ARTIFICIAL PHOTOSYNTHESIS—FUELS FROM SUNLIGHT, WATER AND CARBON DIOXIDE

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NATIONAL ACADEMIES BOARD ON CHEMICAL SCIENCES AND TECHNOLOGY

March 7th, 2018
Artificial Photosynthesis

Natural Photosynthesis

Photosynthesis
4 Photons $\rightarrow$ 1 NADPH
(48 Photons/glucose)

Artificial Photosynthesis
2 Photons $\rightarrow$ 1 Hydrogen atom
6-12 Photons $\rightarrow$ 1 Hydrocarbon
Artificial Photosynthesis

Hydrogen evolution reaction (HER)

\[ 2H^+ + 2e^- \rightarrow H_2(g) \]

Oxygen evolution reaction (OER)

\[ H_2O \rightarrow \frac{1}{2}O_2(g) + 2H^+ + 2e^- \]

CO₂ reduction reaction (CO₂RR)

\[ \begin{align*}
CO_2 + H_2O & \rightarrow HCOOH + \frac{1}{2}O_2 \\
CO_2 + H_2O & \rightarrow HCHO + O_2 \\
CO_2 + 2H_2O & \rightarrow CH_3OH + 3/2 O_2 \\
CO_2 + 2H_2O & \rightarrow CH_4 + 2O_2
\end{align*} \]

Artificial Photosynthesis

2 Photons \rightarrow 1 Hydrogen atom
6-12 Photons \rightarrow 1 Hydrocarbon
JCAP is developing scientific foundation for conversion of CO$_2$ to hydrocarbon fuels using solar energy.

+ 120,000 terawatts

The world uses only a small fraction of solar energy the Earth receives from the Sun.

Solar Energy + CO$_2$ + H$_2$O ➔ CO$_2$ + H$_2$O

Solar-driven CO$_2$ reduction

CO$_2$ air capture and recycling

Route to drop-in hydrocarbon transportation fuel

Catalyst

Target reduction products:
- Alkanes
- Alkenes
- Primary alcohols
JCAP – an Integrated Partnership for Solar Fuels Research

- Faculty and Senior Scientist Principal Investigators: 32
- Nobel Laureate: 1
- National Academies of Science and Engineering Members: 12
- National Medal of Science Recipient: 1
- American Academy of Arts and Sciences Members: 8
JCAP – an Integrated Partnership for Solar Fuels Research

Jorgensen Laboratory @ Caltech

Chu Hall @ LBNL
JCAP – an Integrated Partnership for Solar Fuels Research

ACADEMIC/LAB/EFRC PARTNERSHIPS

INDUSTRIAL INTERACTIONS

ENABLING CAPABILITIES AND PARTNERSHIPS

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Solar fuels: water-splitting

**Discovery**
- Photoelectrode materials and corrosion protection
- High throughput experimentation
- Membrane separators

**Measurement and mechanisms**
- Catalyst benchmarking
- In situ and operando studies
- Catalytic structures and mechanisms

**Integration and demonstration**
- Multiphysics modeling
- Prototype designs
- Demonstrations of robust >10% efficient water splitting

**Materials**

**Devices**

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High throughput materials discovery

Cr, Mn, Cu and V based ternary oxide photoanodes

- **Phase stability**: \( \Delta H < 50 \text{ meV/atom} \)
- **PBE+U band gap**: \( 0.2 \text{ eV} < E_g < 3.5 \text{ eV} \)
  - *Semi-empirical U’s*
- **HSE band gap**: \( 1.2 \text{ eV} < E_g < 3.2 \text{ eV} \)
- **Band edge energies**
- **Stability in water**
  - *Pourbaix diagrams*

- **MP database**
- **HSE, bulk**
- **PBE+U, surface**
High throughput discovery of stable oxide-based photoanodes

Scientific Achievement
Computation, synthesis, and spectroscopy are used to identify and study the earth-abundant Cu and Mn vanadates as a highly promising light absorbers for photocatalytic water splitting.

Significance and Impact
The detailed understanding of $\beta$-Mn$_2$V$_2$O$_7$ reveals that it is a unique metal oxide semiconductor due to its desirable band gap and near-perfect band alignment to the standard potentials for water splitting. The additional discovery of 4 CuO-V$_2$O$_5$ phases with band gap below 2 eV marks a vast expansion of the known photoelectrocatalyst for efficient solar fuel generation.

Research Details
– A density functional theory (DFT) was used to understand the structural, electronic, and magnetic properties of Mn and Cu vanadates.
– The optical and photoelectrochemical properties of these phases were mapped using combinatorial chemistry and high throughput experimentation.
– Photoelectrochemical characterization revealed excellent stability and opportunities for improving the photoelectrocatalytic activity to enable efficient photo-driven water splitting.

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High throughput discovery of stable oxide-based photoanodes

- Stitching complementary techniques together accelerates hypothesis-based discoveries

Pipeline execution summary:
- Out of the 15 hits there are 12 discoveries (3 of 15 were already reported)
- The 88% hit rate upon successful synthesis provide credence to the design criteria and the computational workflow
- These experimentally-verified predictions foundationally demonstrate that high throughput computation can accelerate experimental discovery of functional materials.

Varying the electronic band character in complex oxides enables tuning of the band gap energy and band positions.
Stable High Efficiency Water Splitting Prototypes

A >10% efficient, stable, unassisted solar-driven water-splitting in a monolithic photoelectrochemical system integrating

• Oxide-protected tandem junction photoabsorbers,
• Earth-abundant electrocatalysts, and
• Anion exchange membranes.

CX Xiang and Erik Verlage assemble a monolithically integrated III-V device, protected by a TiO$_2$ stabilization layer, which performs unassisted solar water splitting with hydrogen fuel and oxygen.

Fully integrated, highly efficient solar-fuel prototypes with gas separations

All earth-abundant electrocatalysts for operation in 1.0 M NaOH (aq.):
- NiMo for hydrogen evolution reaction (HER)
- NiO_x for oxygen evolution reaction (OER)

- Fully integrated prototypes exhibited a solar-to-hydrogen conversion efficiency close to 10%.
- Minimal product crossover achieved by incorporation of an anion exchange membrane (AEM)

19.3% Efficiency Water Splitting Device


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Rapid Advances in Efficiency for Water Splitting


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PEC device: performance limits

\[ V_{PEC}(j) = \sum_i V_{PV_i}(j) - V_{cat,a}(j) - V_{cat,c}(j) - V_{series}(j) \geq E_{rxn} \]

PV Voltage: \[ V_{PV}(j) = \frac{n_d k_B T}{q} \ln \left( \frac{j}{j_0} + 1 \right) \]

Catalyst Voltage: \[ V_{cat}(j) = \frac{RT}{\alpha n_e F} \sinh^{-1} \left( \frac{j}{2 j_{0,cat}} \right) \]

Device operating point: \[ V_{op}(j_{op}) = E_{rxn} \]

Water splitting PEC efficiency: \[ \eta_{PEC} = \frac{j_{op} E_{rxn} f_{FE}}{P_{in}} \]

PEC device: performance limits of ‘real’ devices

- Absorption of 90% of incident photons above the bandgap of the semiconductor
- An external radiative efficiency (ERE) of 3% (typical III-V)
- Catalytic exchange current densities of 1 mA·cm⁻² (HER) and 10⁻³ mA·cm⁻² (OER); consistent with the best reported values for Pt and IrO₂
- Diode ideality factor, $n_d$, of 1.
- The electrochemical potential for water-splitting at standard conditions, $E_{rxn} = 1.23$ V.
- Unity Faradaic efficiency.

Single Junction: $\eta=15.1\%$, $E_g=2.05 \text{eV}$

Dual Junction: $\eta=28.3\%$, $E_g=1.59$, 0.92eV

A 1 GW Solar Hydrogen Plant Model

A 1 GW Solar Hydrogen Plant Model

Energy Returned on Energy Invested: Sensitivity Analysis

Solar-to-hydrogen efficiency
Life span of PEC cell
Photocell fabrication energy use
Life span of balance of system
Other cell materials energy use
Primary energy-to-electricity conversion
Panel heat requirement
Capacity factor of facility
Oxygen collected
Solar transmittance loss
Compressor basic power use
Cell degradation threshold
Gas blower power use
Other cell fabrication energy use
Panels per blower

Base case: 1.7

WORSE

BETTER

The CO₂ Utilization Landscape

Current emissions:

- 10 GtC/yr
  - 0.6 GtC/yr Manufacturing
  - 0.9 GtC/yr Land use change
  - 8.5 GtC/yr Fuels combustion

Some possible non-atmospheric ends:

- 3.8 GtC/yr Coal and other solid fuels
- 3.6 GtC/yr Liquid fuels
- 2.0 GtC/yr Methane and other gas
- 0.1 GtC/yr Other chemicals

Consumable Materials [2, 3] Carbon recycling

- 3.0 GtC/yr C-based concrete substitute
- 1.4 GtC/yr C-based steel substitute
- 0.8 GtC/yr CaCO₃-based cement substitute
- 0.2 GtC/yr Polymers

Non-Consumable Materials [4, 5, 6, 7, 8] Useful sequestration

- 0.7-0.9 GtC/yr Enhanced oil recovery
- 0.6-2.2 GtC/yr Biomass storage (biochar)
- 0.5-1.8 GtC/yr Geologic storage
- 0.1-2.0 GtC/yr Deep ocean injection

Store it

Pure Sequestration [9, 10, 11, 12]

GCC = 1 billion metric tons of carbon equivalent, i.e. 1 Gt MeqH = 12.01/(12.01+16.00+4*1.01) Gt = 0.37 GtC.

1 Assuming cement is composed of CaCO₃, and the aggregate is composed of 50% CaCO₃ by mass.
2 Assuming a steel substitute that is similar in composition to carbon fiber, i.e. 90% C by mass.
3 Assuming cement is composed of CaCO₃.
4 Estimated feasible scale-up rates by 2050, excluding geoengineering approaches. Shaded bars indicate the upper range of estimates.
The CO$_2$ Utilization Landscape

- Focus on processes able to capture, reduce or sequester 1 GtCO$_2$/yr scale
- 1 of the top 5 Priorities: Synthetic Transformations of CO$_2$
- Recommendations:
  - Reduce the cost of carbon-free/neutral energy in the form of heat/electricity
  - Focus on fundamentals of electrocatalysis and photoelectrocatalysis
  - Identify catalysts made of abundant elements that reduce the overpotentials for CO$_2$RR and OER at high reaction rates.
The CO₂ Utilization Landscape
Routes to fuels from CO$_2$: Comparing Approaches

Approaches to reduction of CO$_2$ to fuels:

**Thermocatalysis**
- Advantages:
  - Mature technology; heat only required as energy input
- Disadvantages:
  - High capital cost and intrinsically large-scale for plant; efficiency < 100%

**Electrocatalysis**
- Advantages:
  - Room temperature operation, high FE and throughput for certain products (e.g., CO, HCOO$^-$)
- Disadvantages:
  - Limited throughput, low selectivity and STF efficiency for alkane and alcohol fuels

**Photocatalysis**
- Advantages:
  - Low capital cost, scalable, uses sunlight as direct energy input
- Disadvantages:
  - Low efficiency and selectivity, product separation

**Biocatalysis**
- Advantages:
  - Low capital cost; near room temperature; near neutral pH operation
- Disadvantages:
  - Limited durability (bacteria die after 30 days); limited pH range, low throughput
Many chemical conversions from syngas to products, including gasoline via Fischer-Tropsch
Many chemical conversions from methanol to products, including gasoline
Methanol is an achievable product from CO$_2$R PEC

F-T has 50-60% thermal energy conversion efficiency

Methanol synthesis has 50-60% thermal energy conversion efficiency

Methanol-to-gasoline (MTG) has 95% thermal energy conversion efficiency

Why not just make CO and H₂ and use thermochemistry to do the rest?

- High capital cost for thermochemical plant
- Fischer-Tropsch thermal conversion efficiency 50-60%
- Requires source of hydrogen using process other than steam reforming (PEC water splitting technology development ongoing)

Japanese Gas to Liquids Pilot Plant, Niigata City, Japan
Production scale: 500 barrels/day

Need for direct, selective CO₂R catalysis strategies under mild P & T conditions that have potential for scalable production of fuels from sunlight with low capital cost.
Copper: our best heterogeneous CO$_2$R catalyst ... so far

Selectivity is a major issue

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Methane</th>
<th>Methanol</th>
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<tr>
<td>Fe</td>
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</tbody>
</table>

Catalyst Surface Structure

Mechanisms for achieving selectivity in CO₂ Reduction

Electrocatalysis Strategies

Photocatalysis Strategies

- Multi-site surfaces
- Confinement
- Tethering/Functionalization
- Electrolyte engineering
- Interfacial sites

- Thermal
- Plasmon Resonance
- Hot Carrier

- p-type Semicond.

JCAP Center for Artificial Photosynthesis

Caltech
Theory Developments

Kinetics and Mechanisms

- Free Energy (eV)
  - Initial
  - Transition State
  - Final
- Position (Å)
  - Solute Electrolyte Interface

- W.A. Goddard et al., JACS, 2016, 138, 483-486.

Catalyst Screening

- Microkinetic Rate at -1 V
- J.K. Nørskov et al., ACS Catalysis, 2016, 6, 4428-4437.

Electrochemical Interface and Higher Order Methods

- Solute Electrolyte Interface
- Position (Å)

W.A. Goddard et al., JACS, 2016, 138, 483-486.
Experimental developments

Catalyst Composition

Catalyst Surface Structure

Catalyst Morphology

Electrolyte Composition and Ionomer-Catalyst

Catalyst and Reaction Intermediate Characterization

J.T. Feaster, C. Hahn, and T.F. Jaramillo et al., 2016.


Tuning selectivity of copper with molecules to make multicarbon products

Addition of N-aryl pyridinium molecules enhances the selectivity for C≥2 products to ~80%.
(ethylene, ethanol and propanol)

A Sustainable Energy Landscape

Summary

- **JCAP developing a strategy for selective EC-CO₂ reduction**: multifunctional cathode that combines multiple active sites, functional coatings, additives, nanoscale confining volumes
- **Mechanism discovery**: initial focus predominantly on Cu and Cu alloys
- **Materials discovery**:
  - bimetallic alloy candidates screened and synthesized
  - oxide photoanode theory/experimental effort achieves high predictive yield
- **Integration** – OER at ‘mild’ pH and membranes
- **Prototyping**: testbeds for EC and PEC CO₂RR in liquid electrolytes and vapor (GDE)
- **Devices**: with high Faradaic efficiency for C2 (ethylene, ethanol) products