Solar hydrogen production by photoelectrochemical (PEC) water-splitting: Advancing technology through the synergistic activities of the PEC working group (PEC WG)

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This presentation does not contain any proprietary, confidential, or otherwise restricted information.
The US DOE PEC Working Group approach towards efficient and durable solar H₂ production
Storing solar energy in the form of chemical bonds

H₂O \rightarrow \text{‘Black Box’ Device/Process} \rightarrow \text{sunlight} \rightarrow \text{H}_2, \text{O}_2
(Photo-)electrochemical schemes

Scheme 1: Separate devices for electricity generation and for H₂ production.

Scheme 2: One integrated device for solar harvesting and H₂ production.
Techno-Economics: PV-electrolysis

- “Electrolysis: Information and Opportunities for Electric Power Utilities”
  DOE-NREL Technical Report, NREL/TP-581-40605
  September 2006

- www.solarbuzz.com (February 20, 2012)

\[ \text{1000 kg H}_2/\text{day} \]

\[ \text{USA gasoline (2013): } $8.89/\text{kg} \]

\[ \text{Industrial Solar: } $17.39/\text{kg} \]

\[ \text{Electricity Costs: } $0.166/\text{kWh (2012)} \]

\[ \text{500 kW system sunny climate} \]

\[ \text{Commercial: } $5.40/\text{kg} \]

\[ \text{Industrial: } $4.09/\text{kg} \]

\[ \text{Electricity Costs: } $0.069/\text{kWh in 2005} \]

\[ \text{Decommissioning, Raw Material and Other Variable Costs: } $0.37/\text{kg} \]

\[ \text{Fixed O&M: } $1.30/\text{kg} \]

\[ \text{Capital Costs: } $3.68/\text{kg} \]
A world record PEC device

World Record Photoelectrolysis Device  

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

Operated for the U.S. Department of Energy by Midwest Research Institute • Battelle • Bechtel
The big question

Q: Can H₂ production by solar PEC water-splitting ever be cost-effective?

To answer this question, we need a techno-economic analysis!

Four reactor types

Type 1: Single Bed Particle Suspension
STH Efficiency 10%

Type 2: Dual Bed Particle Suspension
STH Efficiency 5%

Type 3: Fixed Panel Array
STH Efficiency 10%

Type 4: Tracking Concentrator Array
STH Efficiency 15%
Which system is the most cost-effective?

Recall that 1 kg of $H_2$ is the energy equivalent of 1 gallon of gasoline.

Sensitivity Analysis

How does the $/kg H_2$ change if we modify our assumptions on material performance?

**Type 1**
- **Base Case**: 10%, 1x, 5 years
- **Efficiency**: 15/10/5 %
- **Particle Cost Multiplier**: 0.1/1/20x
- **Lifetime**: 10/5/1 years

**Cost Sensitivity (\$ per kg H_2)**
- Base Case: $1.63
- Efficiency: $1.49
- Particle Cost Multiplier: $1.61
- Lifetime: $1.61

**Type 2**
- **Base Case**: 5.0%, 1x, 5 years
- **Efficiency**: 7.5/5.0/2.5 %
- **Particle Cost Multiplier**: 0.1/1/20x
- **Lifetime**: 10/5/1 years

**Cost Sensitivity (\$ per kg H_2)**
- Base Case: $3.20
- Efficiency: $2.53
- Particle Cost Multiplier: $3.13
- Lifetime: $3.17

**Type 3**
- **Base Case**: 10%, 153 $/m^2, 10 years
- **Efficiency**: 20/10/5 %
- **PEC Cell Cost**: 80/153/200 $/m^2
- **Lifetime**: 20/10/5 years

**Cost Sensitivity (\$ per kg H_2)**
- Base Case: $10.36
- Efficiency: $6.14
- PEC Cell Cost: $6.90
- Lifetime: $8.64

**Type 4**
- **Base Case**: 15%, 316 $/m^2, 10 years
- **Efficiency**: 25/15/10 %
- **PEC Cell Cost**: 200/316/450 $/m^2
- **Lifetime**: 20/10/5 years

**Cost Sensitivity (\$ per kg H_2)**
- Base Case: $4.05
- Efficiency: $2.85
- PEC Cell Cost: $3.70
- Lifetime: $3.85
Just how feasible are the efficiency assumptions in the techno-economic analysis (STH 10-25%)?
### Modeling ‘Realistic’ PEC efficiencies

#### Device Options

<table>
<thead>
<tr>
<th>Solid-state $V_{oc}$</th>
<th>Catalyst Activity</th>
<th>Shunt</th>
<th>Absorber Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High $V_{oc}$ ($\sim$470mV loss)</td>
<td>Precious metal (Pt/Ru)</td>
<td>Zero shunt losses ($R_{sh} = \infty \Omega$)</td>
</tr>
<tr>
<td></td>
<td>Low $V_{oc}$ ($\sim$590mV loss)</td>
<td>Non-precious metal (MoS$_2$/MnO$_x$)</td>
<td>“Significant” shunt losses ($R_{sh} = 100 \Omega$)</td>
</tr>
</tbody>
</table>

Calculated theoretical limits for a ‘realistic’ STH efficiency as a function of bandgap, taking into account:

- Reaction overpotentials ($H_2$ and $O_2$)
- Entropic losses ($V_{ph} < E_g$)
- Shunts

Can reach 10-11 % STH with $E_g \sim 2.3$ eV
Single-absorber devices

**Calculated theoretical limits for a ‘realistic’ STH efficiency as a function of bandgap, taking into account:**

- **Reaction overpotentials** \((H_2 \text{ and } O_2)\)
- **Entropic losses** \((V_{ph} < E_g)\)
- **Shunts**

![Diagram of a single-absorber device](image)

Multi-junction or Tandem Devices

Calculated theoretical limits for a ‘realistic’ STH efficiency as a function of bandgap, taking into account:

- Reaction overpotentials \((H_2 \text{ and } O_2)\)
- Entropic losses \((V_{ph} < E_g)\)
- Shunts

Can reach ~ 25 % STH with \(E_{g1} \sim 1.2 \text{ eV}\) & \(E_{g2} \sim 1.8 \text{ eV}\)

Calculated theoretical limits for a ‘realistic’ STH efficiency as a function of bandgap, taking into account:

- Reaction overpotentials ($H_2$ and $O_2$)
- Entropic losses ($V_{ph} < E_g$)
- Shunts

Can reach 15% STH with $E_{g1} \sim 1.6$ eV & $E_{g2} \sim 1.6$ eV

The US DOE PEC Working Group approach towards efficient and durable solar H₂ production

**DOE Targets:**
- >1000h @ STH 10-25%
- Projected PEC Cost: $2 - 4/kg H₂
Approach #1 (NREL): Stabilizing High Efficiency Materials & Devices

• High Efficiency
  o Work with single-crystal (high purity) semiconductors composed of Group IIIA and VA p-block elements (III-V)
  o Unrivaled photovoltaic efficiencies

• GaInP₂/GaAs Tandem
  o Only demonstrated system that exceeds unbiased 10% solar-to-hydrogen target
    - 12.4% with Pt-black counter electrode, >16% with RuO₂ CE
  o Metal organic chemical vapor deposition (MOCVD) synthesis
    - Synthesis by NREL’s III-V team

• Focus: Improve Durability
  o High efficiency III-V’s prone to degradation during PEC operation
  o Need enhanced corrosion resistance to meet both efficiency and durability targets

p-GaInP₂/GaAs tandem after 24 hours of operation in 3M H₂SO₄

The MVS/HNEI research team is accelerating the development of three important thin-film material classes with high potential for reaching low-cost H₂ PEC production.

Development of new metal oxides

2.2eV CuWO₄

Chalcogenides bandgap engineering

CuWO₄-CNT nanocomposite

CuₓGa₁₋ₓSe₂

CuInₓGa₁₋ₓS₂

1.6 eV 2.0 eV 2.2 eV 2.4 eV
Approach #3 (Stanford Univ.): 3rd Generation Device Structures, High Surface Area Scaffolds for PEC Materials

Conventional Planar Devices
- Thick hematite layer
- Dense ITO layer
- Glass

Low IQE (long charge trans.)
High loading (high OD)
Low device performance

HSE Support
- Dense ITO layer
- Glass

High IQE (short charge trans.)
Low loading (low OD)
High device performance

Interfacial Engineering
- Ti-Hematite | HSE-ITO
- ALD TMT Tin Oxide
- Post annealed ALD TDMA Tin Oxide
- Spray Tin Oxide
- As-prepared ALD TDMA Tin Oxide

6x improvement in J\text{photo} from SnO\text{2} interfacial layer

Graphs show:
- Photo current onset
- Dark current onset
- Saturated photo current

No SnO\text{2}

6x improvement in J\text{photo} from SnO\text{2} interfacial layer

HSE

Low load

High load
Theory at the molecular-scale (LLNL): Ab-initio molecular dynamics (MD) to investigate the electrode-electrolyte interface

Ab-initio molecular dynamics simulations of water-InP and water-GaP interfaces

Experimental observation: Pt loading on GaP(001) improves the conversion efficiency *only a little* [ChemPhysChem 13, 3053 (2012)]
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Summary

• Technologically, PEC water-splitting has already been accomplished.

• A techno-economic analysis shows that it is possible to reach cost targets if materials with appropriate properties can be developed.

• A feasibility study shows that these properties are within reach based on the current state of materials development.

• The PEC WG is collaborating synergistically to accelerate R&D efforts.

DOE Targets:
>1000h @STH 10-25%
Projected PEC Cost:
$2 - 4/kg H₂