GLOBAL CLIMATE AND ENERGY PROJECT | STANFORD UNIVERSITY

Energy Tutorial:
Synthetic Fuels 101

GCEP RESEARCH SYMPOSIUM 2014 | STANFORD, CA

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GLOBAL CHALLENGES – GLOBAL SOLUTIONS – GLOBAL OPPORTUNITIES

The goal for today

To discuss unconventional, emerging technologies that could produce fuels in a renewable, sustainable manner.

Our definition of "Synthetic Fuels" for today's purpose.

Some previous GCEP Energy 101 Tutorials that are complementary to the material presented today:

Solar Energy 101	Prof. Nathan Lewis
Solar Cells 101	Prof. Michael McGehee
Electrocatalysis 101	Prof. Thomas F. Jaramillo

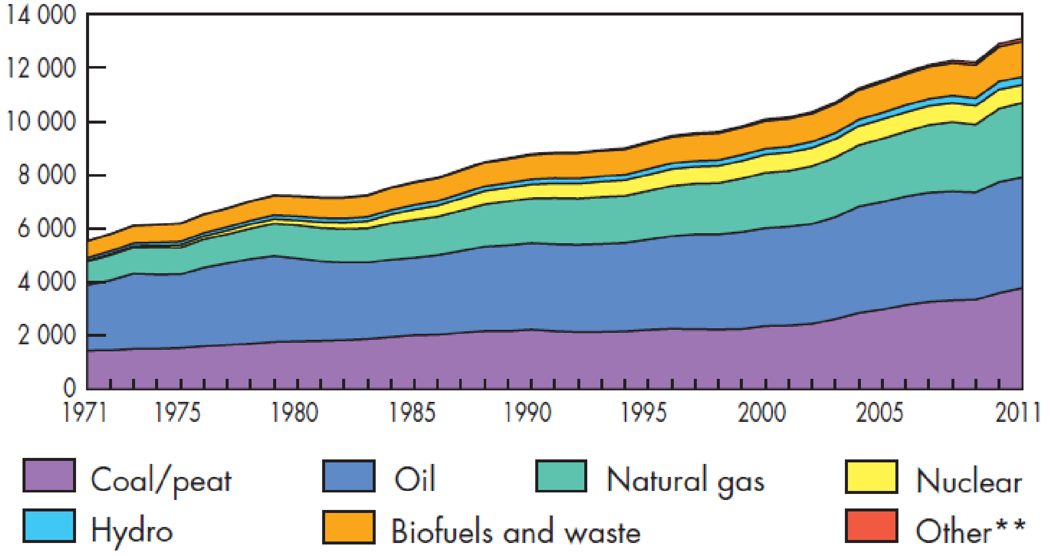
Outline

- Fossil fuels
- Pathways to renewable, synthetic fuels
- Overview of thermodynamics & efficiency
- Electrochemical & Photo-electrochemical pathways
  - Hydrogen fuels
    - Lab-based devices
    - Techno-economics of large-scale facilities
    - Chemical & physical factors at play → modeling efficiency
  - Extending to carbon-based fuels
- Summary

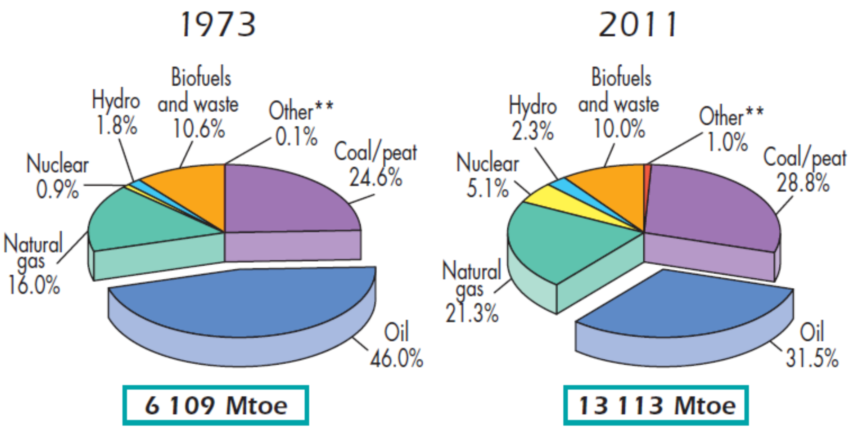
Total primary energy supply: The facts

World

World* total primary energy supply from 1971 to 2011 by fuel (Mtoe)



- Today: 17 TW of power.
- 80% comes from fossil fuels (oil, coal, natural gas).
- oil : coal : natural gas ≈ 1 : 1 : 1.



*World includes international aviation and international marine bunkers.
**Other includes geothermal, solar, wind, heat, etc.

International Energy Agency (IEA) “Key World Energy Statistics” (2013)

Fossil fuels: An amazing resource

- Consider petroleum/gasoline
  - Massive world-wide resource, extremely abundant
    - Provides ~ 5 TW of power across the globe (out of 17 TW total)
  - Huge energy density
    - Can drive a car 500 miles on one tank of gas, or fly a commercial jet half-way around the earth.
    - A full tank of gasoline in a car is approximately equivalent to:
      - The potential energy of 1 million gallons of water at 200 ft elevation
      - The electrical energy stored in 80,000 iPhone 6 batteries
  - High power density
    - Can power anything… automobiles, trucks, shipping vessels, commercial and military aircraft….
    - The power transfer in filling up your car at the pump is approximately 5 MW.
  - Yet very chemically stable
    - When you drive your car, do you worry about it exploding?
  - Easy to store and to transport
    - Approx. 100,000 miles of gasoline pipeline in the USA.
    - As a liquid fuel it can fit into any size and shape of container with ease.
  - Cost
    - How do the 'high' gas prices of today (~ $3-$4/gallon) compare with other consumer goods? Bottled water? Milk? Orange juice?
  - Convenience
    - Have you ever timed yourself at the gas pump? How long does it take to fill the tank?

No wonder why we consume so much petroleum!
This is also why fossil fuels are so hard to beat….

Gasoline and related hydrocarbons

<u># of carbon atoms</u>

Heavier

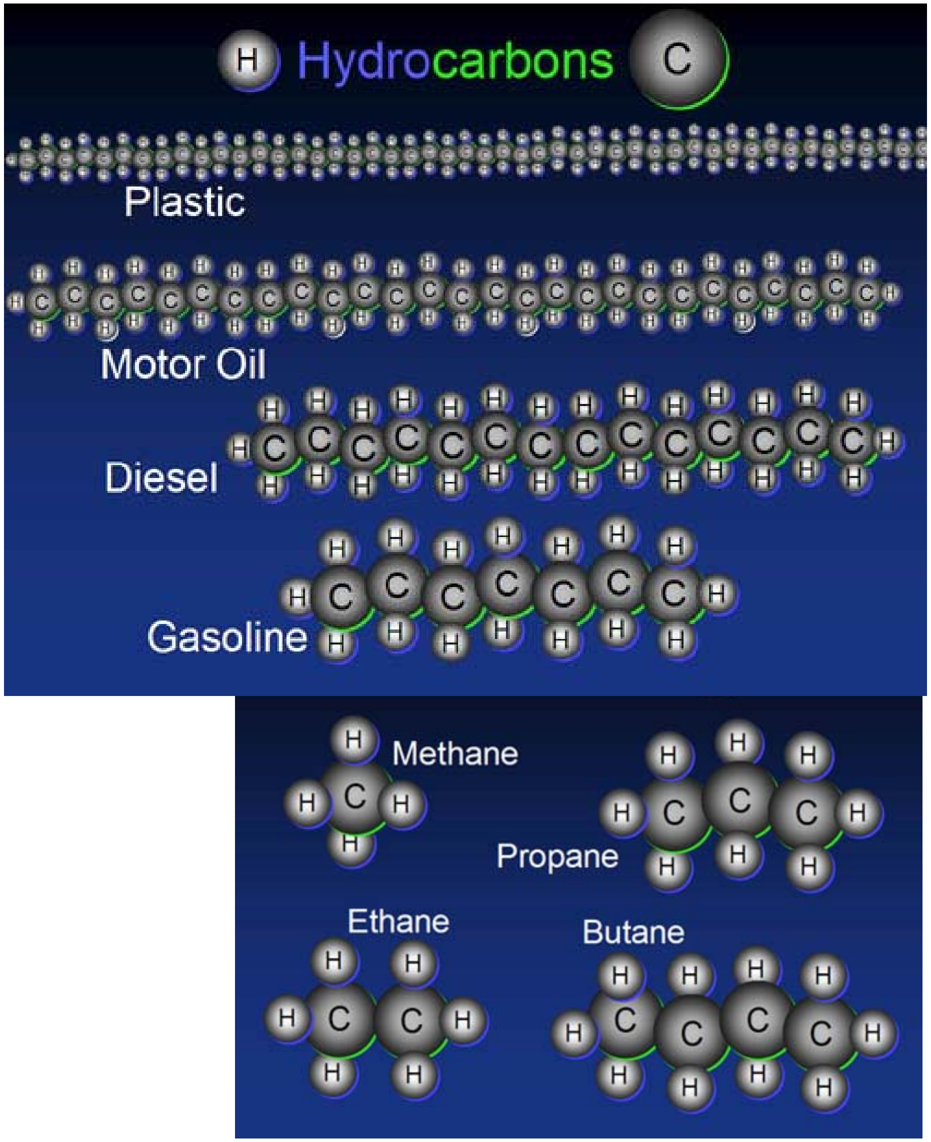
100-10,000

15-25

7-18

5-9

1-4



Petroleum Refining

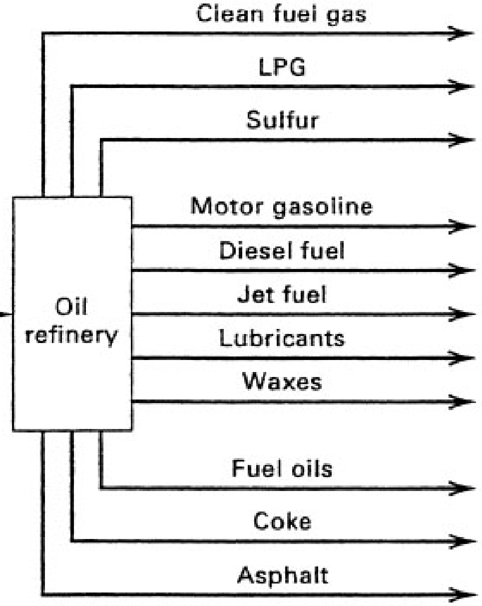
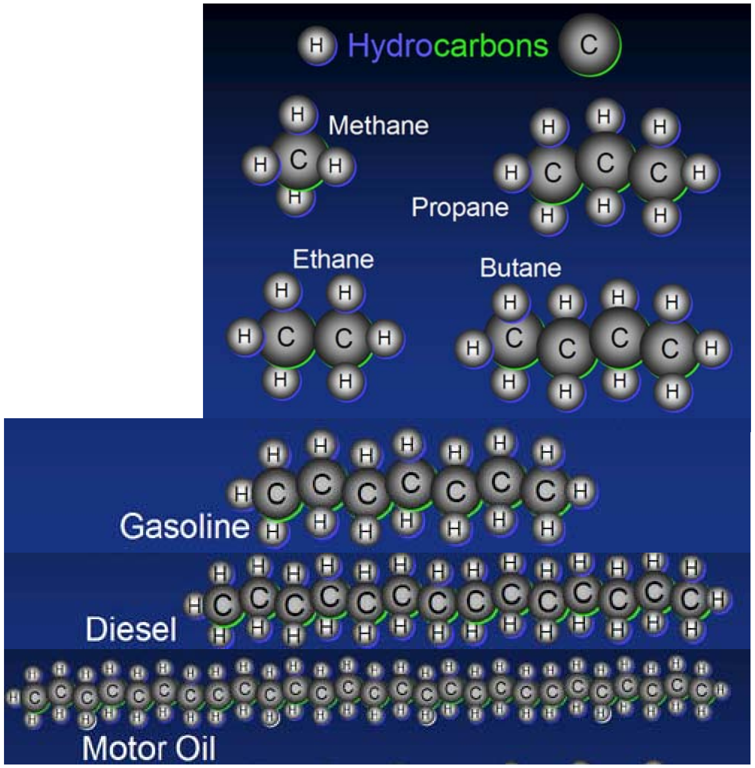


Figure 1.1 Refinery for converting crude oil into a variety of marketable products.

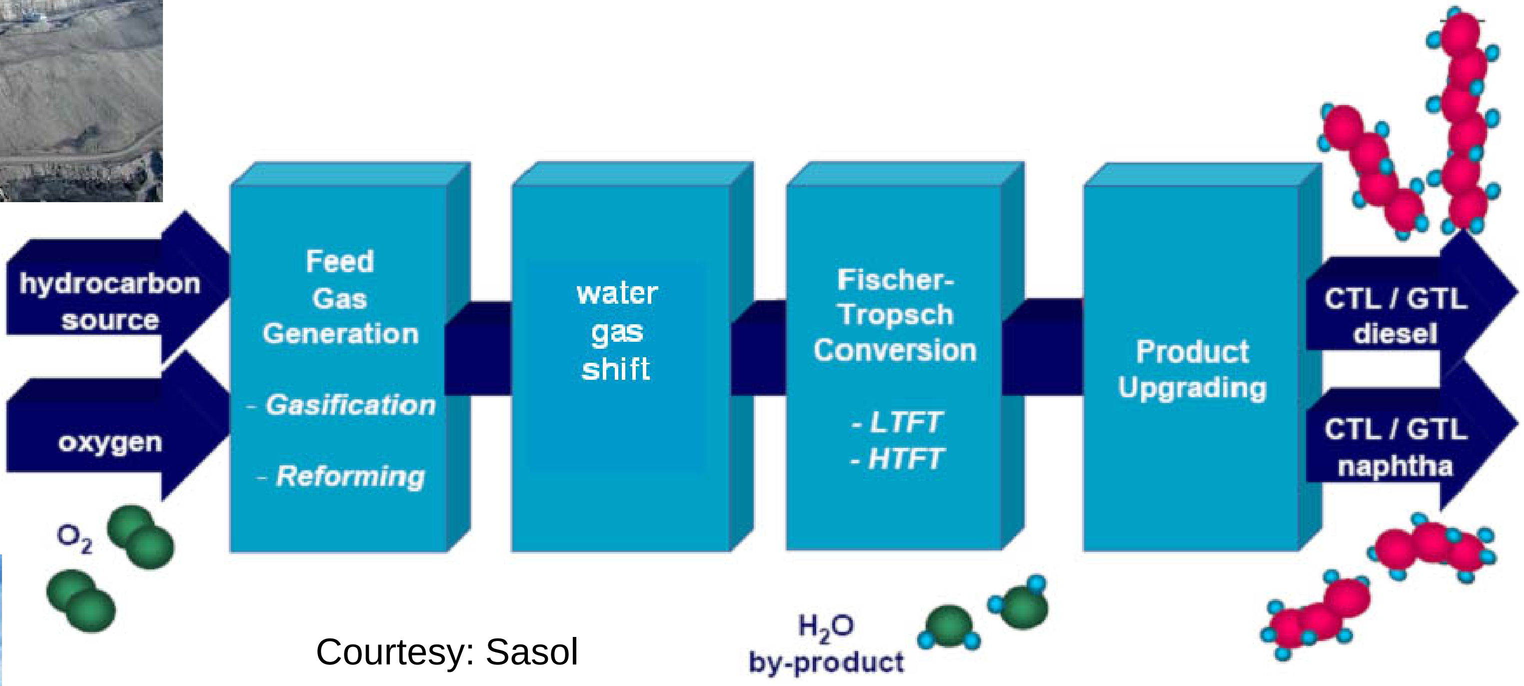


Recommended viewing:
The History Channel "Modern Marvels" series
- "Gasoline" (2002)
- "Secrets of Oil" (2008)

A “conventional” approach to synthetic fuels

Coal

Biomass



hydrocarbon source

oxygen

O_2

Feed Gas Generation

- *Gasification*

- *Reforming*

water gas shift

Fischer-Tropsch Conversion

- *LTFT*

- *HTFT*

H_2O by-product

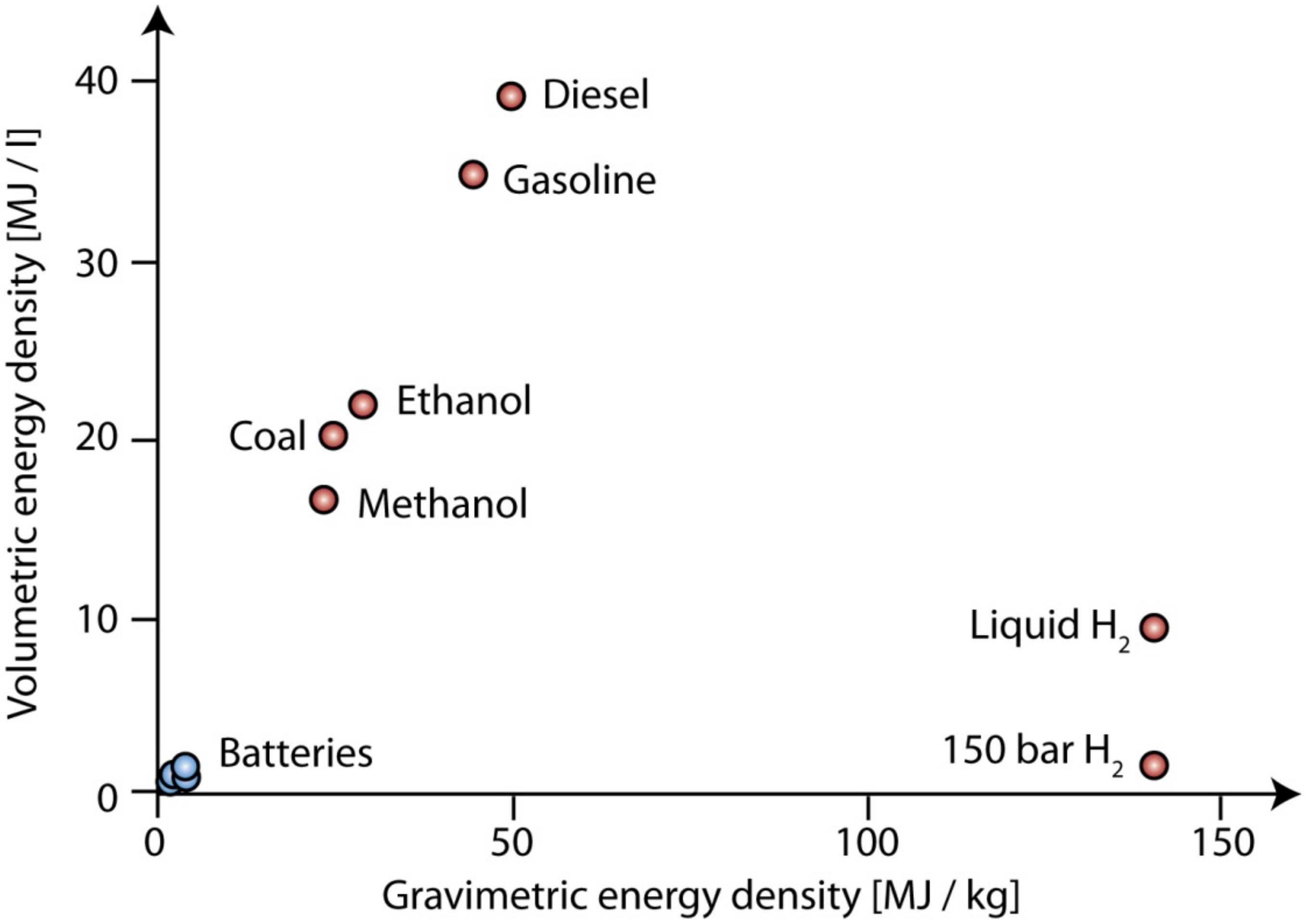
Product Upgrading

CTL / GTL diesel

CTL / GTL naphtha

Courtesy: Sasol

Energy Density

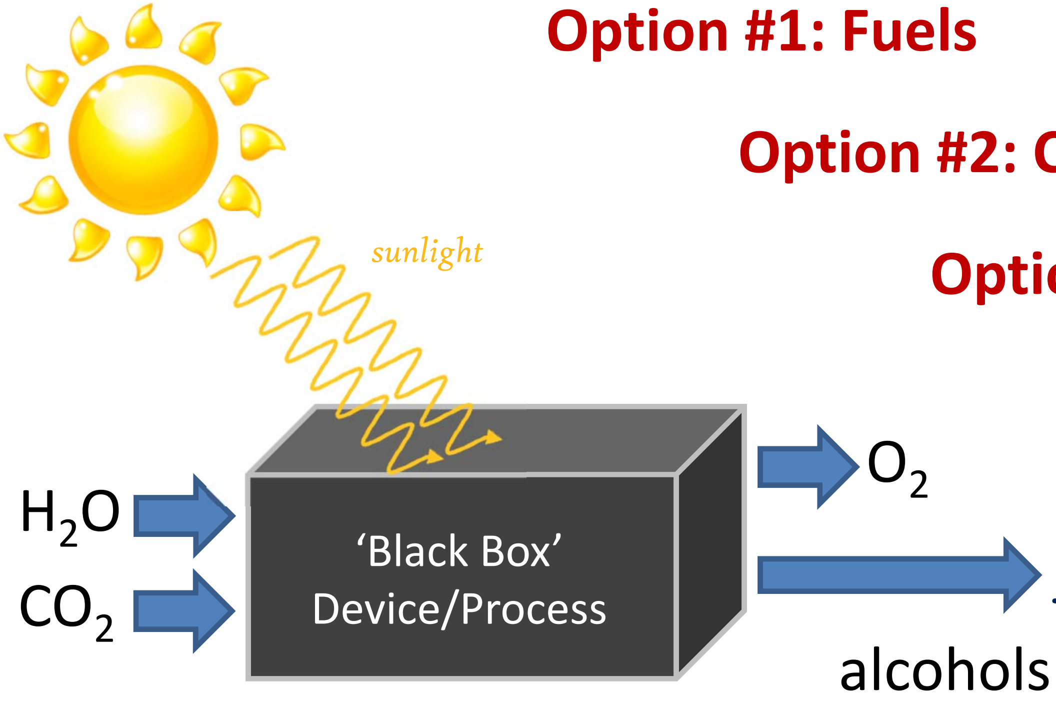


The broad vision:
Renewable production of fuels and chemicals

Option #1: Fuels

Option #2: Chemical Products

Option #3: Chemical Precursors



- Hydrogen (H_2)
- Carbon monoxide (CO)

alcohols

- Methanol (CH_3OH)
- Ethanol (C_2H_5OH)
- Butanol (C_4H_9OH)

hydrocarbons

- Methane (CH_4)
- Ethylene (C_2H_4)
- Gasoline (C5-C9)
- Diesel (C7-C15)
- Others…

Many possible schemes for solar fuels

Photobiologic → engineered organisms that synthesize fuels

Figure 6 Certain algae, whose chlorophyll give a green colour to the fluid, produce hydrogen in the presence of light. In engineered systems available today, 24% of the photosynthetic product is hydrogen rather than glucose. The photosynthesis process itself is about 1% efficient in converting light into chemical energy[10].

NREL

Photochemical → metallorganic absorbers and redox mediators

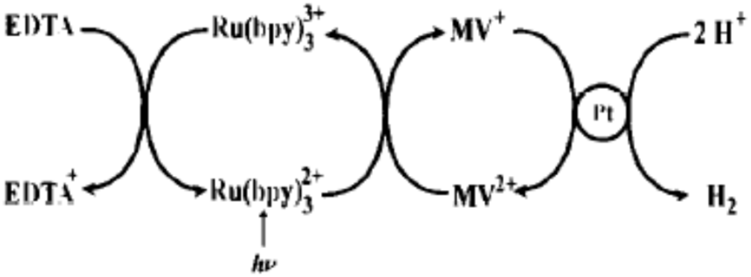
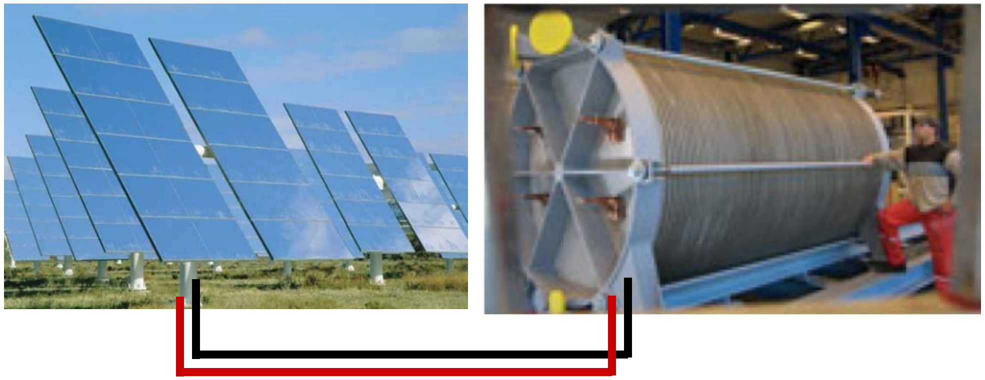


Fig. 3. Scheme for the photochemical generation of hydrogen in a reduction half reaction.

Solar thermal → heterogeneous catalysis.

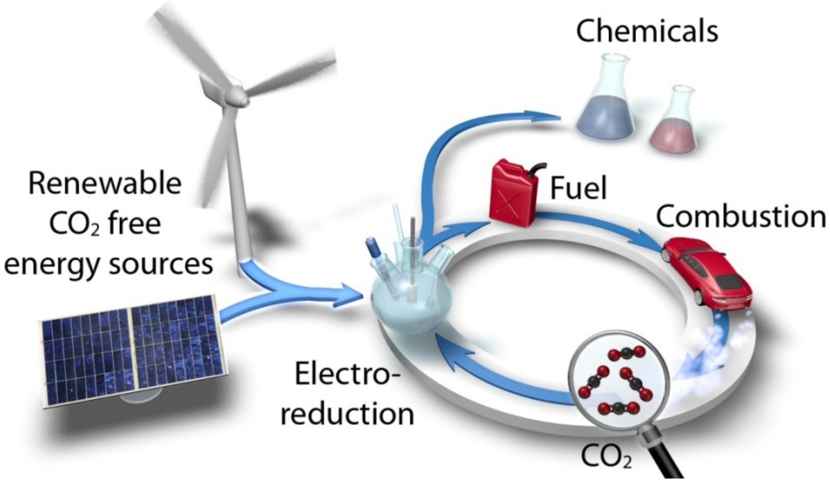
11 MW near Seville

Solar electricity → electrocatalysis

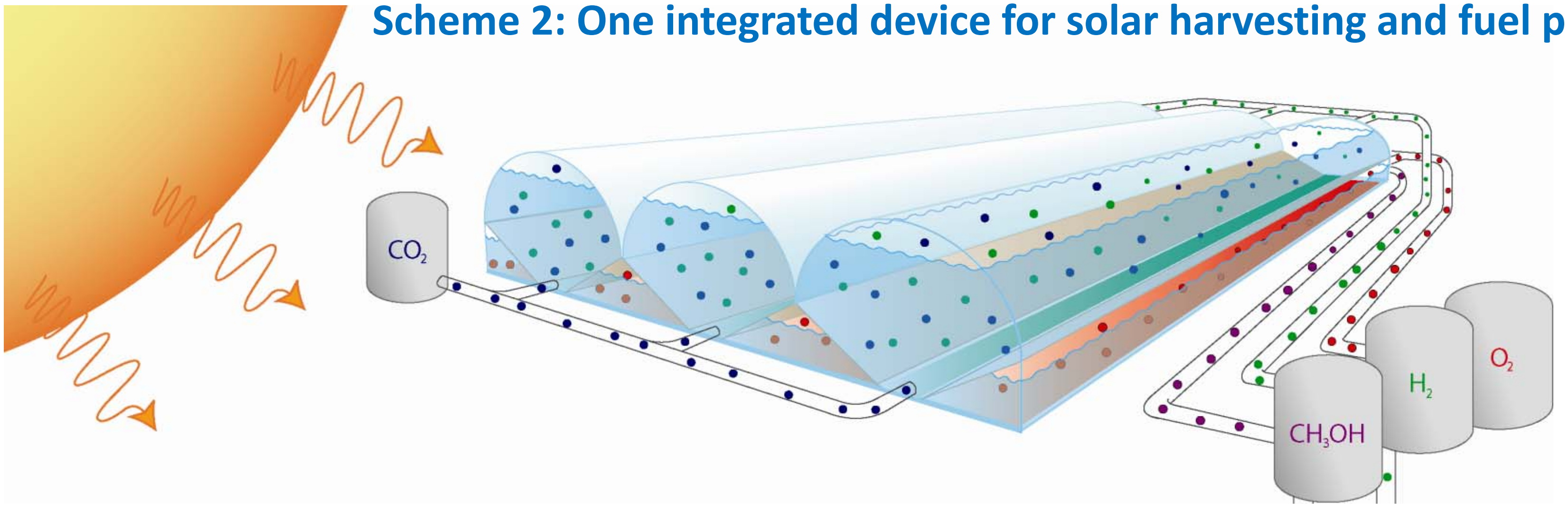


(Photo-)Electrochemical Pathways

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



Scheme 2: One integrated device for solar harvesting and fuel production.



Thermodynamic considerations for (photo-)electrochemical conversions related to energy

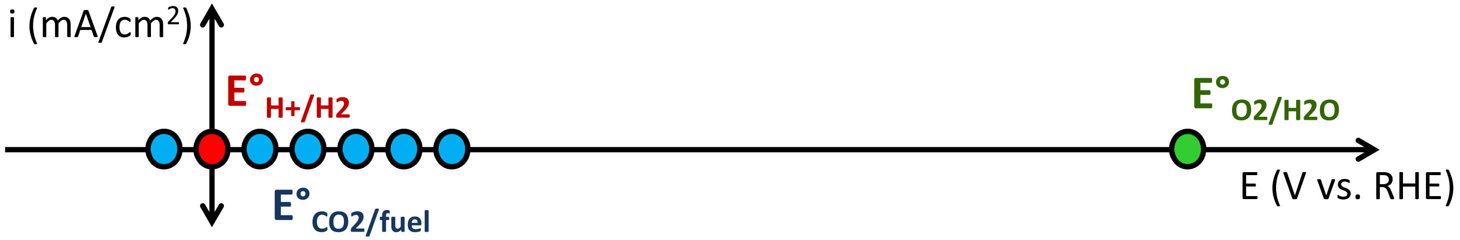
Y. Hori, “Electrochemical CO_2 reduction on metal electrodes” *Modern Aspects of Electrochemistry*, Number 42, edited by C. Vayenas et. al., Springer, NY (2008)

Cathode: “Fuel synthesis” Reactions

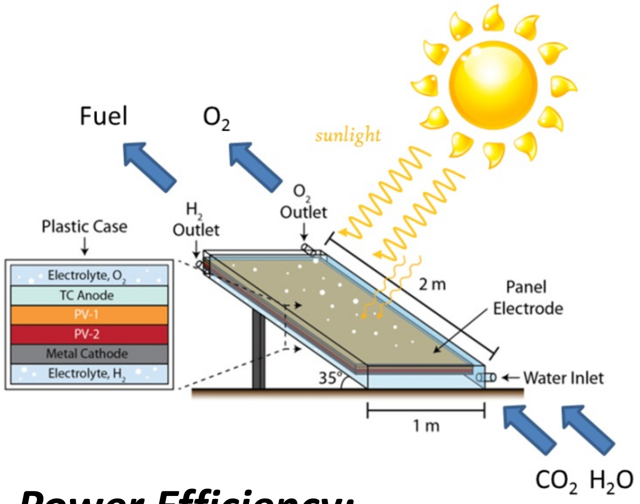
	Reaction	E^0 vs. RHE
Cathode	$2H^+ + 2e^- \rightarrow H_2$	0.00 V
Cathode	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	- 0.11 V
Cathode	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	+ 0.02 V
Cathode	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	+ 0.16 V
Cathode	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	+ 0.07 V
Cathode	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	+ 0.08 V
Cathode	$3CO_2 + 18H^+ + 18e^- \rightarrow C_3H_7OH + 5H_2O$	+ 0.09 V
Anode	$O_2 + 4H^+ + 4e^- \leftarrow 2H_2O$	+ 1.23 V

Anode: The “Balancing” Reaction

All values are close to the H_2 evolution potential (0.00 V).



Calculating STF Efficiency



Summed over all fuels

Rate at which each fuel is produced

chemical energy within each fuel

Power Efficiency:

$$\frac{Power\ Out}{Power\ In} = \frac{Rate\ of\ chemical\ energy\ production}{Power\ input\ from\ solar\ energy} = \left[\frac{\sum_i \left(\frac{mmol\ fuel_i}{second}\right)\left(\Delta G_i \frac{J}{mol}\right)}{\left(P_{total}\frac{mW}{cm^2}\right)\left(Area\ cm^2\right)}\right]$$

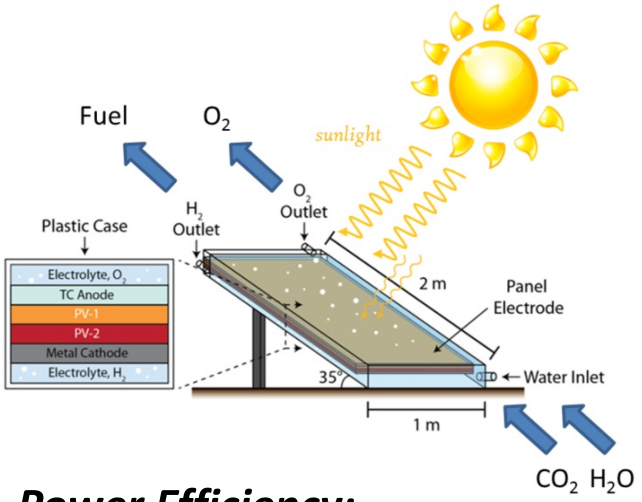
e.g. AM1.5 solar radiation (100 mW/cm^2)

Insolated area of the device

Alternatively one can express fuel production rate in mA/cm^2 and ΔG as a cell potential (V):

$$\frac{Power\ Out}{Power\ In} = \frac{Rate\ of\ chemical\ energy\ production}{Power\ input\ from\ solar\ energy} = \left[\frac{\sum_i \left(\frac{mA\ fuel_i}{cm^2}\right)\left(\Delta G_i\ V\right)}{\left(P_{total}\frac{mW}{cm^2}\right)}\right]$$

Example: Solar-to-hydrogen (STH) Efficiency



Summed over all fuels

Rate at which each fuel is produced

chemical energy within each fuel

Power Efficiency:

$$\frac{Power\ Out}{Power\ In} = \frac{Rate\ of\ chemical\ energy\ production}{Power\ input\ from\ solar\ energy} = \left[\frac{\left(\frac{mmol\ H_2}{second}\right)\left(237{,}000\frac{J}{mol}\right)}{\left(P_{total}\frac{mW}{cm^2}\right)\left(Area\ cm^2\right)}\right]$$

e.g. AM1.5 solar radiation (100 mW/cm^2)

Insolated area of the device

Alternatively one can express fuel production rate in mA/cm^2 and ΔG as a cell potential (V):

$$\frac{Power\ Out}{Power\ In} = \frac{Rate\ of\ chemical\ energy\ production}{Power\ input\ from\ solar\ energy} = \left[\frac{\sum_i\left(\frac{mA\ H_2}{cm^2}\right)(1.23\ V)}{\left(P_{total}\frac{mW}{cm^2}\right)}\right]$$

Assumes 100% of current goes to water-splitting

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Hydrogen (H_2)

Conventional H_2 production

Fossil-fuel powered
Electrolysis
~\$4-\$5 / kg

Annually
~65 billion kg (2007)
~\$100 billion
2-3% Global Energy Consumption

ExxonMobil Baton Rouge, LA
http://www.exxonmobilbr.com/

H_2

Ammonia Synthesis

Crude Oil Refining

Steam Methane Reforming/
Coal Gasification
~\$1 / kg

[1] Simbolotti, G. International Energy Agency. http://www.iea.org/techno/essentials5.pdf

[2] Midilli, A. & Dincer, I. Int. J. Hydrogen Energy 32 (2007) 511-524

[3] Balat, M. Int. J. Hydrogen Energy 33 (2008) 4013-4029

State of Fuel Cell cars today (Oct 2014)

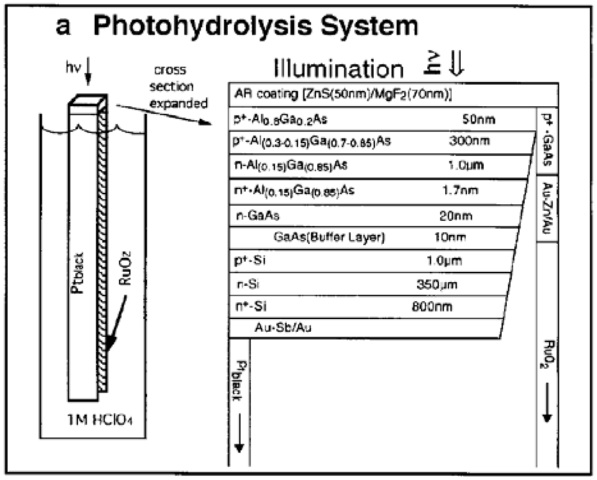
- Test fleets from many major automakers
  - > 3M mi. driven
  - > 27k refuelings
- Toyota FCV, first car to go on sale in 2015
  - MSRP ~$65k

California Fuel Cell Partnership
NREL

Fuel Cell Electric Vehicles are breaking into the market, but cost must come down for mass adoption.

Noteworthy devices for Photoelectrochemical (PEC) H_2 production

AlGaAs/Si

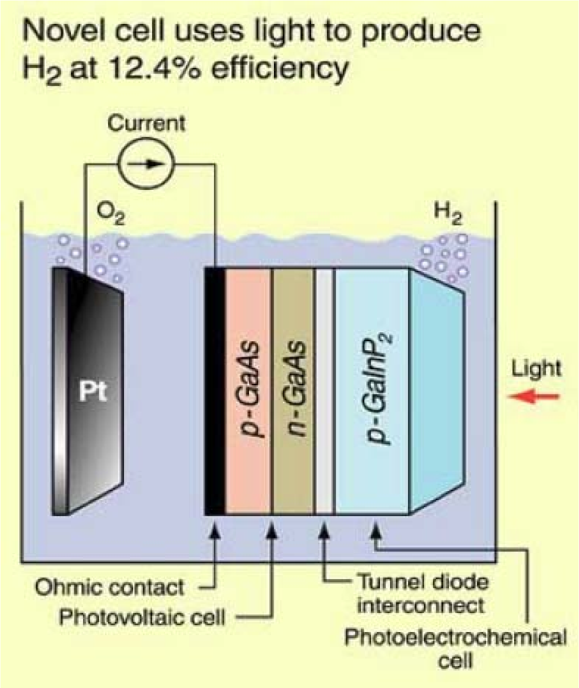


Technion Univ.
Nagoya Inst.
Hahn-Meitner Inst.

18.3 % STH

S. Licht et. al., Journal of Physical Chemistry B 104, 8920-8924 (2000)

GaAs/p-GaInP$_2$

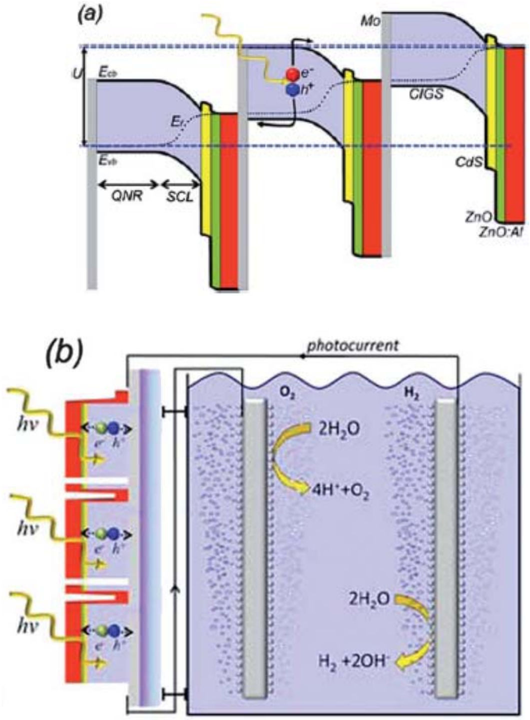


NREL

12.4 % STH

Khaselev, O. & Turner, J. A. *Science* **280**, 425-427 (1998)

3jn-CIGS

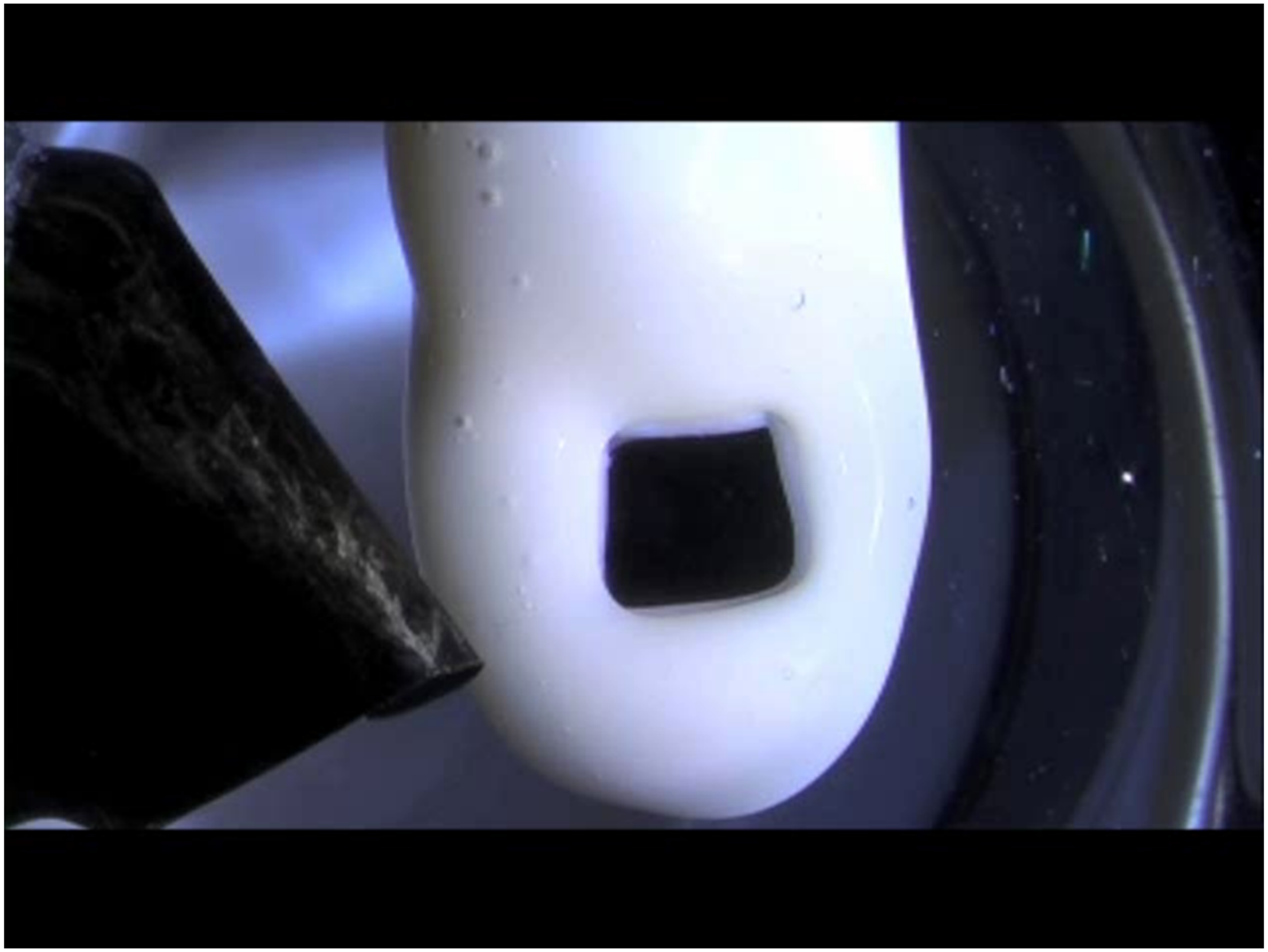


Uppsala University (Sweden)

10 % STH

T. J. Jacobsson, et. al., Energy Environ. Sci., 3676-3683 (2013).

Solar photoelectrochemical (PEC) H_2 production

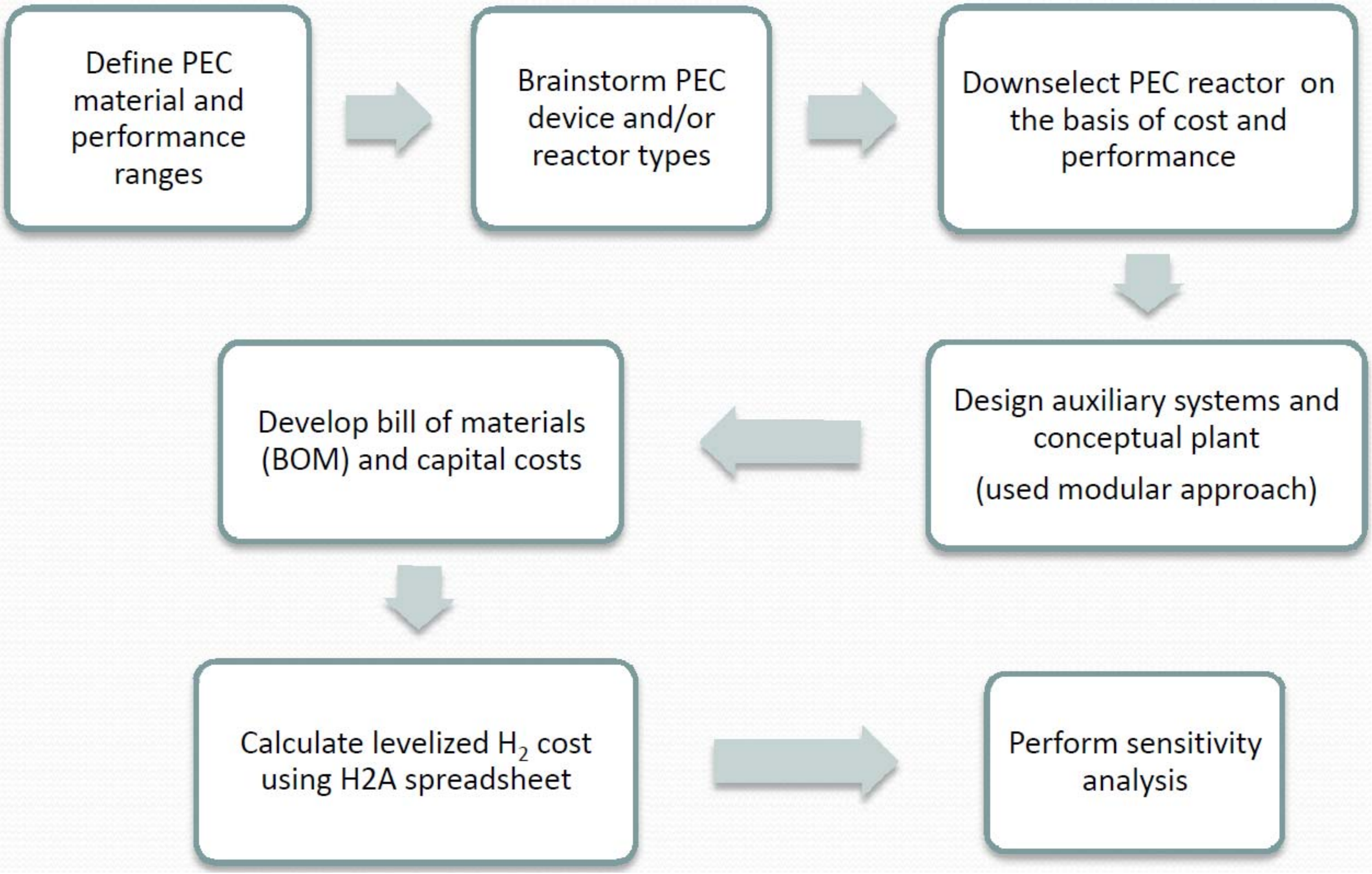


Video courtesy of Dr. Todd Deutsch, NREL

Techno-economics

How much might H_2 cost if produced by large-scale solar PEC water-splitting?

How to conduct a techno-economic analysis



Define PEC material and performance ranges

Brainstorm PEC device and/or reactor types

Downselect PEC reactor on the basis of cost and performance

Design auxiliary systems and conceptual plant

(used modular approach)

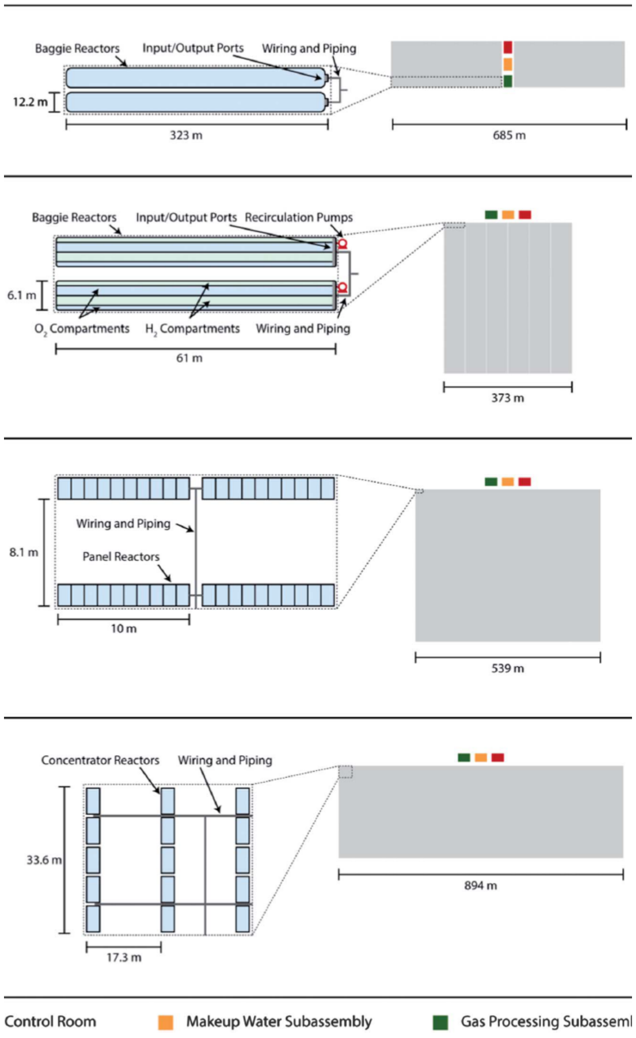
Develop bill of materials (BOM) and capital costs

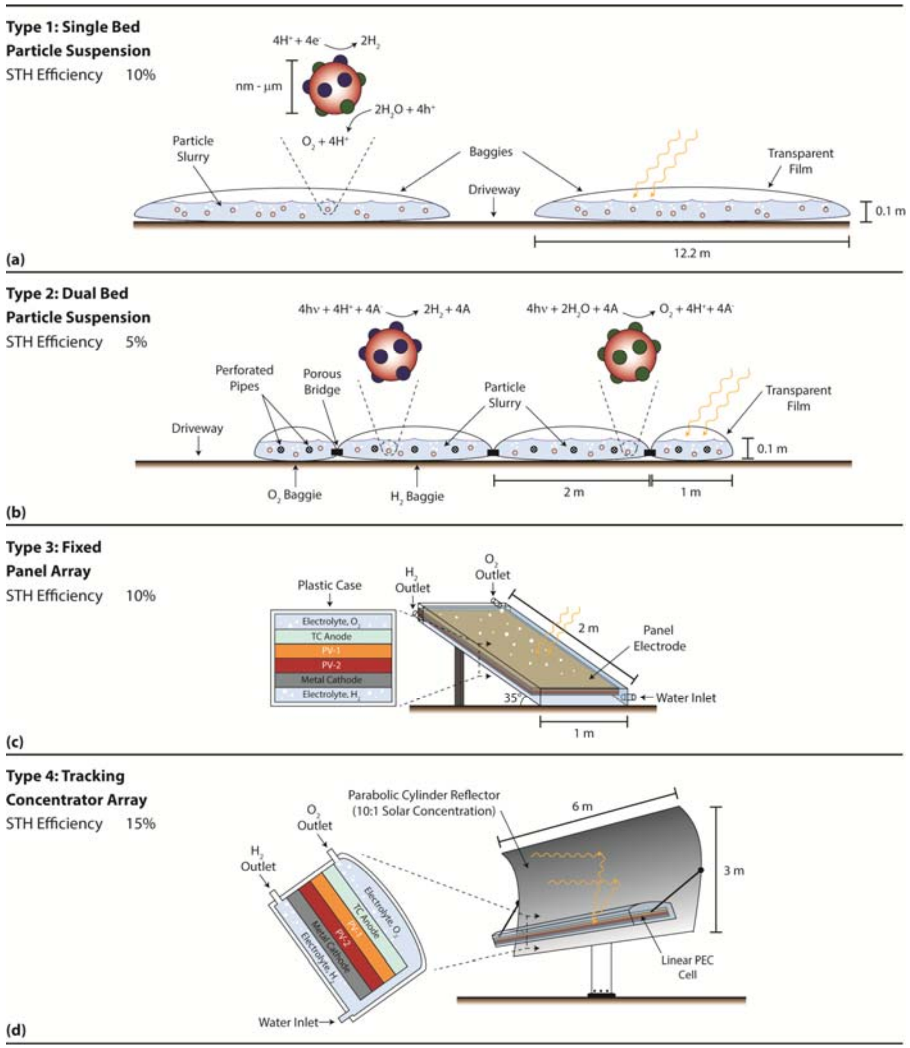
Calculate levelized H_2 cost using H2A spreadsheet

Perform sensitivity analysis

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.

Chemical engineering plant design

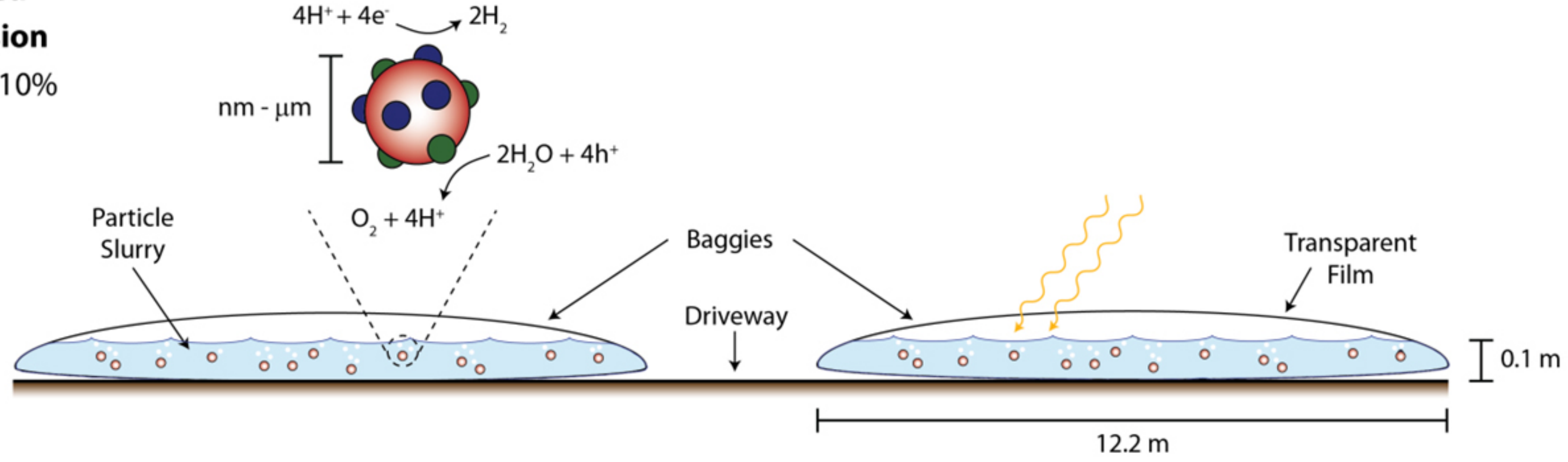




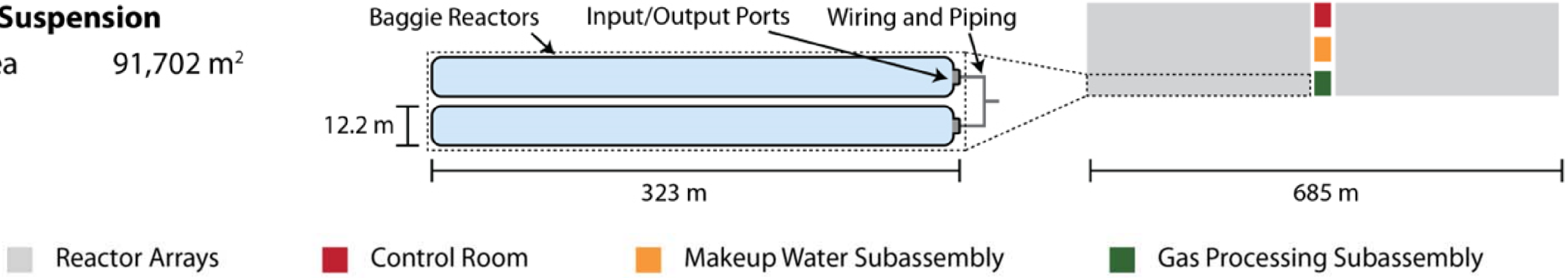
B. Pinaud, J. Benck, L. Seitz, A. Forman, Z. Chen, T. Deutsch, B. James, K. Baum, G. Baum,
S. Ardo, H. Wang, E. Miller & T.F. Jaramillo. *Energy Environ. Sci.* **2013**, 6, 1983-2002

Reactor Type 1: Colloidal Suspension

Type 1: Single Bed
Particle Suspension
STH Efficiency 10%



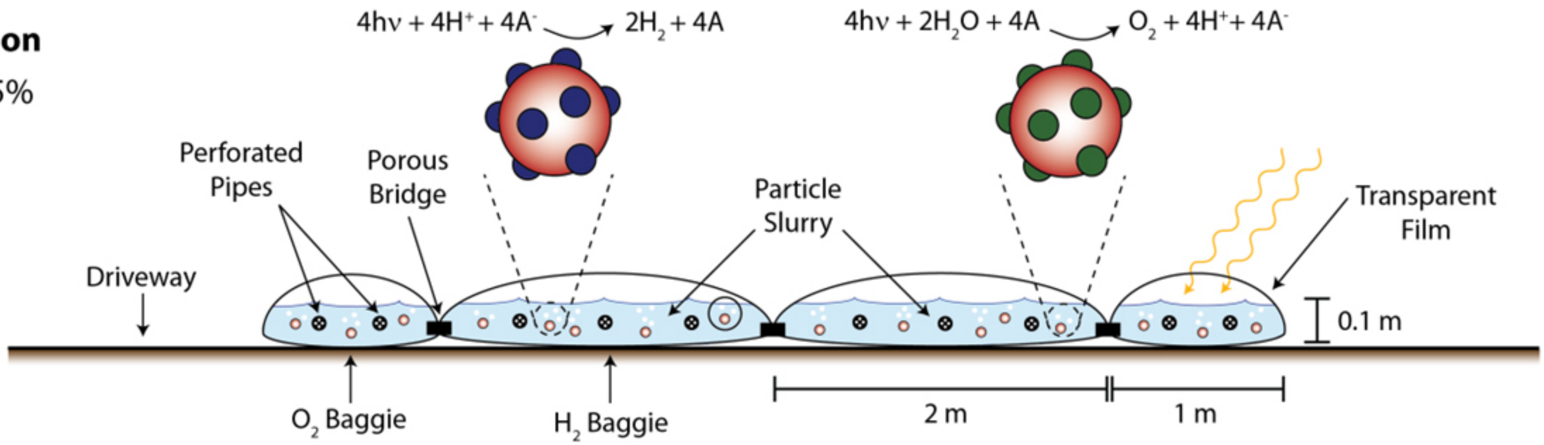
Type 1: Single Bed
Particle Suspension
Plant Area 91,702 m^2



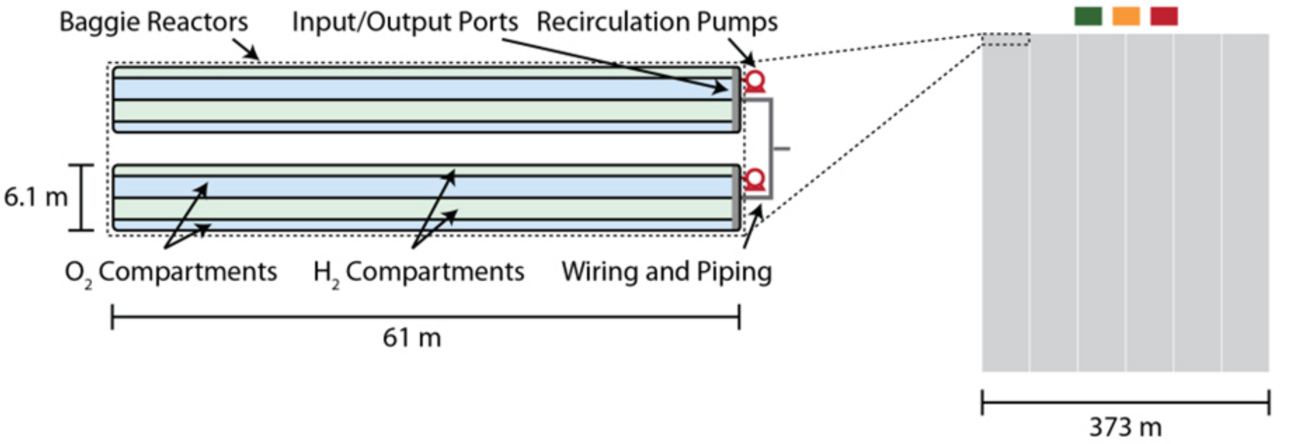
B. Pinaud, J. Benck, L. Seitz, A. Forman, Z. Chen, T. Deutsch, B. James, K. Baum, G. Baum, S. Ardo, H. Wang, E. Miller & T.F. Jaramillo. *Energy Environ. Sci.* **2013**, 6, 1983-2002.

Reactor Type 2: Dual-bed Colloidal Suspension

Type 2: Dual Bed
Particle Suspension
STH Efficiency 5%



Type 2: Dual Bed
Particle Suspension
Plant Area 165,060 m^2



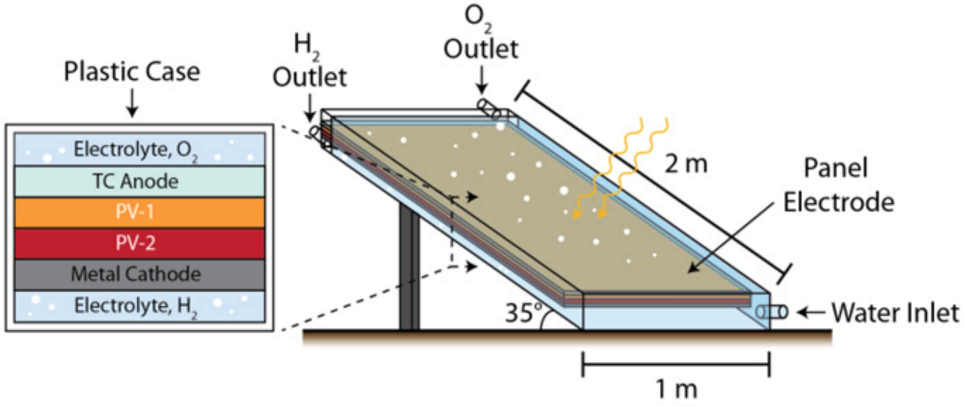
⬜ Reactor Arrays 🟥 Control Room 🟧 Makeup Water Subassembly 🟩 Gas Processing Subassembly

B. Pinaud, J. Benck, L. Seitz, A. Forman, Z. Chen, T. Deutsch, B. James, K. Baum, G. Baum, S. Ardo, H. Wang, E. Miller & T.F. Jaramillo. *Energy Environ. Sci.* **2013**, 6, 1983-2002.

Reactor Type 3: Fixed Panel PEC Array

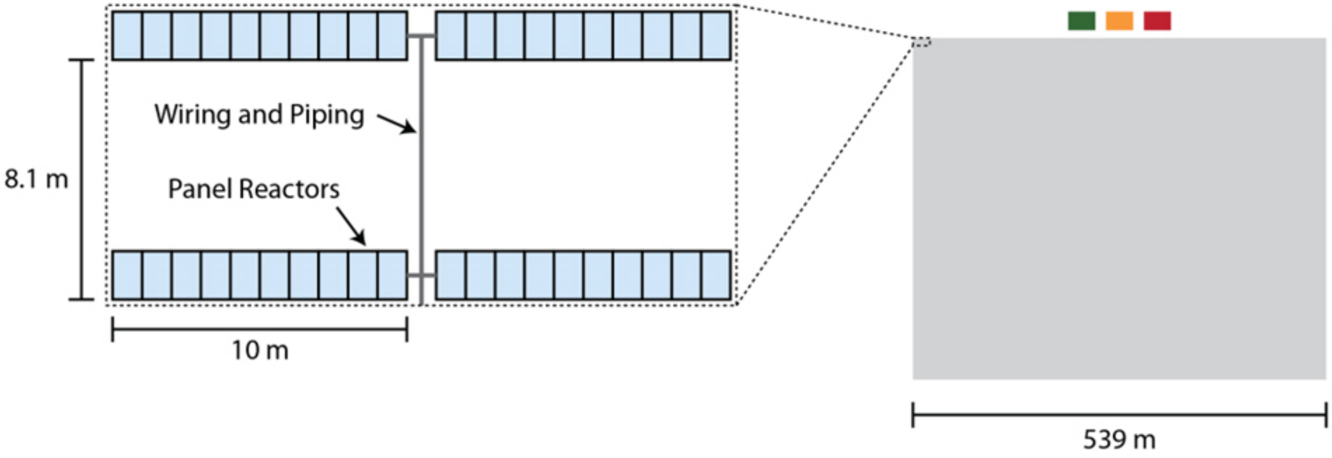
Type 3: Fixed Panel Array

STH Efficiency 10%



Type 3: Fixed Panel Array

Plant Area 219,149 m^2



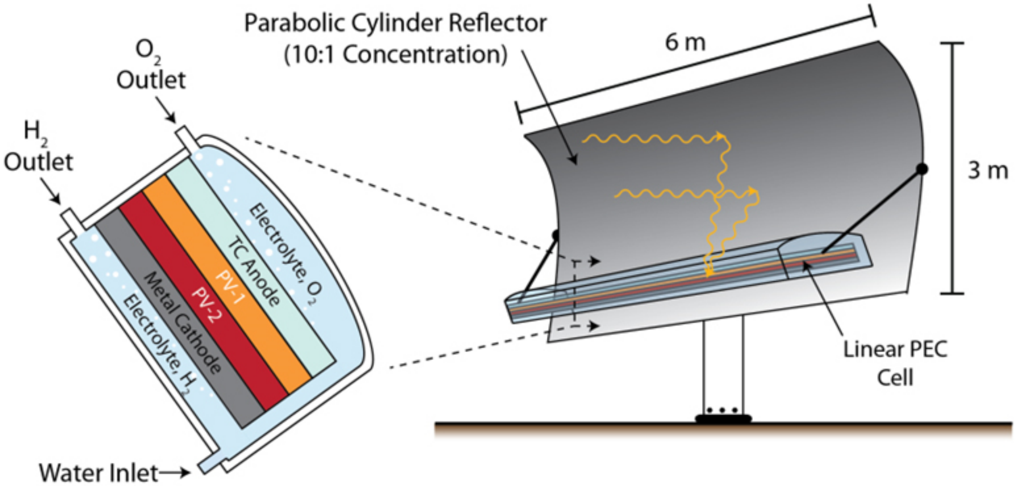
⬜ Reactor Arrays 🟥 Control Room 🟧 Makeup Water Subassembly 🟩 Gas Processing Subassembly

B. Pinaud, J. Benck, L. Seitz, A. Forman, Z. Chen, T. Deutsch, B. James, K. Baum, G. Baum, S. Ardo, H. Wang, E. Miller & T.F. Jaramillo. *Energy Environ. Sci.* **2013**, 6, 1983-2002.

Reactor Type 4: Tracking Concentrator Array

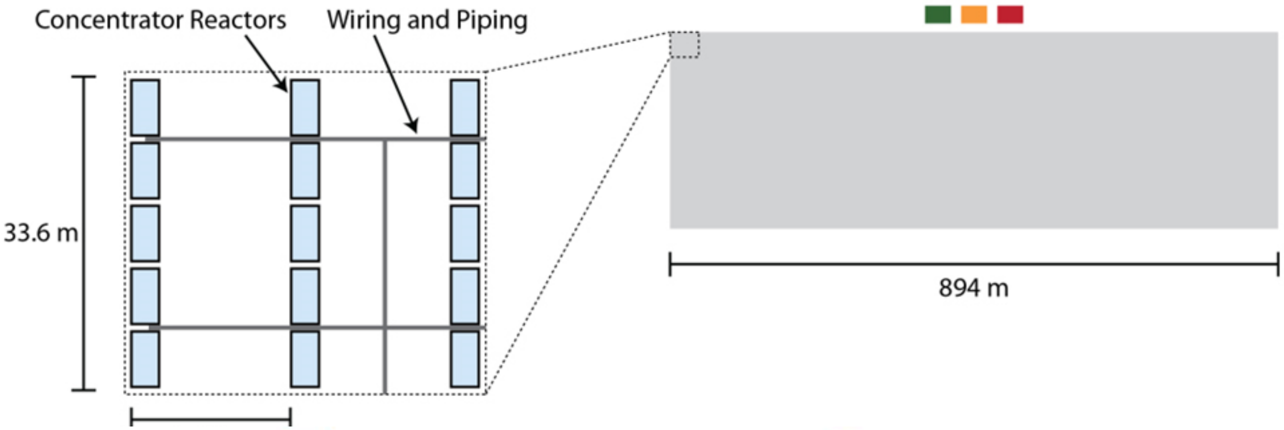
Type 4: Tracking Concentrator Array

STH Efficiency 15%



Type 4: Tracking Concentrator Array

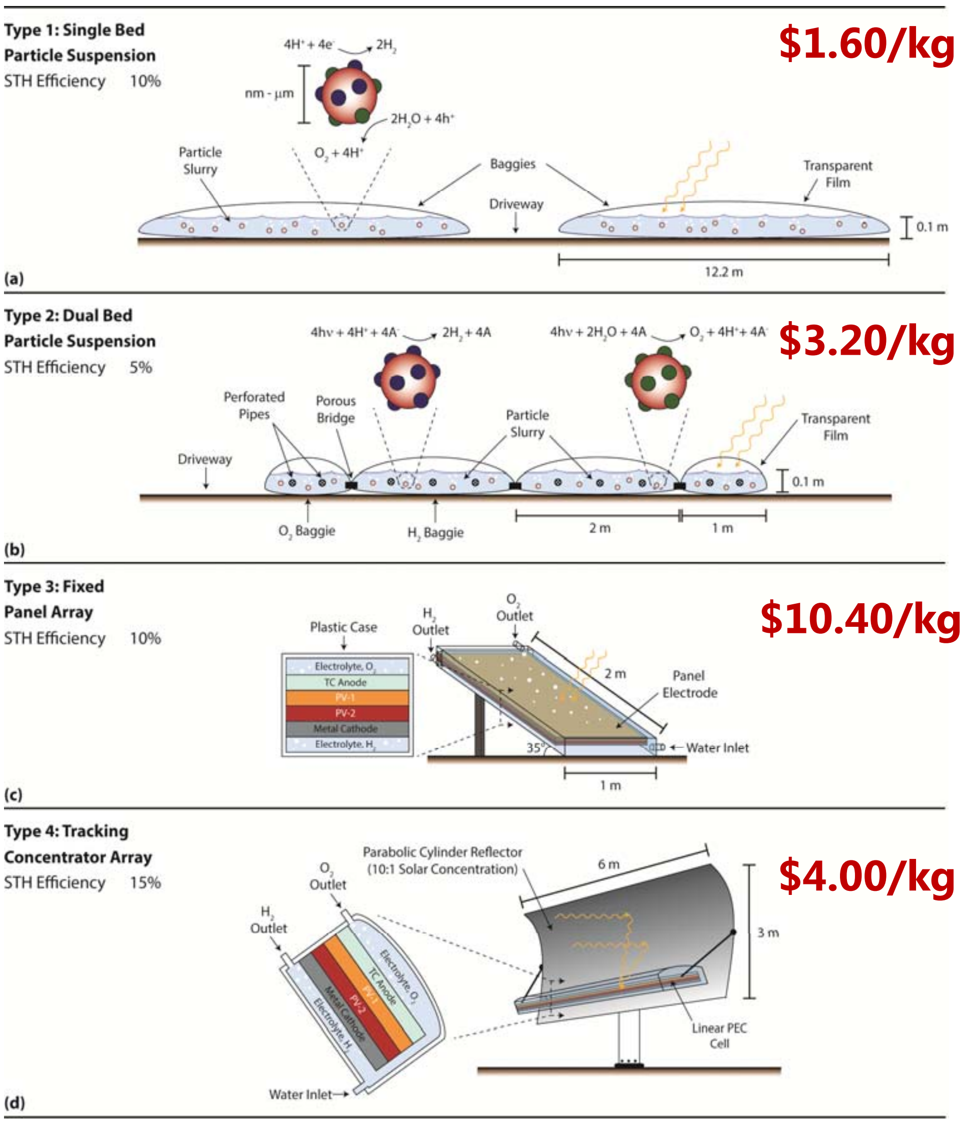
Plant Area 222,881 m²



▨ Reactor Arrays 🟥 Control Room 🟧 Makeup Water Subassembly 🟩 Gas Processing Subassembly

B. Pinaud, J. Benck, L. Seitz, A. Forman, Z. Chen, T. Deutsch, B. James, K. Baum, G. Baum, S. Ardo, H. Wang, E. Miller & T.F. Jaramillo. *Energy Environ. Sci.* **2013**, 6, 1983-2002.

Technoeconomics of Photoelectrochemical H_2



$1.60/kg H_2

$3.20/kg H_2

$10.40/kg H_2

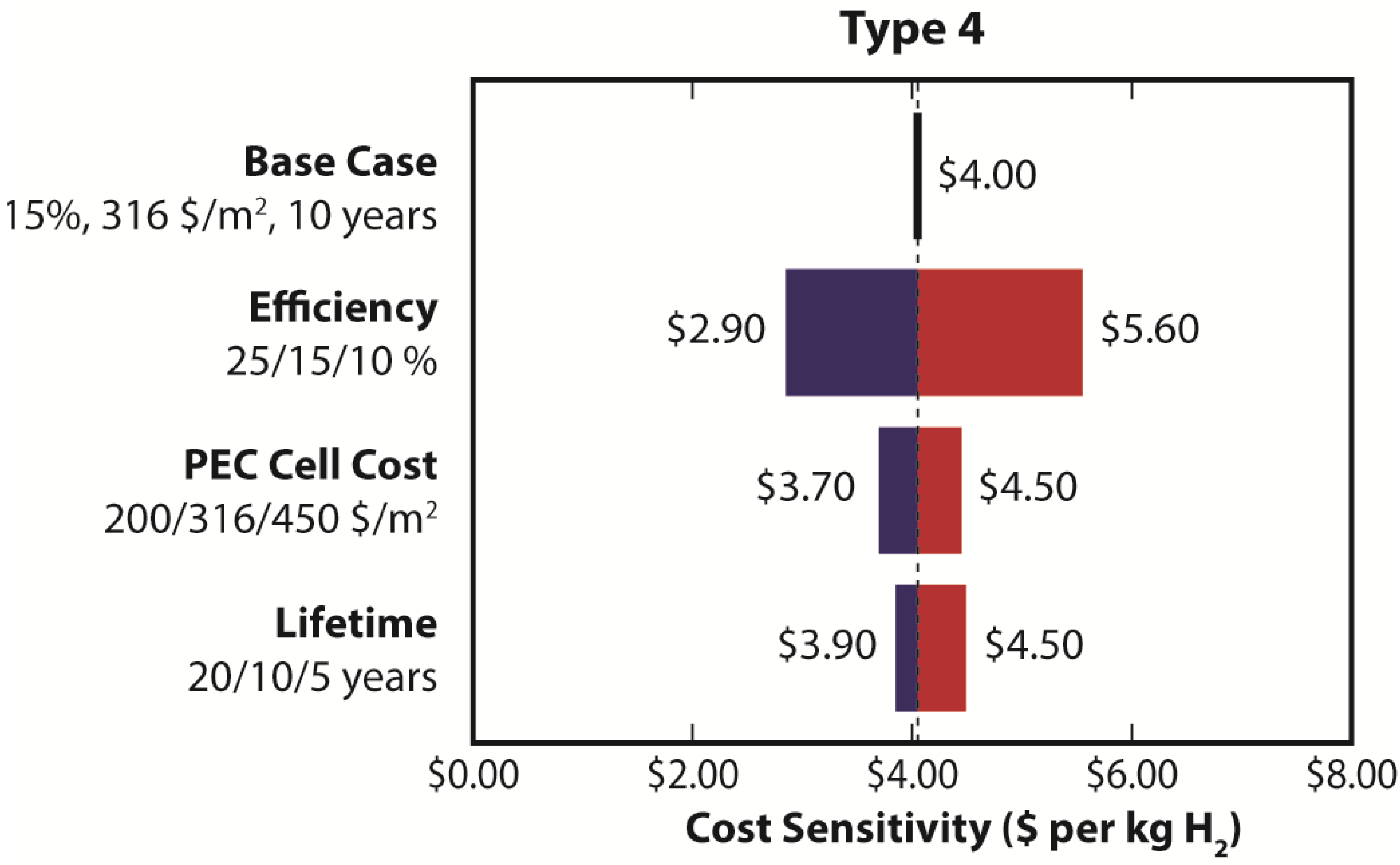
$4.00/kg H_2

- **Particle systems**: Low cost but low demonstrated performance.

Target: $2 – $4/gge

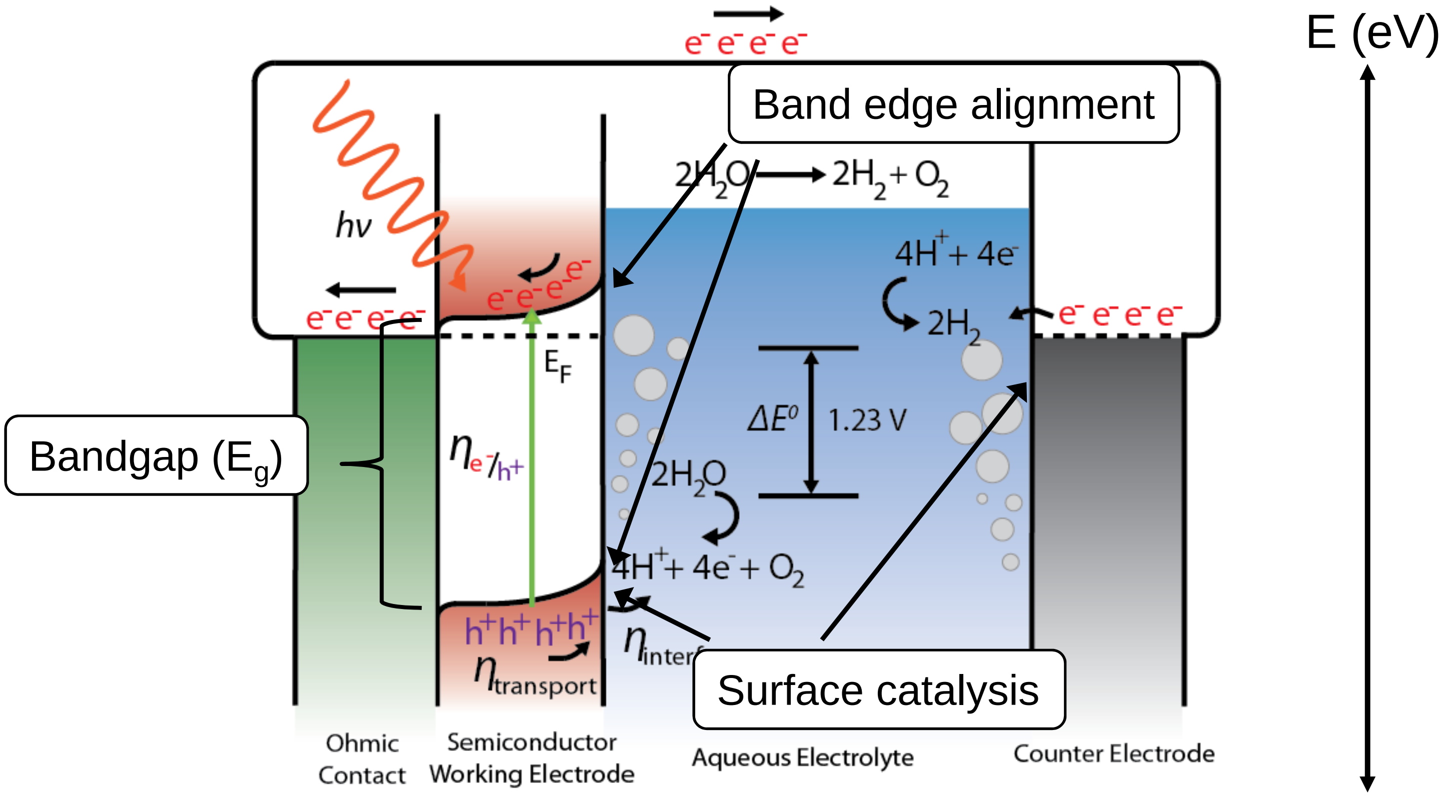
- **Panel systems**: Higher demonstrated bench-scale efficiencies but higher cost.

Sensitivity Analysis: Efficiency is the cost-driver



B. Pinaud, J. Benck, L. Seitz, A. Forman, Z. Chen, T. Deutsch, B. James, K. Baum, G. Baum, S. Ardo, H. Wang, E. Miller & T.F. Jaramillo. *Energy Environ. Sci.* **2013**, 6, 1983-2002.

Band structure of a photoelectrode



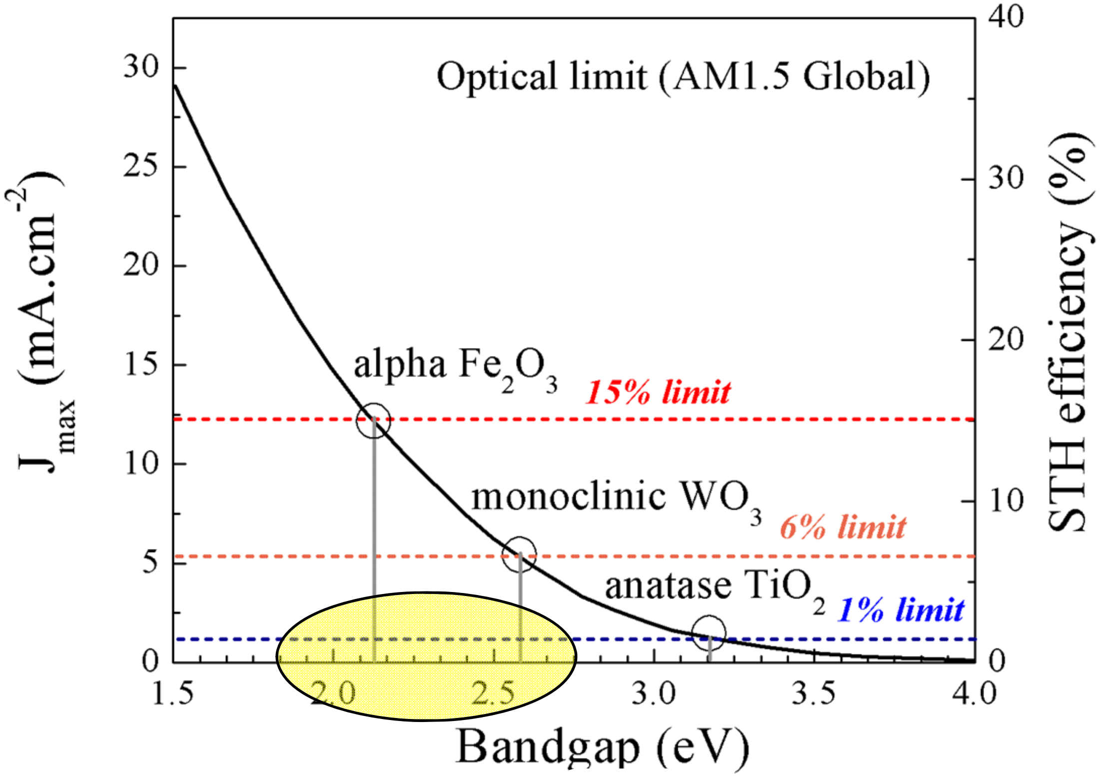
Band edge alignment

Bandgap (E_g)

Surface catalysis

Stability

Maximum STH efficiency vs. bandgap (single-absorber)

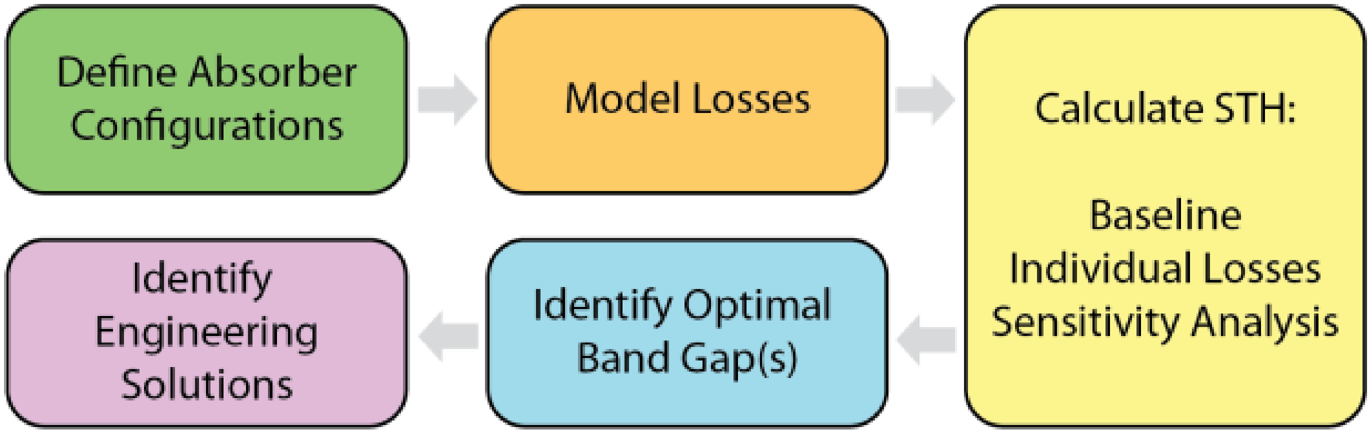


$$\text{Required Bandgap} = \underset{1.23\ \text{V}}{\Delta E^0} + \underset{\sim 400\ \text{mV}}{T\Delta S} + \underset{50\ \text{mV}}{\eta_{HER}} + \underset{400\ \text{mV}}{\eta_{OER}} = \sim 2.0 - 2.5\ \text{eV}$$

Developing materials with appropriate bandgaps is a critical challenge…
But exactly what bandgaps should one target?

Z. Chen, T. F. Jaramillo, T.G. Deutsch, A.K. Schwarsctein, A. J. Forman, N. Gaillard, R. Garland, K. Takanabe C. Heske, M. K. Sunkara, E. W. McFarland, K. Domen, E. L. Miller, J. A. Turner, & H. N. Dinh. *J. Mater. Res*. 25 (1), 2010

Modeling STH efficiencies



Define Absorber Configurations

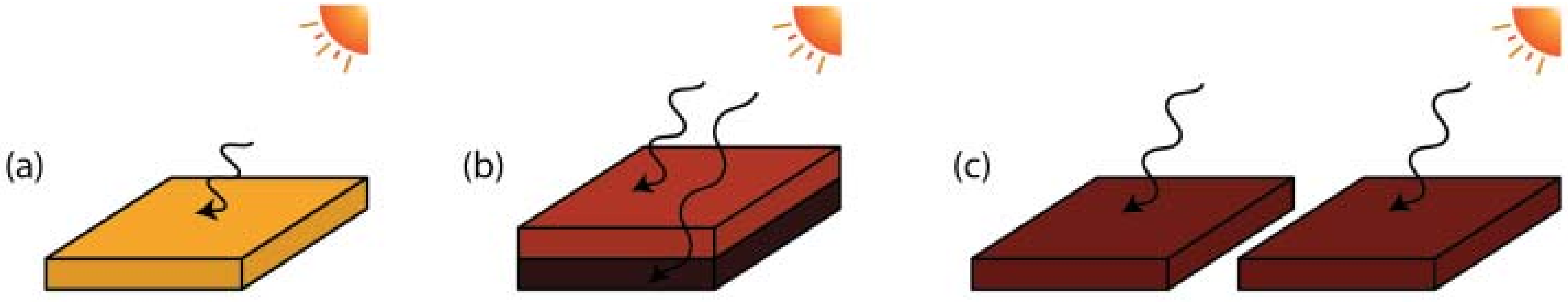
Model Losses

Calculate STH:

Baseline
Individual Losses
Sensitivity Analysis

Identify Optimal Band Gap(s)

Identify Engineering Solutions



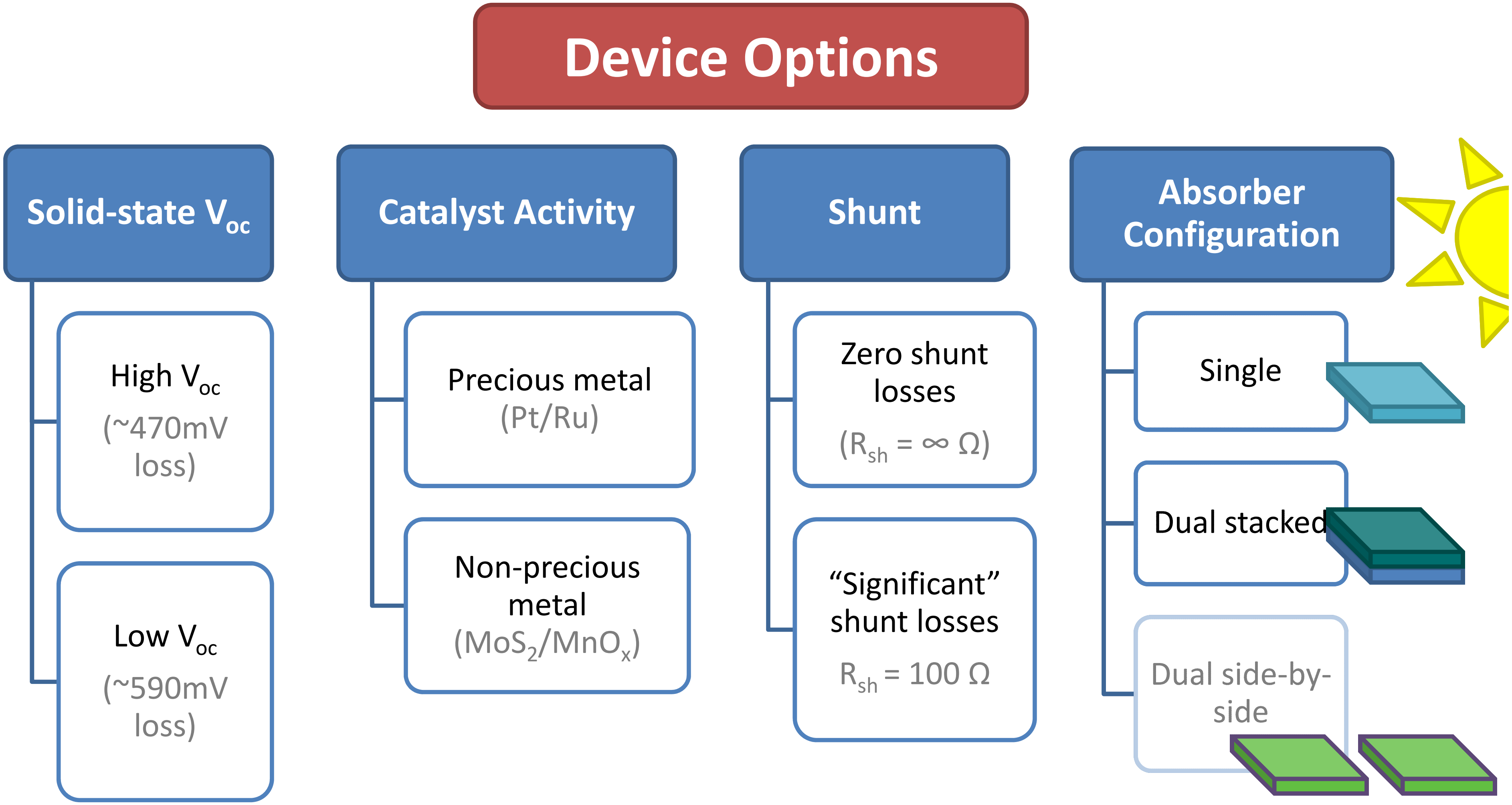
Single Absorber

Dual Stacked Absorber

Dual Side-by-side Absorber

L.C. Seitz, Z. Chen, A.J. Forman, B.A. Pinaud, J.D. Benck, and T.F. Jaramillo, *ChemSusChem*, **7**, 1372-1385 (2014).

Modeling ‘Realistic’ PEC efficiencies



Device Options

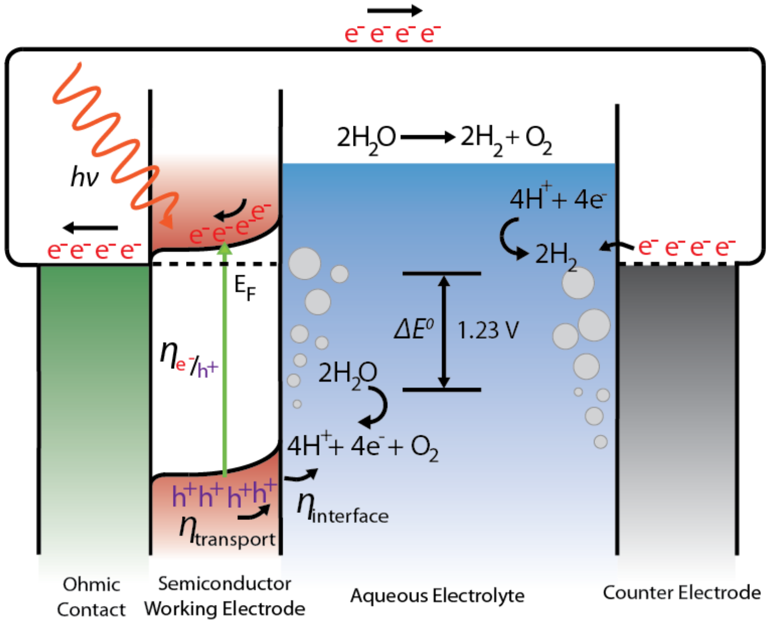
- **Solid-state V_{oc}**
  - High V_{oc} (~470mV loss)
  - Low V_{oc} (~590mV loss)
- **Catalyst Activity**
  - Precious metal (Pt/Ru)
  - Non-precious metal (MoS_2/MnO_x)
- **Shunt**
  - Zero shunt losses ($R_{sh} = \infty\ \Omega$)
  - “Significant” shunt losses $R_{sh} = 100\ \Omega$
- **Absorber Configuration**
  - Single
  - Dual stacked
  - Dual side-by-side

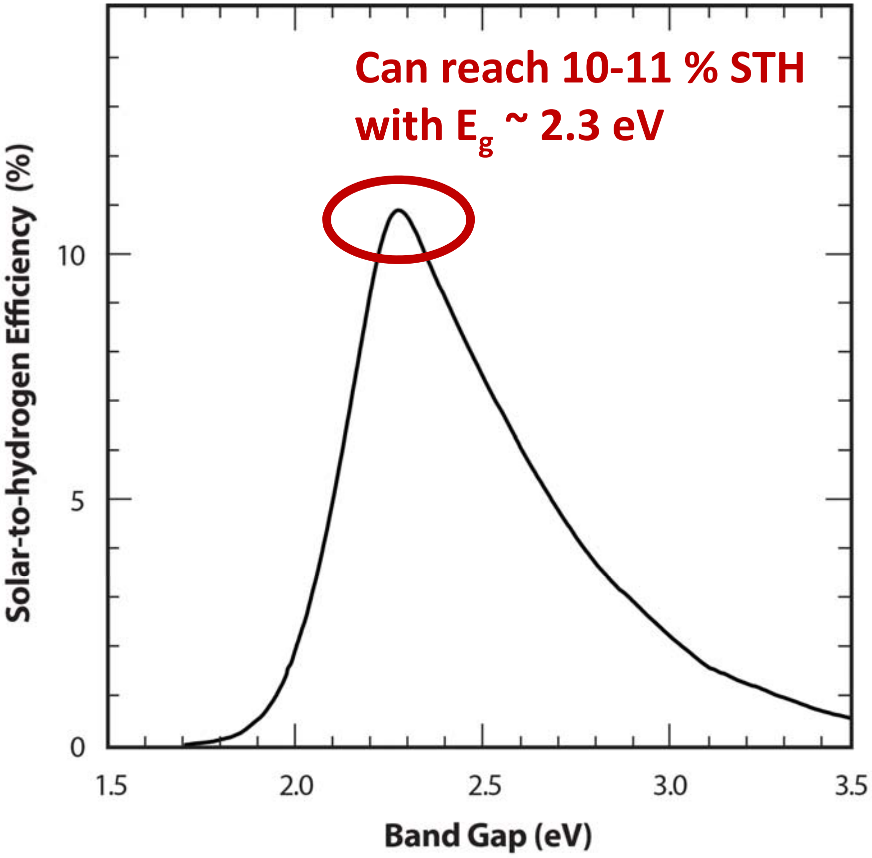
L.C. Seitz, Z. Chen, A.J. Forman, B.A. Pinaud, J.D. Benck, and T.F. Jaramillo, *ChemSusChem*, **7**, 1372-1385 (2014).

Single-absorber devices

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 ~ 2.3 eV

L.C. Seitz, Z. Chen, A.J. Forman, B.A. Pinaud, J.D. Benck, and T.F. Jaramillo, *ChemSusChem*, **7**, 1372-1385 (2014).

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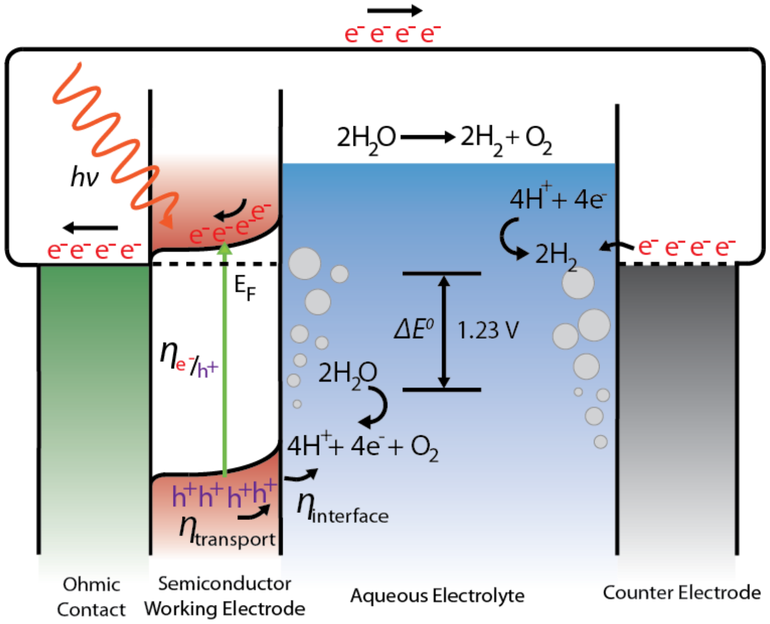
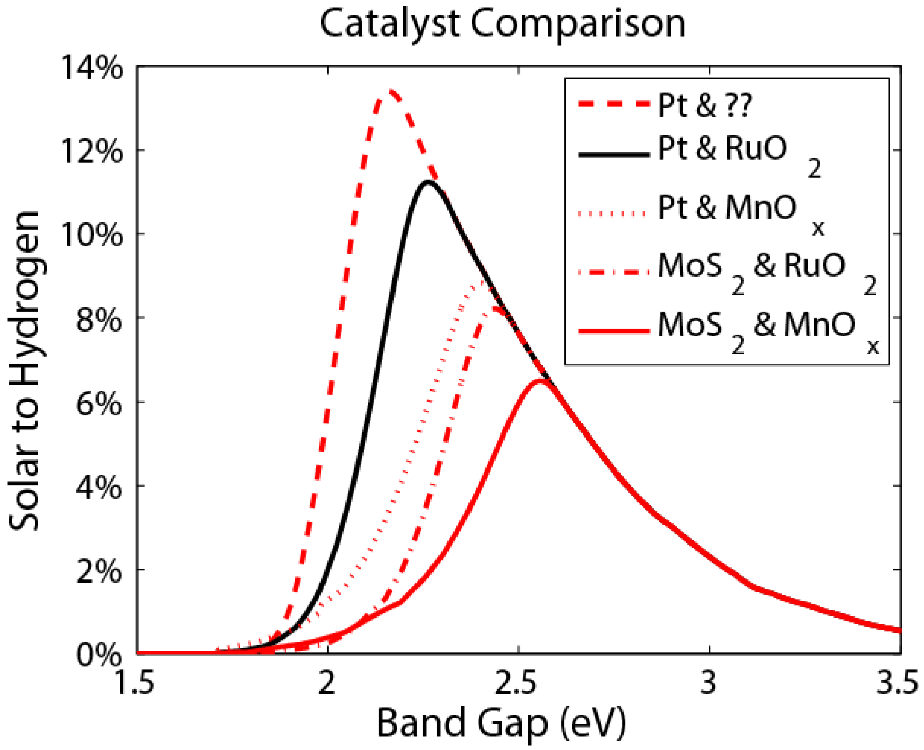
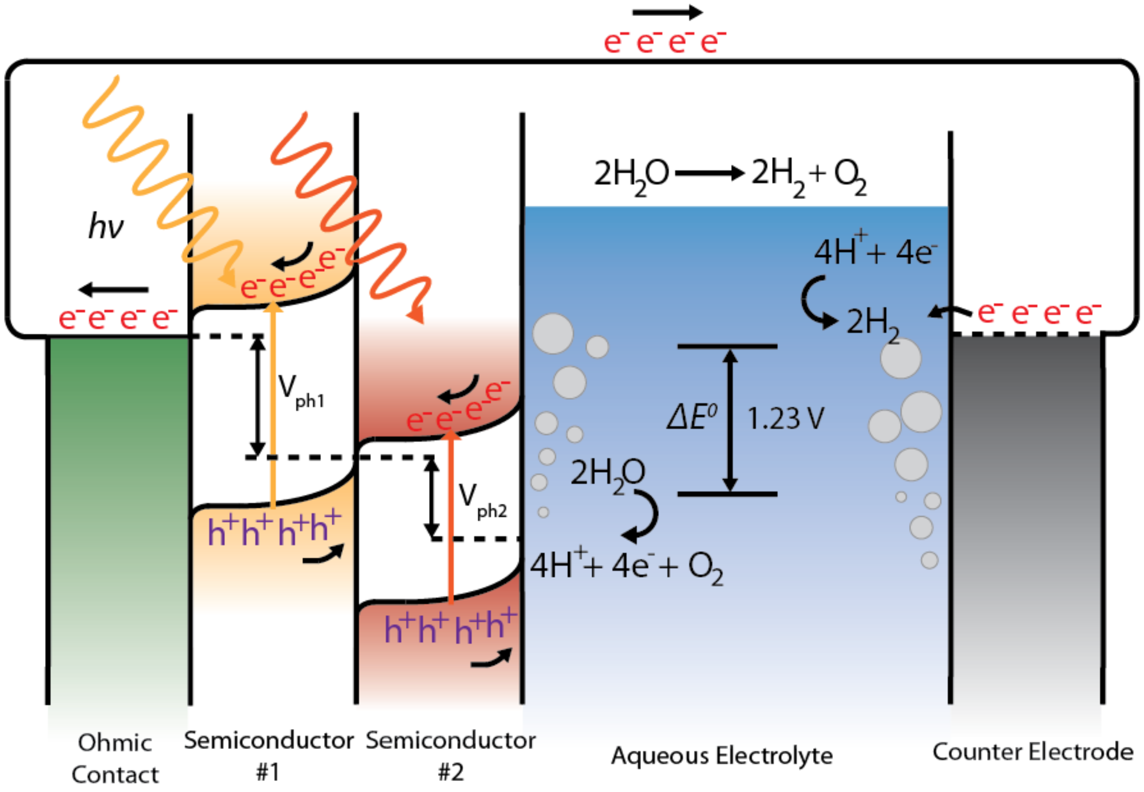


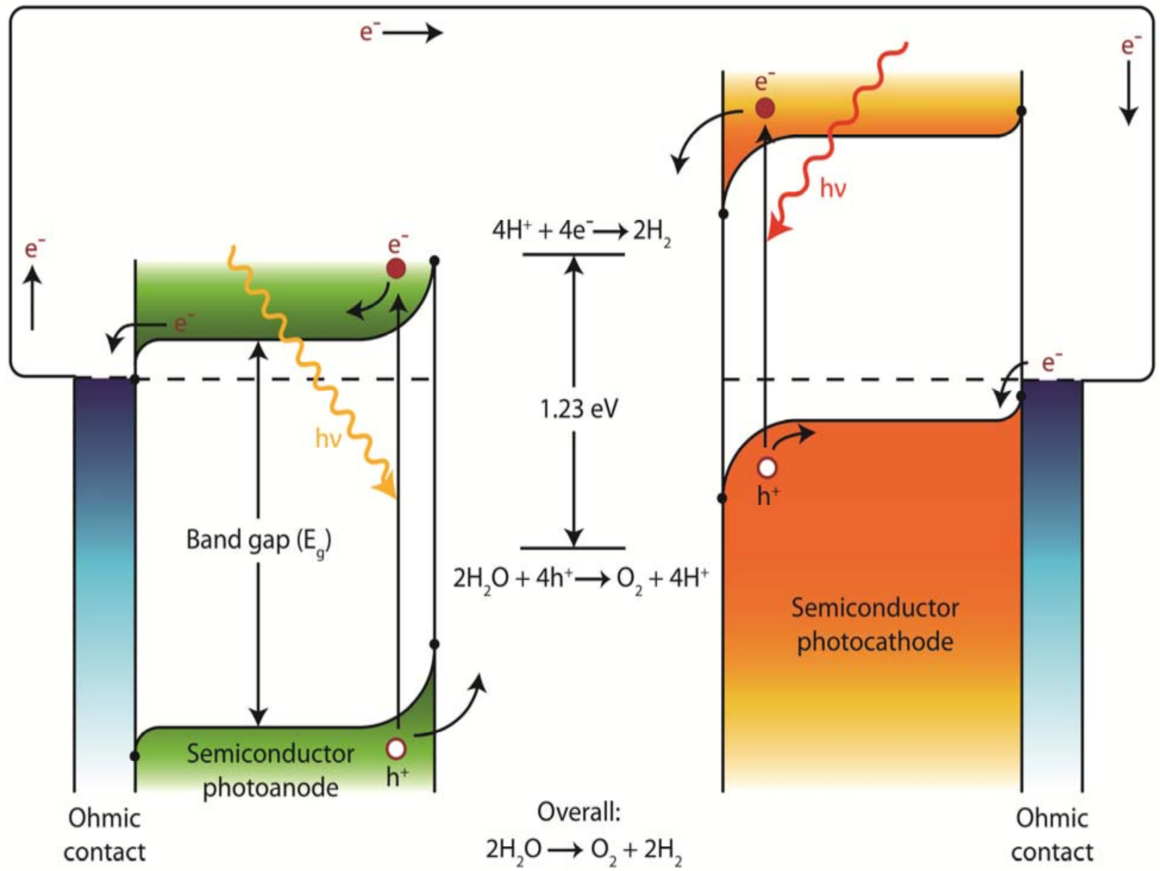


L.C. Seitz, Z. Chen, A.J. Forman, B.A. Pinaud, J.D. Benck, and T.F. Jaramillo, *ChemSusChem*, **7**, 1372-1385 (2014).

Multi-junction devices



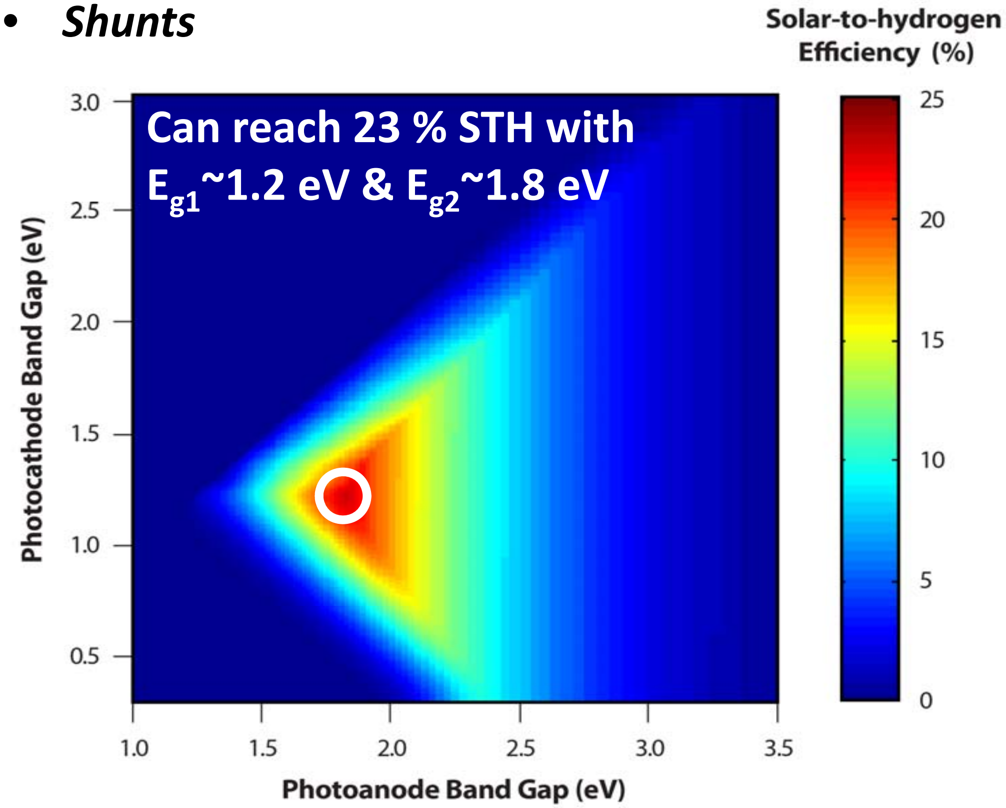
Tandem devices

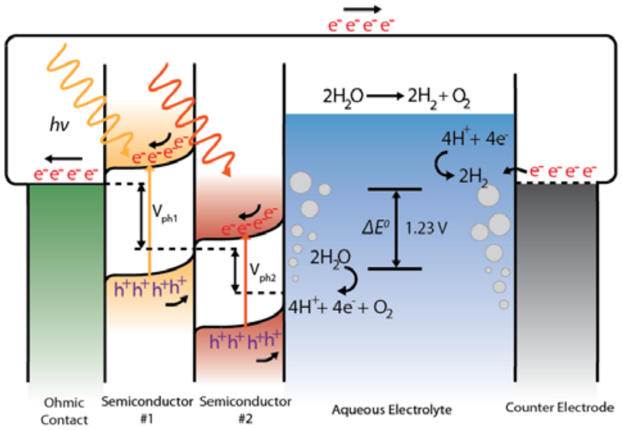


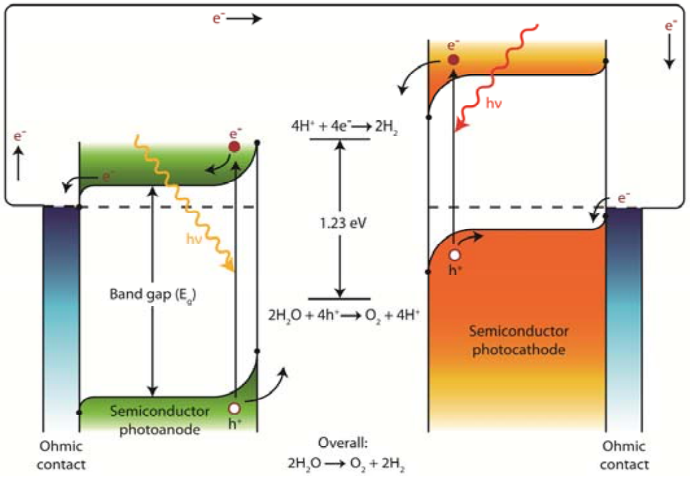
Multi-junction or Tandem Devices

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

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

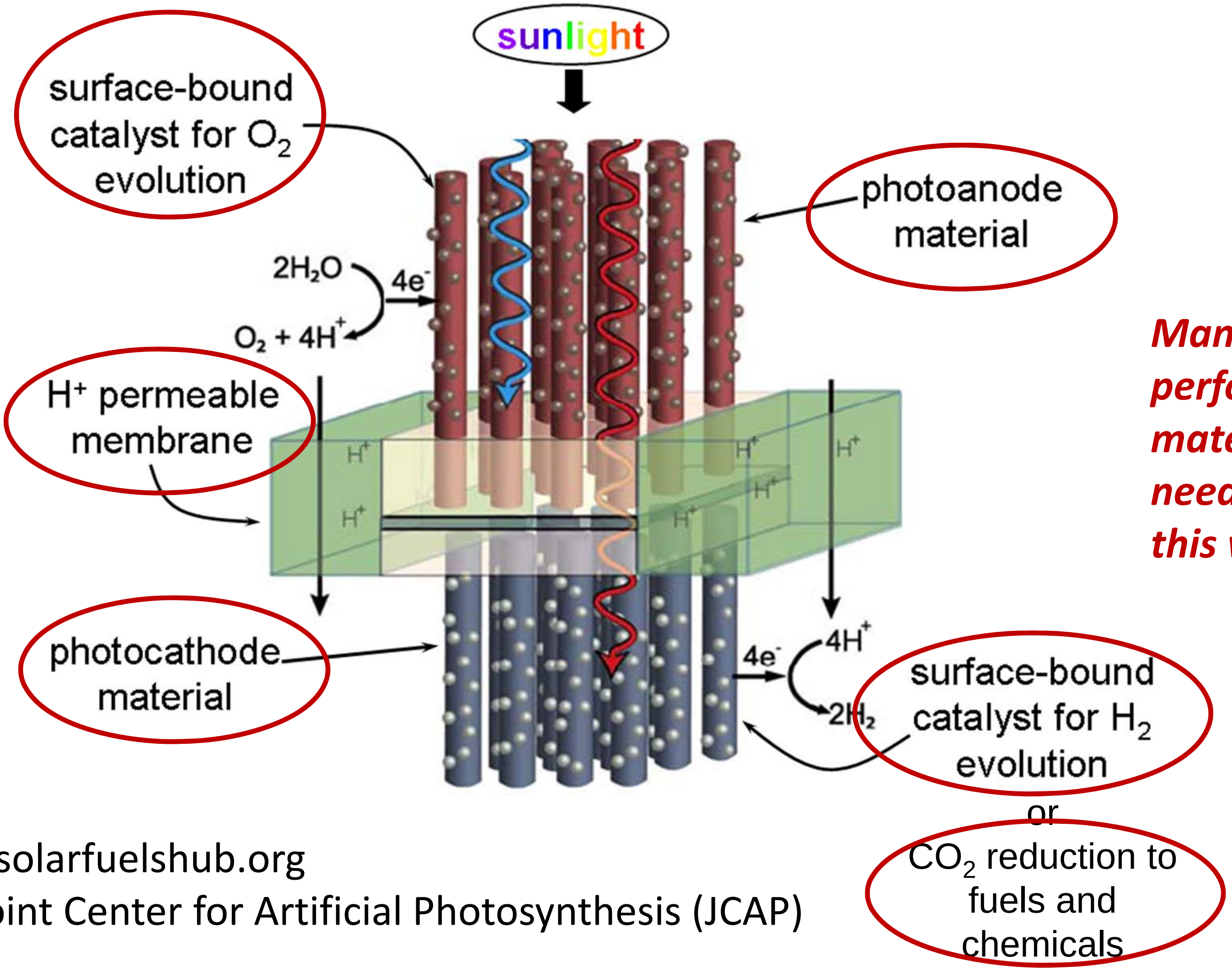

Can reach 23 % STH with E_{g1}~1.2 eV & E_{g2}~1.8 eV





L.C. Seitz, Z. Chen, A.J. Forman, B.A. Pinaud, J.D. Benck, and T.F. Jaramillo, *ChemSusChem*, **7**, 1372-1385 (2014).

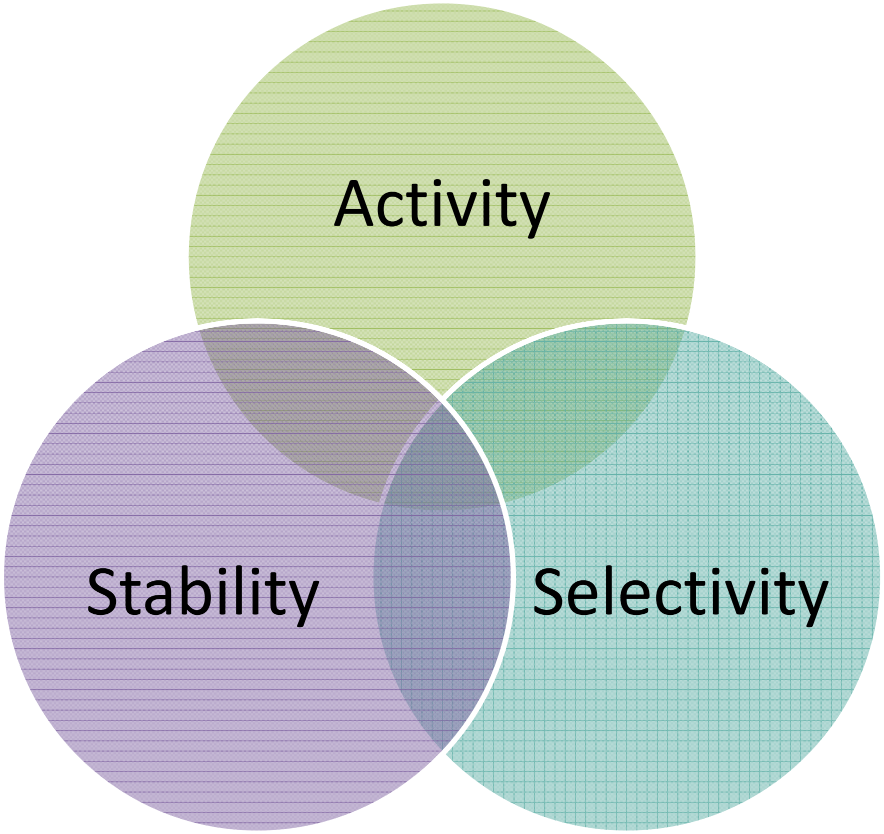
A vision of a solar fuels device



Many high-performance materials are needed to make this work!

www.solarfuelshub.org
The Joint Center for Artificial Photosynthesis (JCAP)

Three primary figures of merit for catalysts



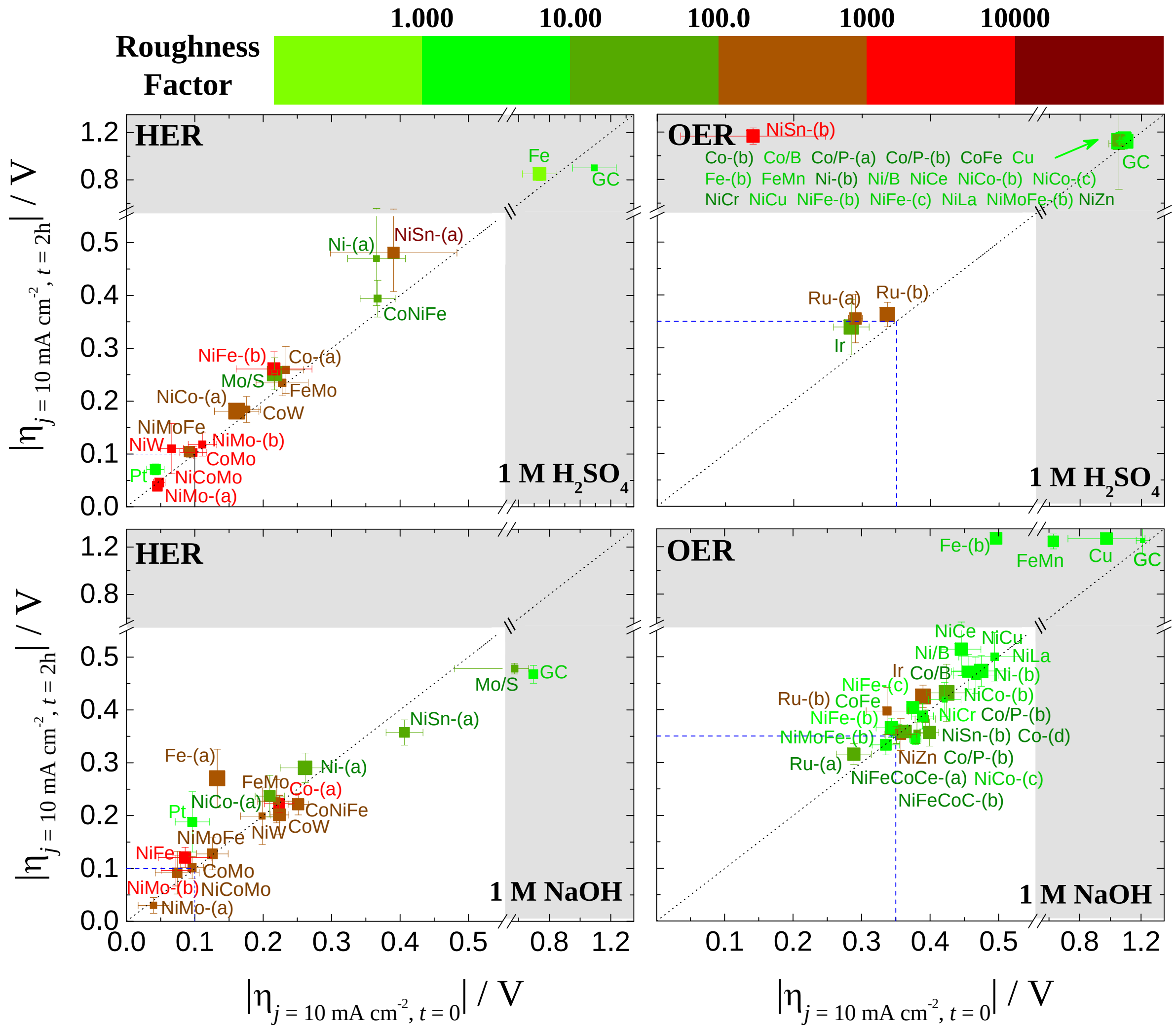
Q: Which of these is most critically needed in catalyst development?

A: It depends on the reaction!

Summary of Electrocatalyst Development

- The hydrogen evolution reaction (HER)
  - Precious metals (e.g. Pt) reach all the important performance metrics.
  - Non-precious metals are not quite as active as Pt, but they might still be feasible.
    - Some are only stable in near-neutral or base (e.g. NiMo).
    - Some are only stable in acid (e.g. metal phosphides or sulfides, e.g. MoS_2).
  - Selectivity for H_2 is excellent for all of these catalysts.
- The oxygen evolution reaction (OER)
  - Lots of room for improvement in activity, even for the best precious-metal based systems (e.g. IrO_2, RuO_2). Some non-precious-metal catalysts are as good or better, but only stable in near-neutral or alkaline conditions (e.g. $FeNiO_x$).
  - Theory has explained why achieving desired activity is so challenging.
  - Dimensionally stable anodes (DSAs) are extremely stable, proven in industrial electrolysis.
  - Selectivity is generally only a concern for seawater electrolysis, where Cl_2 and Br_2 evolution are often favored over O_2 evolution.
- The CO_2 electro-reduction reaction to fuels and chemicals
  - The most challenging of the three reactions, by far. There is a lack of viable candidate catalysts.
  - Producing 2-electron products such as formate or CO is much easier than more reduced products such as hydrocarbons or alcohols.
  - Copper produces an large fraction of hydrocarbons and alcohols, though selectivity is poor for any one product and high overpotentials are needed.
  - Much work needed to make these processes feasible.

Benchmarking H_2 and O_2 catalysts at JCAP



C.C. L. McCrory, S. Jung, I.M. Ferrer, S.M. Chatman, J.C. Peters, and T.F. Jaramillo (submitted, **2014**)

C.C.L. McCrory, S. Jung, J.C. Peters, and T.F. Jaramillo, *Journal of the American Chemical Society*, **135**, 16977-16987 (2013).

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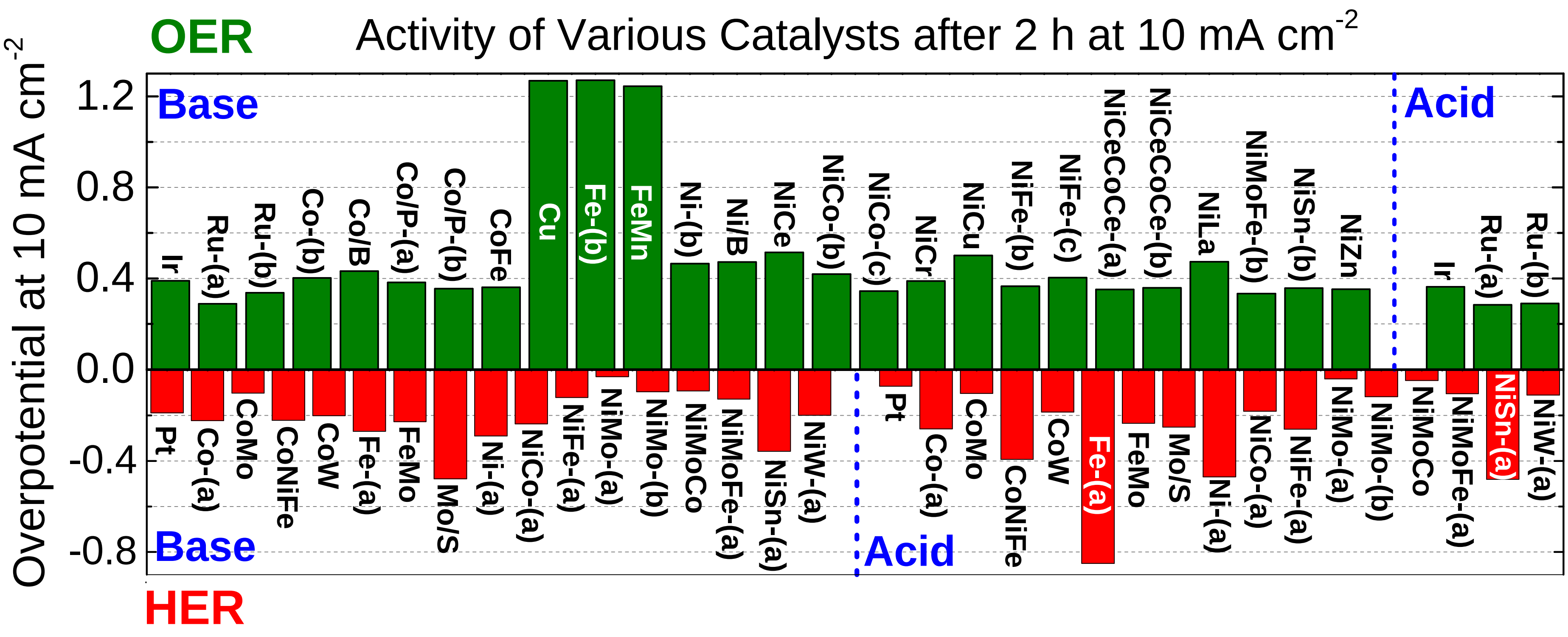


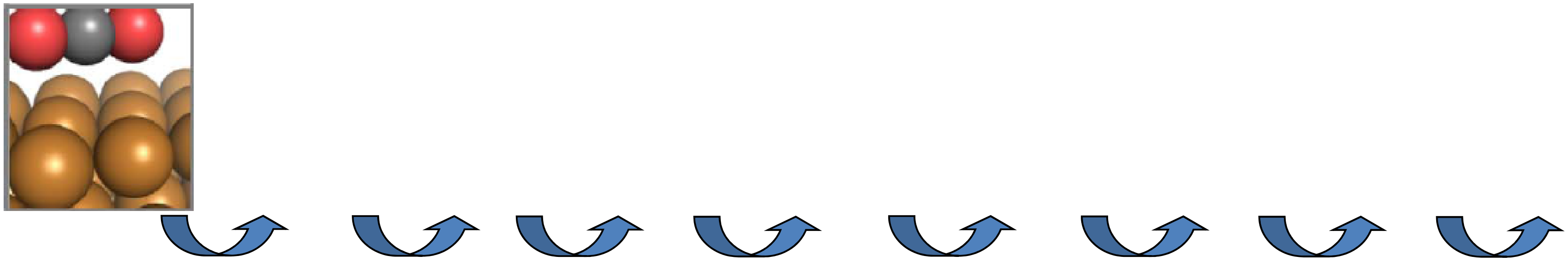
C.C. L. McCrory, S. Jung, I.M. Ferrer, S.M. Chatman, J.C. Peters, and T.F. Jaramillo (submitted, **2014**)
C.C.L. McCrory, S. Jung, J.C. Peters, and T.F. Jaramillo, *Journal of the American Chemical Society*, **135**, 16977-16987 (2013).

Thermodynamics & Kinetics of CO_2 reduction

Y. Hori, “Electrochemical CO_2 reduction on metal electrodes”
within *Modern Aspects of Electrochemistry*, Number 42, Edited by
C. Vayenas et. al., Springer, New York, 2008.

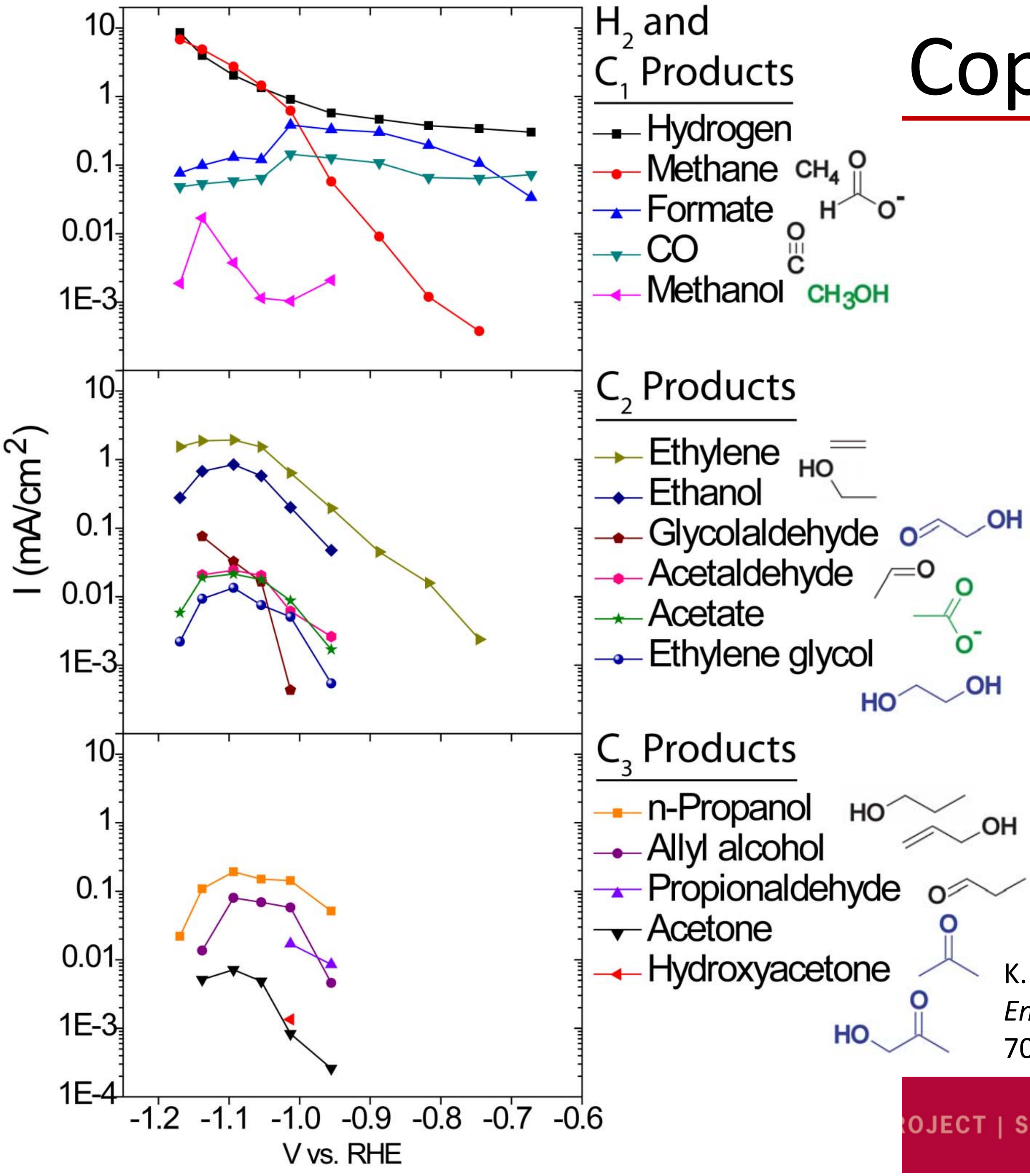
			E^0 vs. RHE
$2H^+ + 2e^-$	$\leftarrow\rightarrow$	H_2	0.00 V
$CO_2 + 2H^+ + 2e^-$	$\leftarrow\rightarrow$	$CO + H_2O$	- 0.11 V
$CO_2 + 8H^+ + 8e^-$	$\leftarrow\rightarrow$	$CH_4 + 2H_2O$	+ 0.16 V
$2CO_2 + 12H^+ + 12e^-$	$\leftarrow\rightarrow$	$C_2H_4 + 4H_2O$	+ 0.07 V
$2CO_2 + 12H^+ + 12e^-$	$\leftarrow\rightarrow$	$C_2H_5OH + 3H_2O$	+ 0.08 V
$3CO_2 + 18H^+ + 18e^-$	$\leftarrow\rightarrow$	$C_3H_7OH + 5H_2O$	+ 0.09 V

All values are close to the H_2 evolution potential (0.00 V).



A. Peterson, F. Abild-Pederson, F. Studt, J. Rossmeisl, J.K. Nørskov, *Energy& Environmental Science* v3 (**2010**) 1311-1315.

Copper catalysts



- CO and formate pull near constant current across voltage range.
- H_2 is mostly constant, then increases at high V.
- CH_4 production rate constantly increasing with Tafel behavior.
- C_2 and C_3 products clearly rise and fall together.

K.P. Kuhl, E. Cave, D.N. Abram, & T.F. Jaramillo, *Energy & Environmental Science*, Vol. 5, pp. 7050-7059, **2012**.

Synthetic Fuels: Take-home messages

- Chemical fuels are a magnificent form of energy storage.
- Researchers in the area of solar fuels aim to develop a way to produce fossil fuel-like molecules from water, CO_2, and solar energy.
- Technologically, this can already be done. However, better catalysts and semiconductors need to be developed if the process is to ever become cost-competitive with fossil fuels.
- A techno-economic analysis for the case of H_2 shows that it is possible to reach that goal if materials with appropriate properties can be developed.
- This is incentive to strengthen our efforts in R&D in this field, keeping our eyes on commercial possibilities as improved materials are developed.