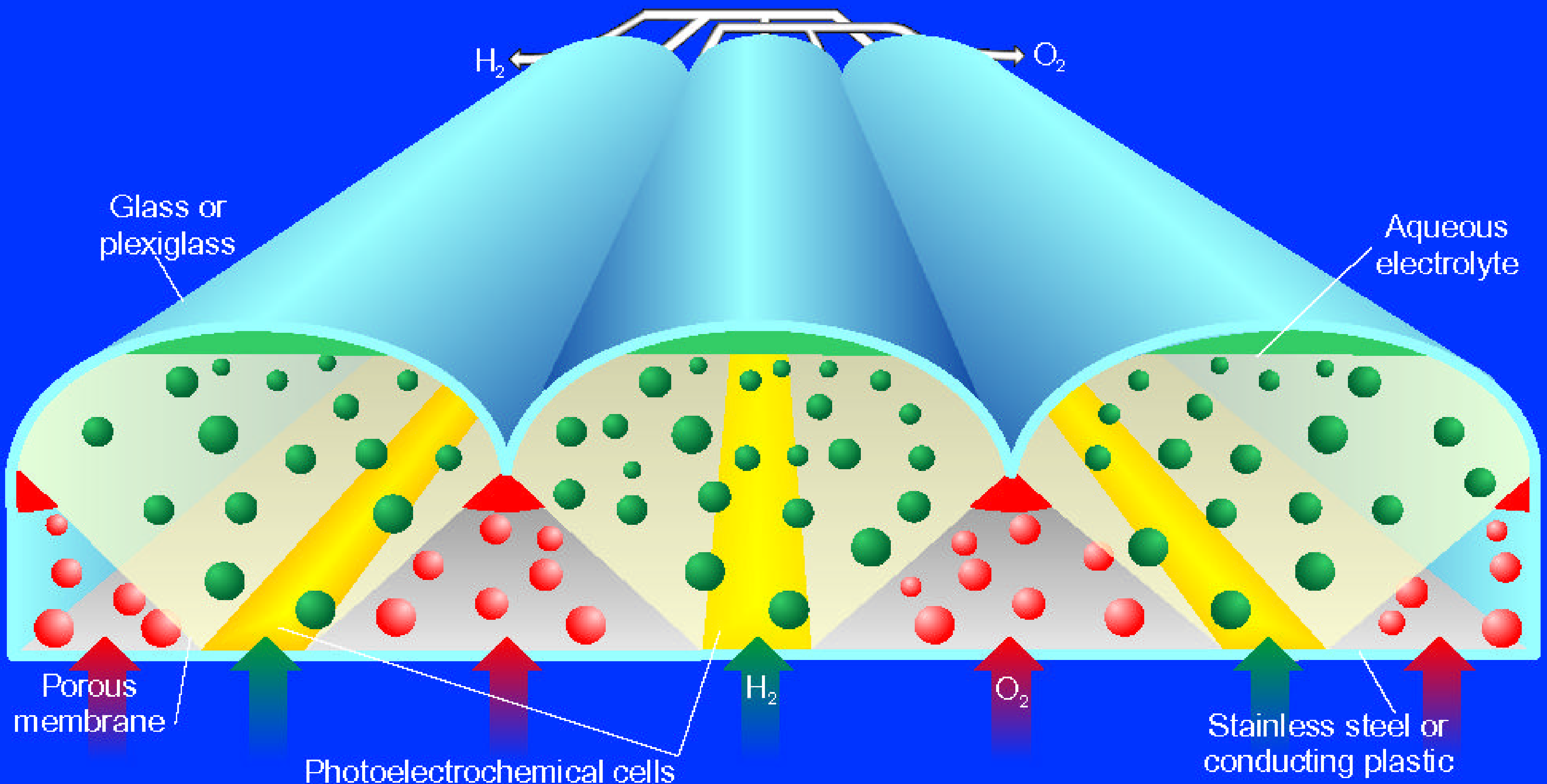
Bak et. al., *Int. J. Hydrogen Energy*, vol 27 (2002) 991-1022

No presently known material is suitable.

Future Directions for PEC Materials Research at NREL

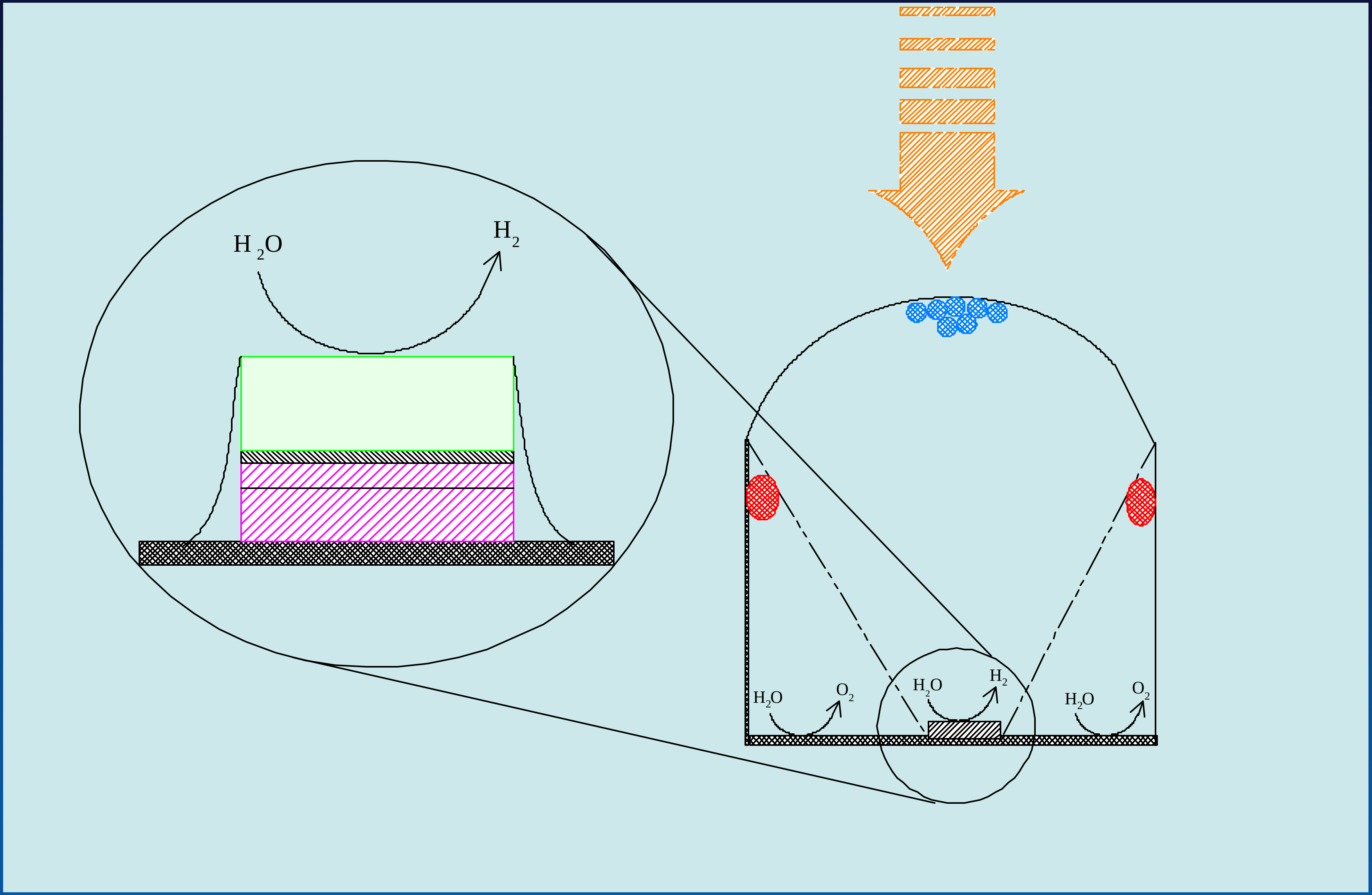
- Computational-combinatorial materials discovery.
  - Inverse band-structure calculations can be used to calculate semiconductor bandgap and band energies from the alloy composition.
  - Combine with calculation of corrosion resistance.
  - Grow new materials with NCPV
- Control of interfacial energetics through surface modification (Office of Science Proposal).

Conceptual Design of a Photoelectrochemical Water Splitting System with Light Concentration



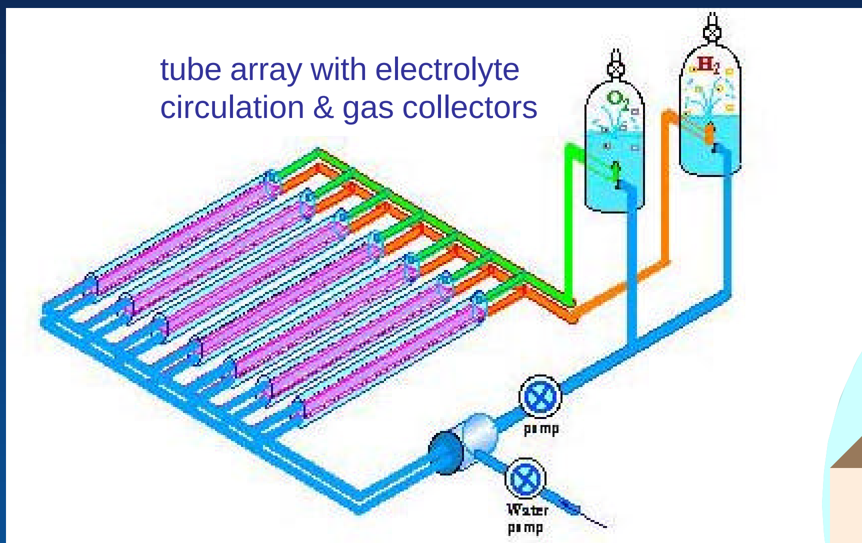
LS-CD24-a375001

PEC Device With Light Concentration

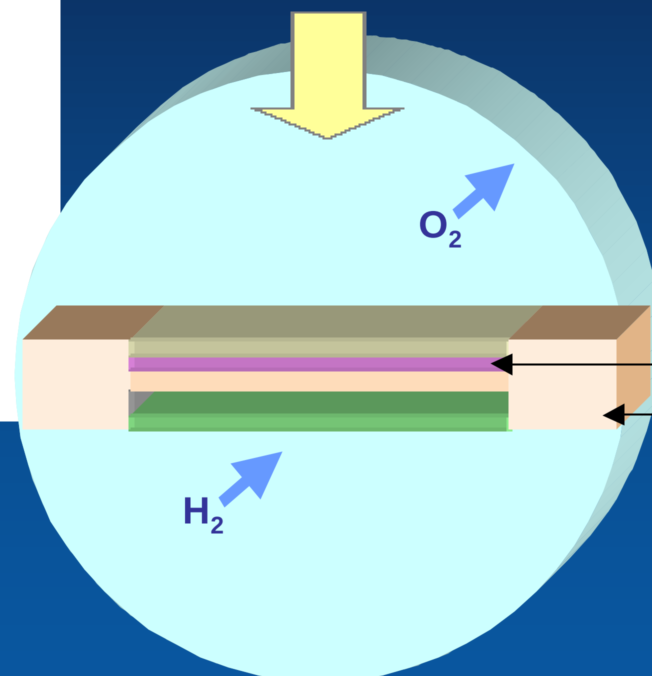


PEC H_2 Approach at HNEI

Multi-photon Planar Photoelectrodes using Low-cost Thin Film Materials



Incident light
(moderate concentration possible)



The PEC Hydrogen Production Lament

(From Gary Hodes)

If it is cheap, it will be inefficient
If it is efficient, it will be expensive
If it is cheap and efficient, it will be unstable
If it is cheap, efficient, and stable, then

Just before you collect your first royalty check,
someone will invent something better than hydrogen, or
You'll die, in which case

In Heaven, hydrogen will be a poisonous useless substance,
or, more likely

in Hell, hydrogen will be unstable under ambient conditions.