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 $\text{H}_2$ production.

**DOE Targets:**
- $>1000\text{h @}\text{STH} 10-25\%$
- Projected PEC Cost: $2 - 4/\text{kg} \text{H}_2$
Storing solar energy in the form of chemical bonds

\[ \text{sunlight} \rightarrow \text{Device/Process} \rightarrow \text{H}_2 \text{O} \rightarrow \text{O}_2 \text{ and H}_2 \]
(Photo-)electrochemical schemes

Scheme 1: Separate devices for electricity generation and for $\text{H}_2$ production.

Scheme 2: One integrated device for solar harvesting and $\text{H}_2$ 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)

![Diagram showing the costs of hydrogen production from solar energy and comparison with USA gasoline costs.]

- **Industrial**
  - $4.09/kg
  - $0.045/kWh

- **Commercial**
  - $5.40/kg
  - $0.069/kWh in 2005

- **Industrial Solar**
  - $17.39/kg
  - $0.166/kWh (2012)
  - 500 kW system
  - sunny climate

- **USA gasoline (2013)**
  - $8.89/kg
A world record PEC device


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

![Experimental Cell](image)

Operated for the U.S. Department of Energy by Midwest Research Institute • Battelle • Bechtel
Q: Can $\text{H}_2$ 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%
- Diagram showing a bed with particles and reaction arrows indicating $4H^+ + 4e^- \rightarrow 2H_2$ and $2H_2O + 4H^+ \rightarrow O_2 + 4H^+$.

**Type 2: Dual Bed Particle Suspension**
- STH Efficiency: 5%
- Diagram showing two beds with perforated pipes and reaction arrows indicating $4hν + 4H^+ + 4A \rightarrow 2H_2 + 4A$ and $4hν + 2H_2O + 4A \rightarrow O_2 + 4H^+ + 4A$.

**Type 3: Fixed Panel Array**
- STH Efficiency: 10%
- Diagram showing a panel with electrolyte, O$_2$, H$_2$, and water inlet and outlet.

**Type 4: Tracking Concentrator Array**
- STH Efficiency: 15%
- Diagram showing a concentrator panel with a parabolic cylinder reflector and linear PEC cell.
Which system is the most cost-effective?

Recall that 1 kg of H₂ is the energy equivalent of 1 gallon of gasoline.

How does the $/kg H_2 change if we modify our assumptions on material performance?
Just how feasible are the efficiency assumptions in the techno-economic analysis (STH 10-25%)?
Modeling ‘Realistic’ PEC efficiencies

Device Options

Solid-state $V_{oc}$
- High $V_{oc}$ (~470mV loss)
- Low $V_{oc}$ (~590mV loss)

Catalyst Activity
- Precious metal (Pt/Ru)
- Non-precious metal (MoS$_2$/MnO$_x$)

Shunt
- Zero shunt losses ($R_{sh} = \infty \Omega$)
- “Significant” shunt losses ($R_{sh} = 100 \Omega$)

Absorber Configuration
- Single
- Dual stacked
- Dual side-by-side

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
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

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:
Stabilize High Efficiency Systems

Approach 2:
Enhance Efficiency in Thin-Film Materials

Approach 3:
Develop 3rd Generation Materials and Structures
Approach #1 (NREL): Stabilizing High Efficiency Materials & Devices

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

- **GaInP$_2$/GaAs Tandem**
  - Only demonstrated system that exceeds unbiased 10% solar-to-hydrogen target
    - 12.4% with Pt-black counter electrode, >16% with RuO$_2$ CE
  - Metal organic chemical vapor deposition (MOCVD) synthesis
    - Synthesis by NREL’s III-V team

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

\[ \text{Efficiency} = \frac{(120 \text{mA/cm}^2 \times 1.23 \text{V}) \times 100}{1190 \text{mW/cm}^2} = 12.4\% \]


- p-GaInP$_2$/GaAs tandem after 24 hours of operation in 3M H$_2$SO$_4$
Approach #2 (MVSystems / HNEI): Improving thin-film efficiency

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

- **a-SiC: surface energetics management**
- **Chalcogenides bandgap engineering**

**2.2eV CuWO₄**

**CuWO₄-CNT nanocomposite**

**Chalcogenides bandgap engineering**

- CuGaSe₂
- 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$_2$ interfacial layer

- Photo current onset
- E (V vs RHE)
- Dark current onset

- Low load
- High load
- HSE

- $J$ (mA/cm$^2$)
- 0.0
- 0.2
- 0.4
- 0.6
- 0.8

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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)]

- InP HB network explores a broader phase space
- GaP HB network prohibits interchange between most topologies

InP-water interface: good h⁺ transport

GaP-water interface: bad h⁺ transport
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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.