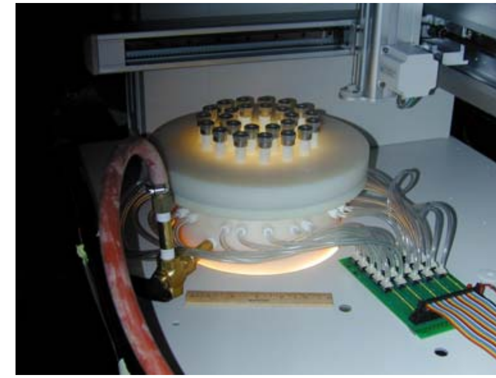
SRI International



Photoelectrochemical Water Splitting

GCEP Hydrogen Workshop

April 14 and 15, Stanford University

D. Brent MacQueen

Brent.macqueen@sri.com

SRI International, Menlo Park CA

Off We Go…

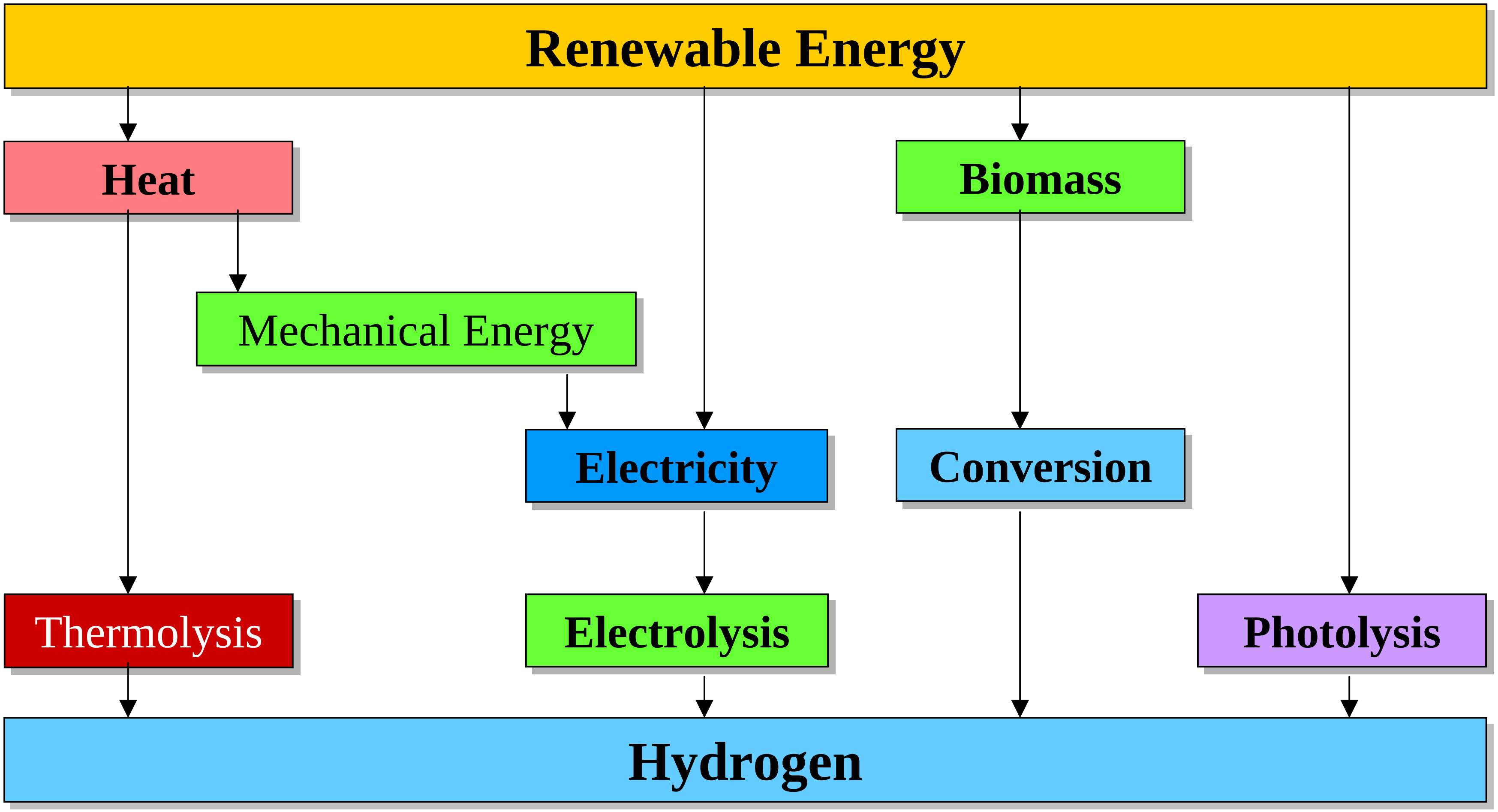
“We are at the peak of the oil age but the beginning of the hydrogen age. Anything else is an interim solution. The transition will be very messy, and will take many technological paths .....but the future will be hydrogen fuel cells.”

Herman Kuipers, Manager of Exploratory Research
Royal Dutch Shell

“General Motors absolutely sees the long-term future of the world being based on a hydrogen economy.”

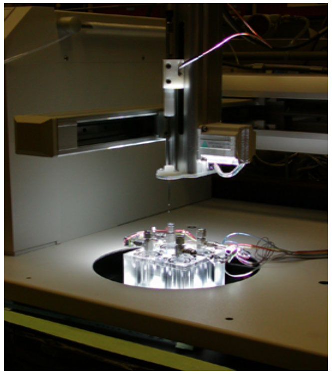
Larry Burns, Director of R&D, General Motors

Sustainable Paths to Hydrogen



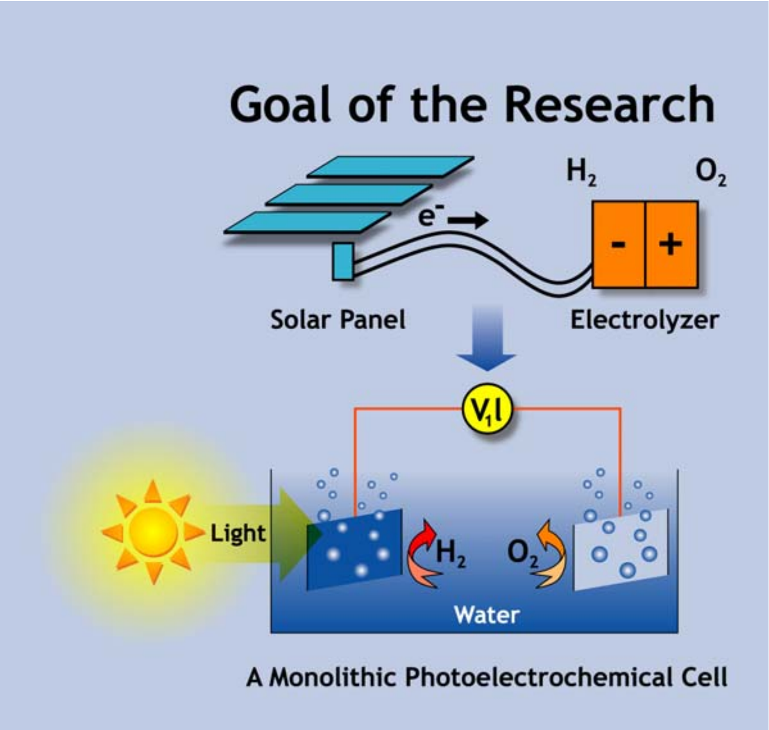
Hydrogen From Visible Light and Water

- **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.**



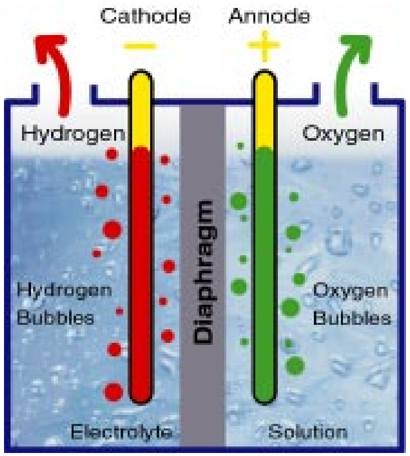
$$2H_2O \xrightarrow{\text{Visible Light}} 2H_2 + O_2$$

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 30% higher than separated system.

Efficiency Considerations



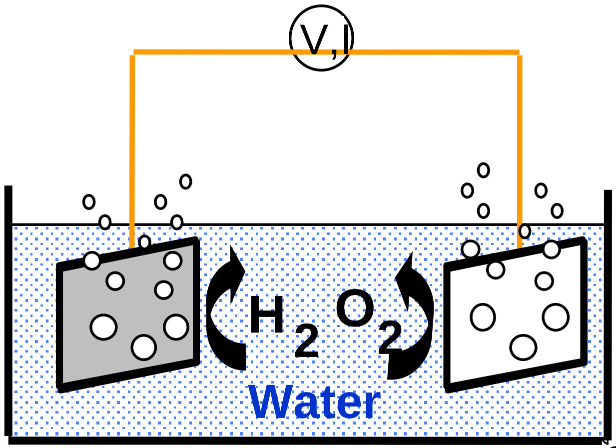
- Energy efficiency of electrolysis =

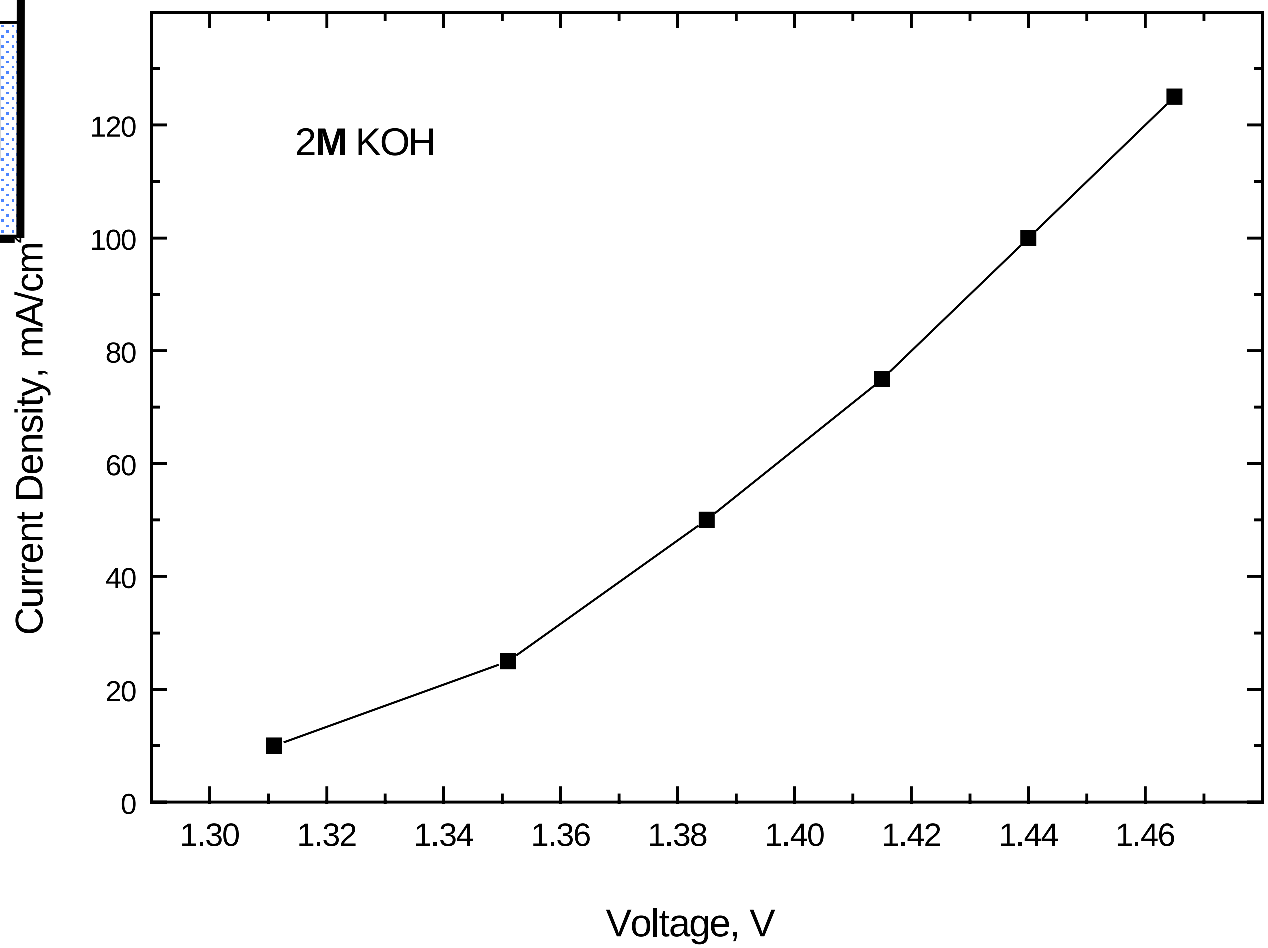
$$\frac{\text{Chemical potential}}{\text{Electrolysis potential}} = \frac{1.23}{1.9} = 65\%$$

- Coupling to a 12% PV array gives a solar-to-hydrogen efficiency of:

.12*.65 = 7.8%

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

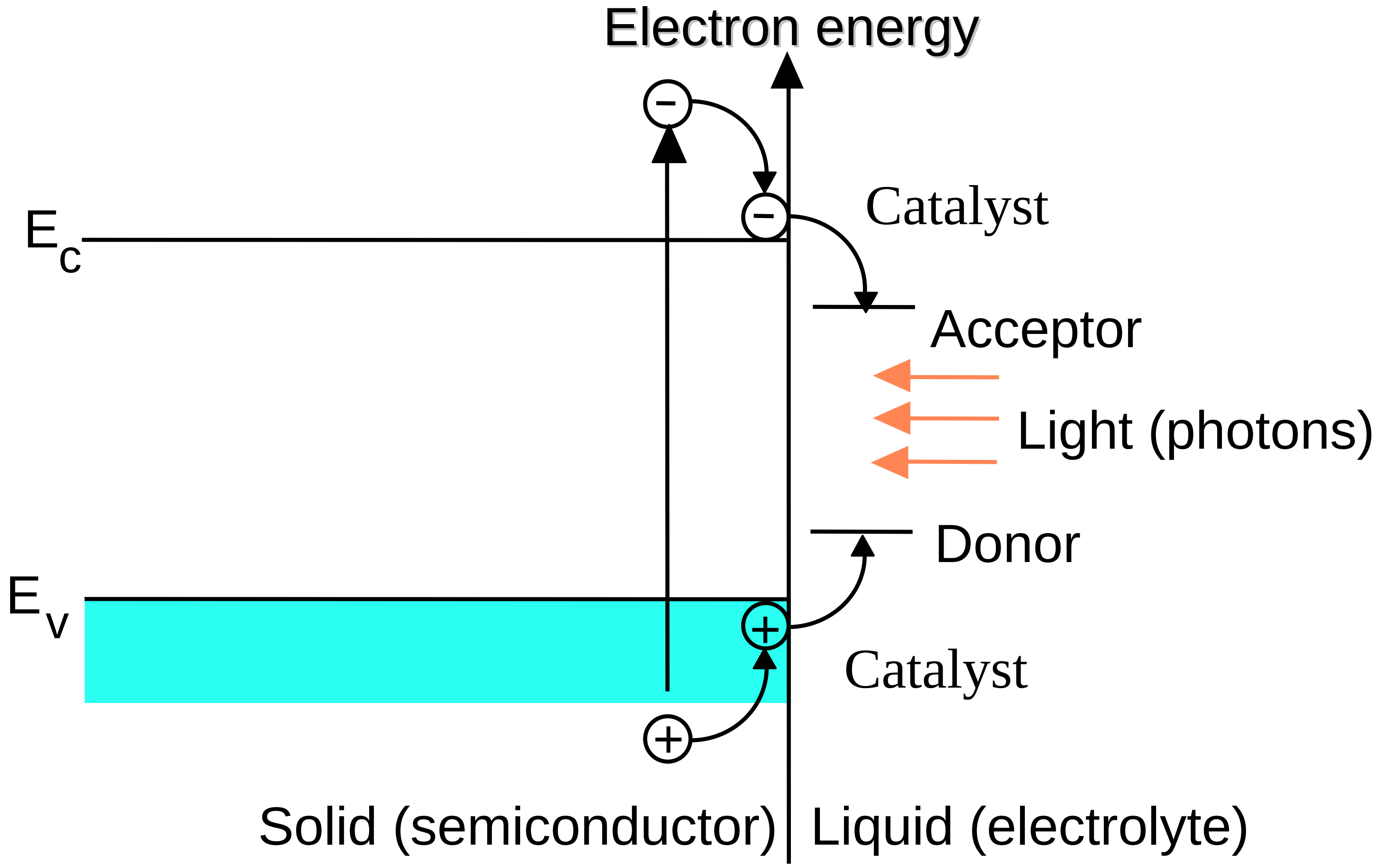




Comparison of PV/Electrolysis with Photoelectrolysis

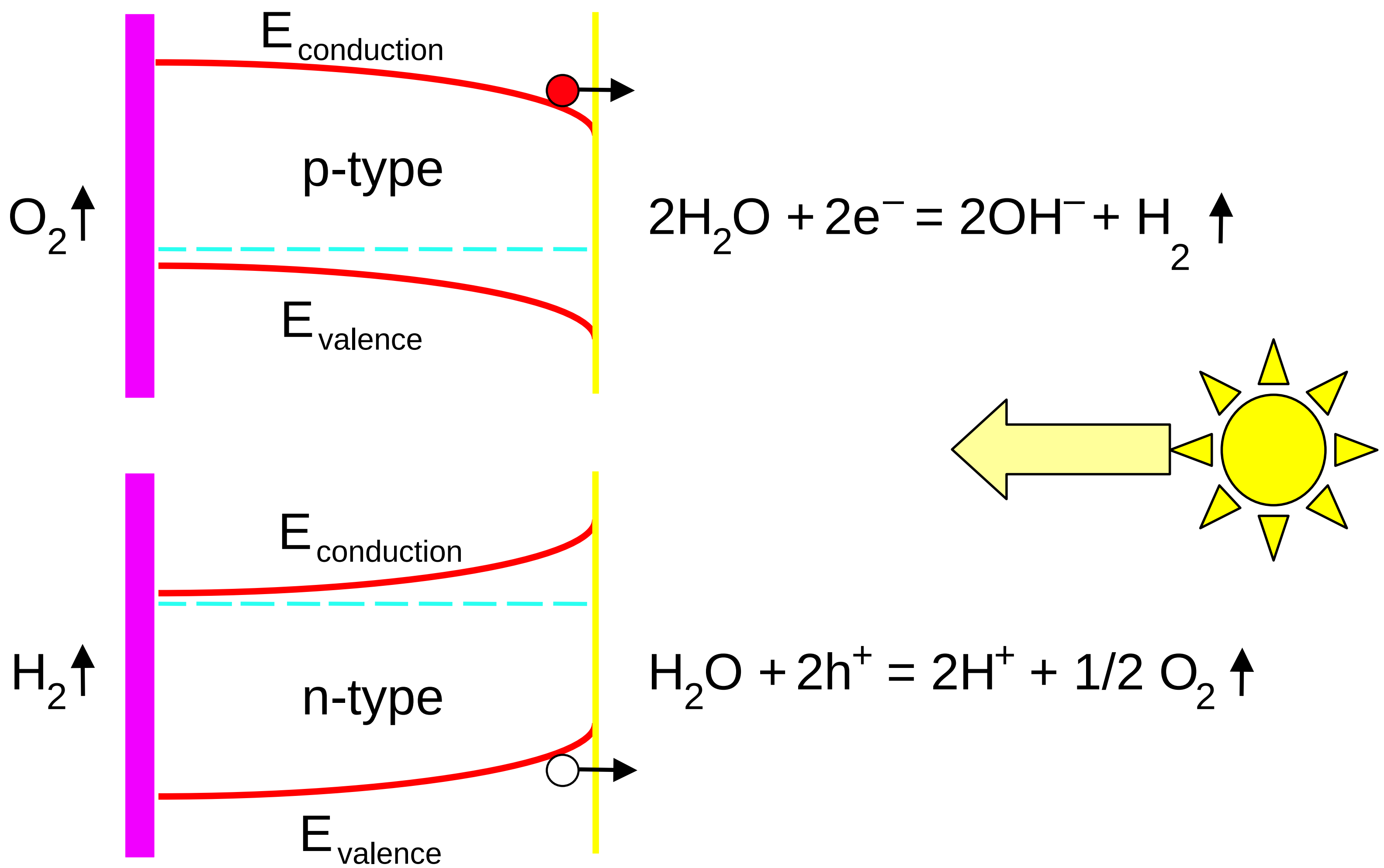
- For 12% PV system with an electrolysis efficiency of 65% (1.9V), we have a solar-to-hydrogen efficiency of 7.8%.
- For a direct conversion system with a base 12% PV efficiency, operating at an equivalent 1.45V, we can have a solar-to-hydrogen efficiency of 10.2%.
  - Equivalent electrolysis efficiency of 85% equals a 30% decrease in coverage area.

PEC 101



Electron energy
E c
Catalyst
Acceptor
Light (photons)
Donor
E v
Catalyst
Solid (semiconductor)
Liquid (electrolyte)

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



Historical Perspective

- First reported direct water splitting: A. Fujishima, K. Honda, *Nature 238, p* 37. 1972,
  - Single crystal TiO_2 with chemical (pH) bias of 840 mV.
- Best unbiased single semiconductor material efficiency to date is ~ 1% (solar-to-hydrogen)
- Best multijunction/PV bias is:
  - 4.5% (M. Grätzel et.al., Nature, 414, p338 2001)
  - 8.5% (S. Kahn et.al., Science, 297, p2243 2002)

Historical Perspective

"Holy Grails of Chemistry", *Accounts of Chemical Research,* vol 28 (1995)

Allen J. Bard & Marye Anne Fox "Artificial Photosynthesis: Solar Splitting of Water to Hydrogen and Oxygen"

Water splitting "Holy Grail" definition: "We want an efficient and long-lived system for splitting water to H_2 and O_2 with light in the terrestrial (AM1.5) solar spectrum at an intensity of one sun. For a practical system, an energy efficiency of at least 10% appears to be necessary. This means that the H_2 and O_2 produced in the system have a fuel value of at least 10% of the solar energy incident on the system….and will not be consumed or degraded under irradiation for at least 10 years."

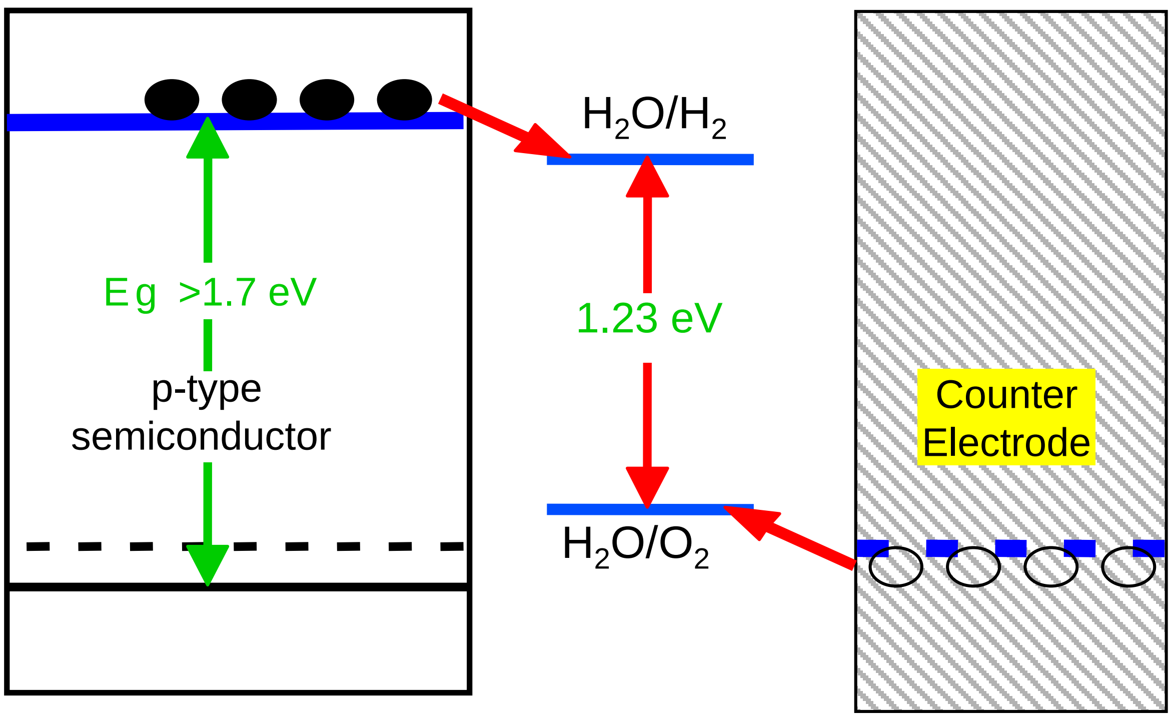
Material and Energetic Requirements

Bandgap

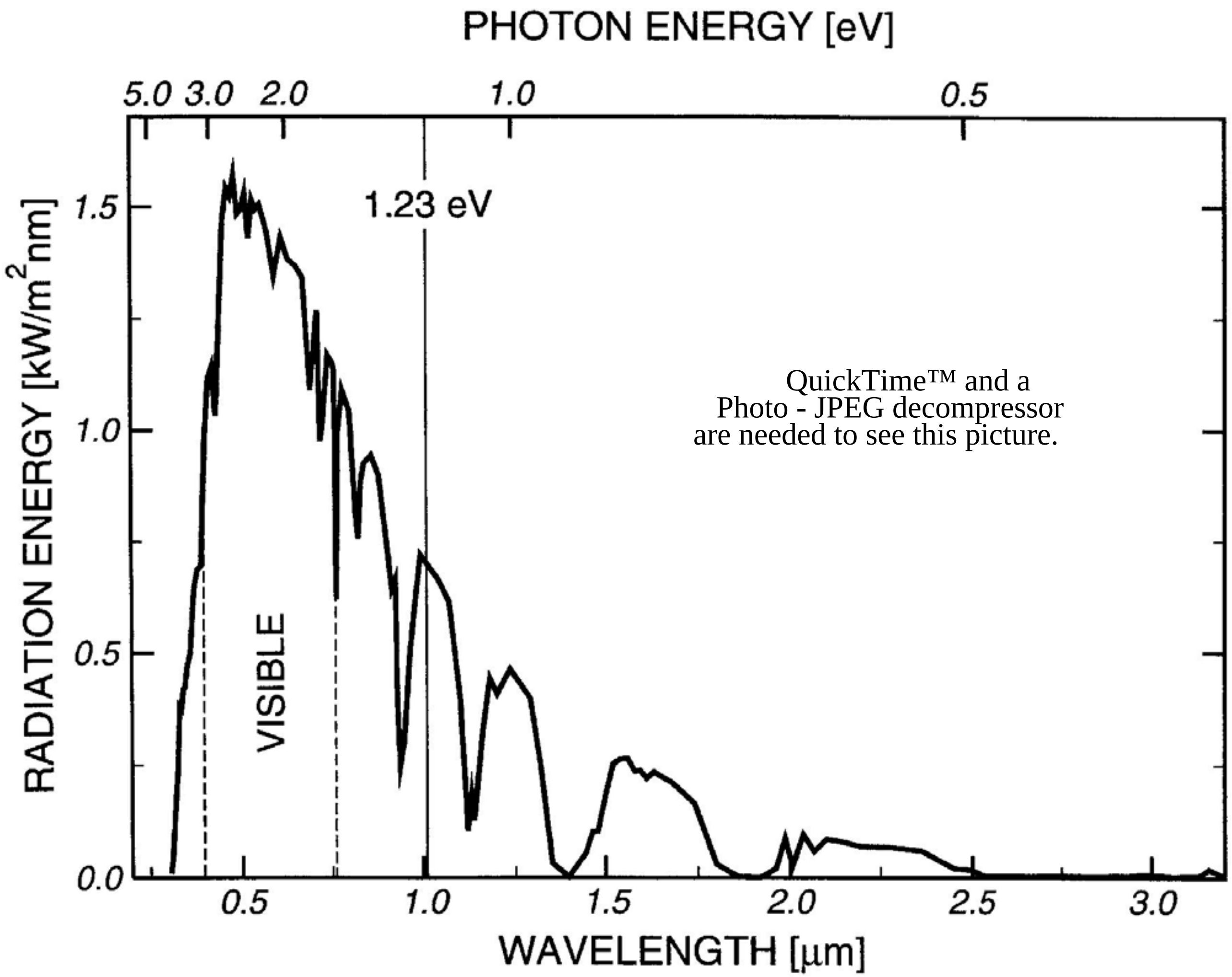
Band edge overlap

Fast charge transfer

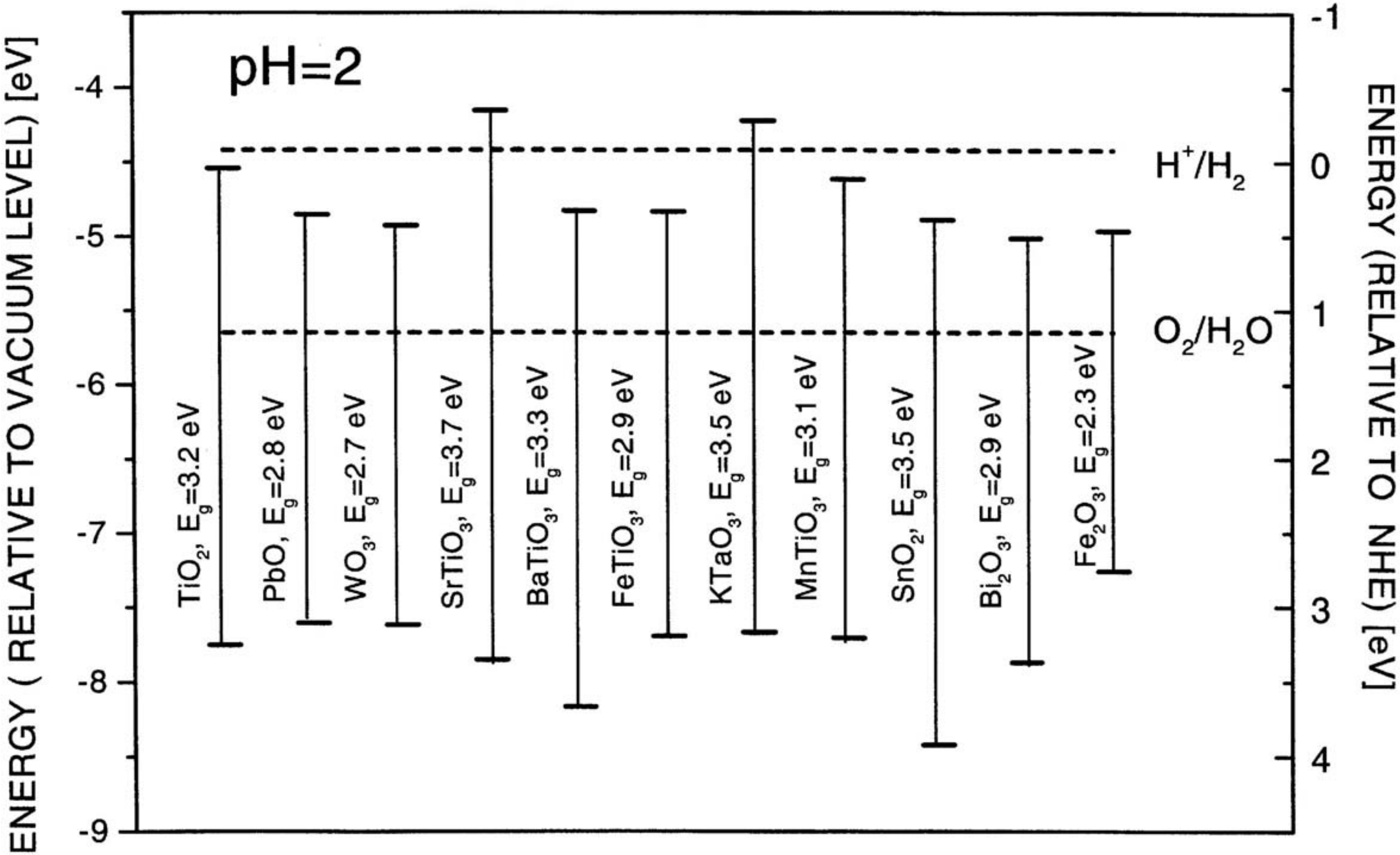
All three energetic conditions must be satisfied SIMULTANEOUSLY + ***Stability***



Bandgap Considerations



Bandedge Energetic Considerations



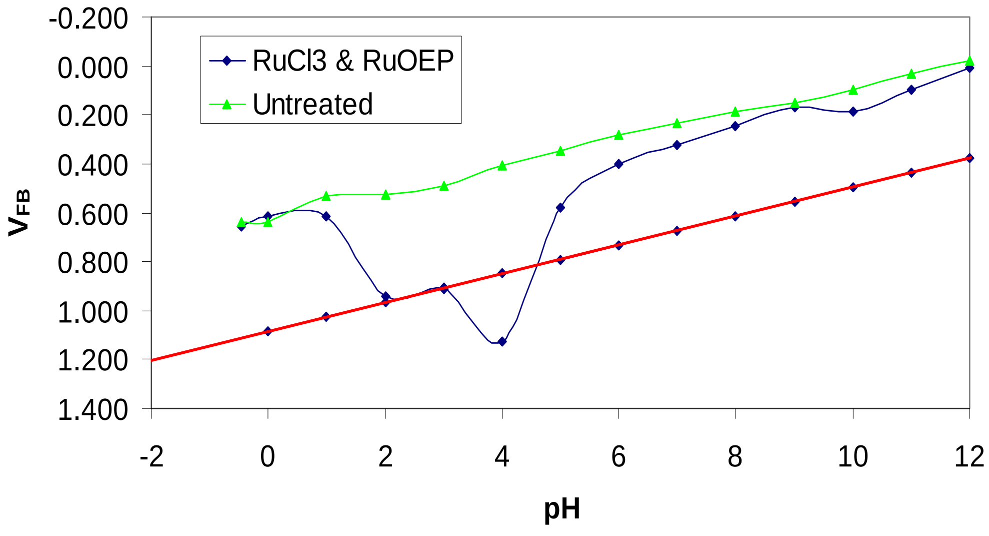
T. Bak, J. Nowotny, M. Rekas, C.C. Sorrell, International Journal of Hydrogen Energy **27** (2002) 991– 1022

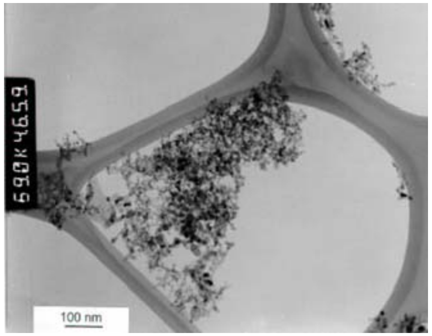
Technical Challenges

- Stability
  - The most photochemically stable semiconductors in aqueous solution are oxides, but their band gaps are either too large for efficient light absorption (~3 eV), or their semiconductor characteristics are poor.
- Efficiency (Bandgap)
  - For reasonable solar efficiencies, the band gap must be less than 2.2 eV, unfortunately, most useful semiconductors with bandgaps in this range are photochemically unstable in water.
- Energetics
  - In contrast to metal electrodes, semiconductor electrodes in contact with liquid electrolytes have fixed energies where the charge carriers enter the solution. So even though a semiconductor electrode may generate sufficient energy to effect an electrochemical reaction, the energetic position of the band edges may prevent it from doing so. For spontaneous water splitting, the oxygen and hydrogen reactions must lie between the valence and conduction band edges, and this is almost never the case.

Technical Challenges (Cont.)

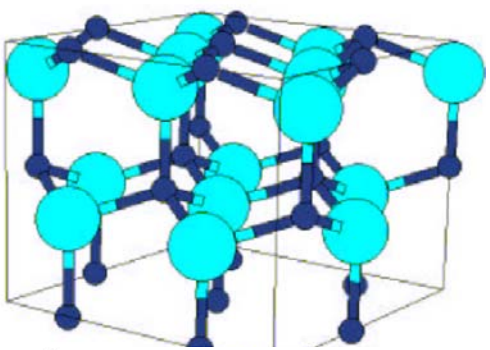
- Catalysts:
  - **Oxygen (most important -- highest energy loss).**
  - **Hydrogen**
  - **Transparency might be necessary**
- Band edge engineering.
- Semiconductor hybrid designs
- Low cost system designs featuring passive controls.

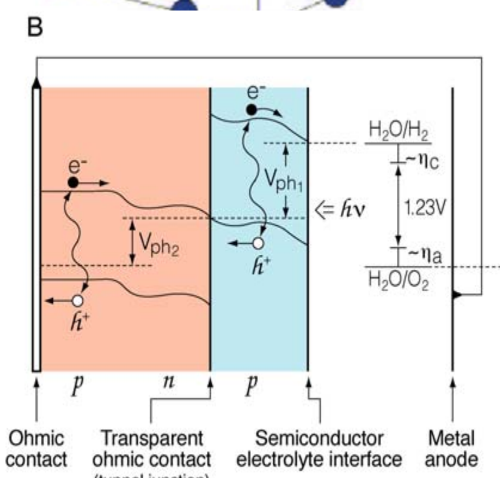


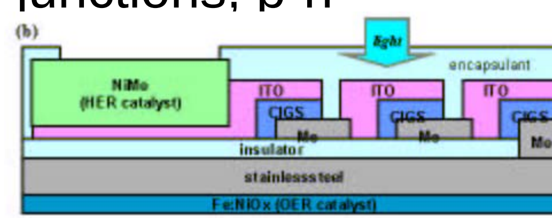


DOE PEC Program Areas of Effort

- 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
- Advanced structures/hybrid designs
  - Tandem cells, triple junctions, p-n combinations.
  - Specialty designs
- Catalysts
- High throughput Screening







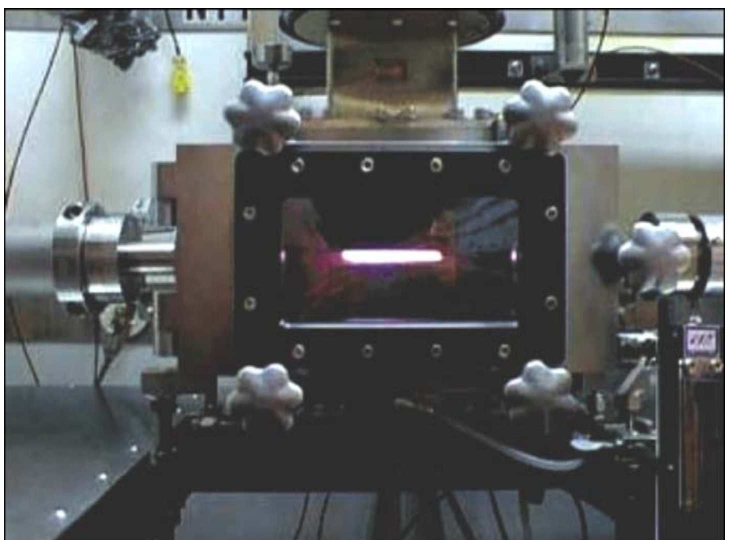
How Do We Advance

- Materials development
  - Rational high throughput screening
  - Standardized Testing
  - Self assembly
- Hybrid Design
- Reliable database of Materials and their properties with respect to PEC
- Accelerated testing protocols
  - How do you predict PEC performance of 10 years?

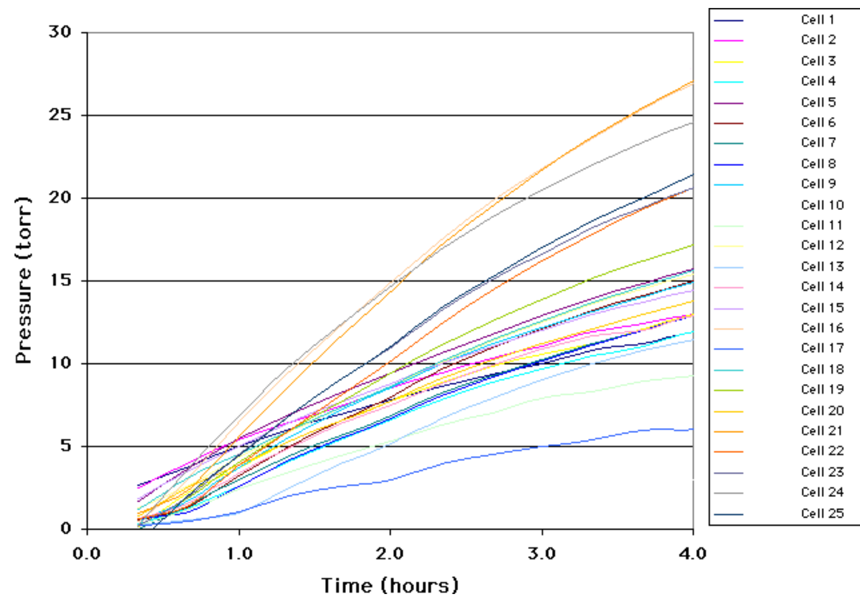
SRI International

Acknowledgments

- GCEP
- DOE (contract DE-FC36-01GO11093)
- John Turner, NREL



Laser Pyrolysis Reactor



Pres. Vs time plot from 25 cell photoreactor