ARTIFICIAL PHOTOSYNTHESIS—THE SELECTIVE CO₂ REDUCTION CHALLENGE

HARRY ATWATER

JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS
ISF-2

July 8th 2017
JCAP Mission

JCAP is developing scientific foundation for conversion of CO₂ 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 + CO₂ + H₂O** → **CO₂ + H₂O**

**Solar-driven CO₂ Reduction**

**CO₂ Air Capture and Recycling**

**Route to drop-in hydrocarbon transportation fuel**

**Target Reduction Products**
- Alkanes
- Alkenes
- Primary Alcohols
### JCAP’s First Phase: Solar Fuels for Water-Splitting

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**Integration and demonstration**

- Multiphysics modeling
- Prototype designs
- Demonstrations of robust >10% efficient water splitting
**JCAP: SOLAR FUELS GENERATORS**

### 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)

- \( CO_2 + H_2O \rightarrow HCOOH + \frac{1}{2}O_2 \)
- \( CO_2 + H_2O \rightarrow HCHO + O_2 \)
- \( CO_2 + 2H_2O \rightarrow CH_3OH + 3/2 O_2 \)
- \( CO_2 + 2H_2O \rightarrow CH_4 + 2O_2 \)
Oxide-Protected Photoanode Device:
A >10% efficient, stable, unassisted solar-driven water-splitting in a monolithic photoelectrochemical system integrating
• 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.

Catalytic Grid Photocathode Device:

State of the Art for PEC Hydrogen Generation – 2015

Reported Solar to Hydrogen Conversion Efficiencies

PV and catalyst configuration:
- 2J, integrated PVs and catalysts
- 2J, integrated PVs, wired catalyst
- 2J, series connected PVs or catalysts
- 3J, integrated PVs and catalysts
- 3J, integrated PVs, wired catalyst
- 3J, series connected PVs or catalysts

Reported STH efficiency (%):

PV materials:
- All III-V
- Partial III-V
- All silicon
- Partial Si
- Oxides and other

>15%

>10%

>5%

PEC HYDROGEN GENERATION PERFORMANCE LIMITS

\[ V_{PEC}(j) = V_{PV}(j) + V_{cat,a}(j) + V_{cat,c}(j) + V_{series}(j) + E_{rxn} \]

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

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

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

**Water splitting PEC efficiency:**  \[ PEC = \frac{j_{op} E_{rxn} f_{FE}}{P_{in}} \]
### Realistic Performance Limits for PEC Hydrogen Generation

- 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 $1 \text{ mA} \cdot \text{cm}^{-2}$ (HER) and $10^{-3} \text{ mA} \cdot \text{cm}^{-2}$ (OER); consistent with the best reported values for Pt and IrO$_2$
- Diode ideality factor, $n_d$, of 1.
- The electrochemical potential for water-splitting at standard conditions, $E_{\text{rxn}} = 1.23 \text{ V}$.
- Unity Faradaic efficiency.

**Single Junction:**

$$\eta = 15.1\%, \quad E_g = 2.05 \text{ eV}$$

**Dual Junction:**

$$\eta = 28.3\%, \quad E_g = 1.59, 0.92 \text{ eV}$$

Fountaine, Lewerenz, Atwater Nature Communications (2016)
GaInP with $E_g = 1.78 \text{ eV}$; GaInAs with $E_g = 1.26 \text{ eV}$

19.3% STH Efficiency Integrated PEC Device

Rapid Advances in Efficiency of Integrated STH PECs

All earth-abundant electrocatalysts: NiO$_x$ for OER in the KBi buffer and CoP$_x$ for HER in 1.0 M H$_2$SO$_4$.

- > 1.0 cm$^2$, > 10% STH conversion efficiency, >100 hour stability was achieved using a tandem photoabsorber in a cell configuration that incorporates a bipolar membrane.
- The acid stable electrocatalyst, CoP, was successfully integrated into the cell.

Bipolar membrane:
- near-unity transfer numbers for proton and hydroxide transport at relatively high operational current densities
- ~400-500 mV voltage loss due to ohmic resistance, water dissociation and water transport processes, further improvements can be made by incorporating water dissociation catalysts at the interface.

K. Sun, R. Liu, E. Verlage, N. S. Lewis, C. Xiang, E&ES (2016)
**Solar-Driven Reduction of CO$_2$ to Formate at 10% Energy Conversion Efficiency**

Schematic illustration of the series connected photoanode and dark cathode for CO$_2$ reduction to formate

- **Photoanode**: InGaP/GaAs/TiO$_2$/NiO$_x$ at pH=14 electrolyte previously used for solar water-splitting.
- **Dark cathode**: Pd/C nanoparticles on Ti mesh in pH=8 bicarbonate solution achieved $\leq 100$ mV overpotential and $>94\%$ Faradaic efficiency at 10 mA cm$^{-2}$.
- **Bipolar membrane** sustained the steady-state pH differential and minimized the product crossovers.

**Relative Scale of Emissions and Potential Uses for CO₂**

**Current emissions:**
- 10 GtC/yr $^{[1]}$
- 0.6 GtC/yr Manufacturing
- 0.9 GtC/yr Land use change
- 8.5 GtC/yr Fuels combustion

**Use it**
- 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$^{1}$
- 1.4 GtC/yr C-based steel substitute$^{2}$
- 0.8 GtC/yr CaCO₃-based cement substitute$^{3}$
- 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**

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GtC = 1 billion metric tons of carbon equivalent, i.e. 1 Gt = $12.01/(2.01+16.00+4*1.01)$ GtC = 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 geengineering approaches. Shaded bars indicate the upper range of estimates.
**THE CO₂ UTILIZATION LANDSCAPE**

- **Focus on processes able to capture, reduce or sequester 1 GtCO₂/yr scale**
- **1 of the top 5 Priorities: Synthetic Transformations of CO₂**
- **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 CO₂RR and OER at high reaction rates.

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**THE CARBON LANDSCAPE**

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Secretary of Energy Advisory Board Report, 12/13/2016
THE $\text{CO}_2$ UTILIZATION LANDSCAPE

(A) Electrochemical → Photochemical → Biochemical → Thermochemical

CO$_2$ feedstock at \$/tC

$\text{H}_2$ $\text{/kg}$

$\text{H}_2 \text{O}$

Biomass (Fossil sources of C or CH$_4$)

Fossil fuel-based energy

CO$_2$ capture and storage

Thermochemical (Reverse Water Gas Shift + Fischer-Tropsch)

Methanol

Ethanol

Hydrocarbon ($$/kg; $$/L)

Carbon-free/netural exergy at $$/kWh

(B) Electrochemical → Photochemical → Biochemical → Thermochemical

CO$_2$ feedstock at \$/tC

$\text{H}_2$ $\text{O}$

$\text{H}_2$ $\text{$/kg}$

Thermochemical (Reverse Water Gas Shift + Fischer-Tropsch)

Methanol

Ethanol

Hydrocarbon ($$/kg; $$/L)

Carbon-free/netural exergy at $$/kWh

(C) Electrochemical → Photochemical → Biochemical → Thermochemical

CO$_2$ feedstock at \$/tC

$\text{H}_2$ $\text{O}$

Fossil sources of C or CH$_4$

Fossil fuel-based energy

Thermochemical (Reverse Water Gas Shift + Fischer-Tropsch)

Methanol

Ethanol

Hydrocarbon ($$/kg; $$/L)

$\text{H}_2$ at $$/kg

SECRETARY OF ENERGY ADVISORY BOARD REPORT, 12/13/2016
**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
**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

*JCAP aims 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.*
**Chemical Syntheses from Syngas and Methanol**

- 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

![Diagram](image)

**Source:** P.L. Spath and D.C. Dayton, Preliminary screening—technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas, National Renewable Energy Laboratory, NREL/TP-510-34929, December, 2003.
Selectivity is a major issue: Competition with HER

Kuhl, Cave, Abram, Jaramillo
POSSIBLE PATHWAYS FOR CO₂ REDUCTION CATALYSIS ON COPPER

C₁ Products: CO₂ Adsorption

- CO₂ → HCOO⁻
- CO₂ → CO, CH₄
- CO₂ → CH₃OH

C₂ Products: CO Dimerization

- CO₂ → C₂H₄
- CO₂ → CH₃CH₂OH

C₁ Products: CO₂ Insertion

- CO₂ → HCOO⁻

Adsorption energies of the key bound intermediates on fcc Cu (211)

Adsorption energies of adsorbates binding through oxygen

OVERCOMING SCALING RELATIONSHIPS FOR CO₂ REDUCTION

**Electrocatalysis Strategies**

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

**Photocatalysis Strategies**

- Thermal
- Plasmon Resonance
- Hot Carrier

**Graphical Representations**

- Schematic diagrams illustrating various strategies for electrocatalysis (left) and photocatalysis (right).

**Key Concepts**

- Electrocatalysis
- Photocatalysis
- Thermal processes
- Plasmon Resonance
- Hot Carrier phenomena

**Additional Details**

- Diagrams highlight the interaction between catalysts, adsorbates, and electrolytes.
- Energy levels (E_F) and fermi levels (E_F) are marked.

**Contextual Information**

- Focus on overcoming scaling relationships in CO₂ reduction.
- Integration of selective CO₂ reduction strategies.
THEORY DEVELOPMENTS

Kinetics and Mechanisms

Transition State

Final

Free Energy (eV)

-1.0 V

-0.8 V

-0.6 V

-0.4 V

-0.2 V

0.0 V

vs RHE

Initial

-1.0 V


Catalyst Screening


J.K. Nørskov et al., *ACS Catalysis*, 2016, 6, 4428-4437.

Electrochemical Interface and Higher Order Methods


Microkinetic Rate at -1 V

Potential Difference [V]


Sustainable CO₂ Reduction
EXPERIMENTAL DEVELOPMENTS

Catalyst Composition

Catalyst Surface Structure

Catalyst Morphology

Electrolyte Composition and Ionomer-Catalyst Interactions

Catalyst and Reaction Intermediate Characterization

Reactor Design

- Oxygenate/Hydrocarbon
- Copper Atomic Percent

- Boundary Layer
- Well-Mixed Layer


Dr. Jakob Kibsgaard

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


0% 20% 40% 60% 80% 100%
0% 20% 40% 60% 80% 100%

0% 20% 40% 60% 80% 100%
0% 20% 40% 60% 80% 100%

0% 20% 40% 60% 80% 100%
0% 20% 40% 60% 80% 100%

**Electrolyte Selection: Choice of Cation**

Use of CsHCO$_3$ buffer increases FE to C$_2$+ products (ethanol, ethylene) on Cu foil

<table>
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<tr>
<th>Electrolyte</th>
<th>FE / %</th>
<th>C$_2$H$_4$ / CH$_4$</th>
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<tr>
<td>Li</td>
<td>86.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Na</td>
<td>66.3</td>
<td>0.3</td>
</tr>
<tr>
<td>K</td>
<td>55.1</td>
<td>0.7</td>
</tr>
<tr>
<td>Rb</td>
<td>32.2</td>
<td>1.8</td>
</tr>
<tr>
<td>Cs</td>
<td>31.1</td>
<td>3.3</td>
</tr>
</tbody>
</table>

1- Propanol, Ethanol, Acetate, Formate, Ethylene, Methane, CO, H$_2$

$-1.0 \text{ V vs RHE in CO}_2$-saturated 0.1 M MHCO$_3$

Singh, M. R.; Kwon, Y.; Lum, Y.; Ager, J. W.; Bell, A. T.  
Scientific Achievement

Identified tandem, bimetallic catalysts for the preferential formation of H$_2$COO over H$_2$.

Significance and Impact

Selective reduction of CO$_2$ to H$_2$COO can be achieved by embedding metal atoms that favor CORR over HER in a host metal that favors CO$_2$ reduction to CO. The CORR catalyst must bind *CHO (or *COH) more tightly than *H.

Research Details

DFT/RPBE/APW was used to calculate the free energy of activation for all elementary steps in CO$_2$ reduction to CO on Au(111) or Ag(111) surfaces and the reduction of CO to H$_2$CO vs H2 on Cu, Ni, Pd, Pt, Co, Rh, and Ir atoms embedded in the host metal surface.

Near-Surface Alloy for Selective Reduction of CO$_2$ to CH$_3$OH

A theoretical prediction: a near-surface alloy (NSA) of a monolayer of Au on bulk W was empirically found to generate CH$_3$OH to the exclusion of other hydrocarbons and alcohols.

Approach

- Combined density-functional theory and adsorption-energy descriptors $\Delta G^\circ_{\text{CO}_2}$, $\Delta G^\circ_{\text{H}}$ and $\Delta G^\circ_{\text{OH}}$ predicted a Au-W-Au NSA that would be CH$_3$OH-product-selective.
- Overlayer NSA films of (0.5 to 3 ML) Au on W were prepared by controlled galvanostatic deposition.

Products from CO$_2$ reduction at -1.2 V(RHE) in 0.1 M KHCO$_3$ were analyzed by Differential Electrochemical Mass Spectrometry (DEMS). Only CH$_3$OH was found.

**Electrochemical Reduction of CO₂ Selectively to Methanol**

Constant-potential DEMS of CO₂ Reduction on Au-W Near-Surface Alloy

<table>
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<th>Theoretical Prognosis</th>
<th>Experimental Result</th>
<th>Future Work:</th>
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<tr>
<td>CH₃OH-Selective</td>
<td>CH₃OH-Selective</td>
<td>Prepare NSA as prescribed by theory</td>
</tr>
<tr>
<td>High Activity</td>
<td>Not yet optimized</td>
<td>Try different substrates with the same NSA</td>
</tr>
<tr>
<td>Low Overvoltage</td>
<td>Not yet optimized</td>
<td>Obtain complete and quantitative product analysis</td>
</tr>
<tr>
<td>HER Suppression</td>
<td>Not yet optimized</td>
<td>Have theory scrutinized by other theory groups</td>
</tr>
</tbody>
</table>

Polarization curves, Cu – theory vs experiment

\[ \log(j \text{ (mA/cm}^2) \]

\[ P_{\text{CO(g)}} = 1 \text{ mbar} \]

\[ \text{Voltage (V)} \]

- CO\textsubscript{2}RR experiment
- (211) surface
- (111) surface
- (100) surface
- 5\% (211) surface + 95\% (111) surface


Kuhl, Cave, Abram, Jaramillo,
Energy & Environmental Science 5, 7050 (2012).
EPITAXIAL GROWTH USING PHYSICAL VAPOR DEPOSITION

Directing growth orientation utilizing interfacial energy


E-beam Evaporation

Normalized XRD Intensity (a.u.)

4”
TEXTURE OF Cu THIN FILMS

Effects of Surface Structure on C-C Coupling Selectivity

C-C coupling is favored on under-coordinated sites. Epitaxial Cu thin films are single-crystal analogous for C-C coupling selectivity.

Cu(751) has the lowest number of nearest neighbors, and is the least likely to have adsorbed H* adjacent to C2 intermediates. PCET instead of hydride transfer leads to less structure sensitivity.
OECSTM: Cu Reconstruction at CO$_2$R Conditions (-0.9 V/0.1 M KOH)

Cu(pc) \[ t = 0 \text{ m} \] → Cu(111) \[ t = 30 \text{ m} \] → Cu(100) \[ t = 60 \text{ m} \]

Cu(111) \[ t = 0 \text{ m} \] → Cu(100) \[ t = 60 \text{ m} \]

Cu(110) \[ t = 0 \text{ m} \] → Disordered Cu(111) \[ t = 30 \text{ m} \] → Cu(100) \[ t = 60 \text{ m} \]

REGULATING CO-REDUCTION SELECTIVITY BY CONTROL OF SURFACE STRUCTURE

Ethanol-product Selectivity of Post-ORC
Cu(pc)-[Cu(100)] at -1.0 V in 0.1 M KOH

CO-to-C$_2$H$_5$OH on Cu(511)

Surface Lattice Model
Cu(S)-[3(100)x{111}] or Cu(511)

Y.-G. Kim, J. H. Baricuatro, A. Javier and M. P. Soriaga, J.Electroanal. Chem. 780 pp 290-295 (2106)
High Throughput Discovery of Photoanodes

Design Materials & Interface with MP Database
Joint project with the Materials Project to design photoanodes and identify candidate materials.

High Throughput Computation
Judicious choice of functional to rapidly evaluate the electronic structure and Pourbaix stability of hundreds of materials

High Throughput Experimentation
Identify synthesis conditions, generate composition maps of optical and photoelectrochemical properties.

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 provides 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.

BIPHASIC OER CATALYST INTEGRATED ON Si

Onset potential for water oxidation of <1V versus RHE and a saturation current density of 37.5 mA/cm²:

More Co(OH)₂ component increases with increasing photoelectron take-off angle → surface layer:

No detectable transfer of Co from the film into solution after 72 hr.

A new electrochemical CO$_2$ test bed implements isolates the fuel-containing electrolyte produced at the cathode from the anode and produces a stream of liquid products.

Cell design validated with 2-D Multiphysics modeling and experimentally implemented.

Separation efficiency as high as 90% demonstrated.

MULTIPHYSICS MODELING: VIRTUAL INTEGRATOR AND TESTING PLATFORM

Optimize geometries of prototype designs

Evaluate viability of new design concepts

Understand cell performance in real-life environment

Define operational conditions and constraints

Guide materials development

Multiscale model

Theory
20 mA/cm² is feasible with 1 atm CO₂ or equivalent high concentration locally
For aqueous: pH 7.5 to 8.5 shows lowest total losses while maintaining selectivity towards CO₂ reduction

Key is local CO₂ concentration

A strategy for selective EC-CO$_2$ reduction: multifunctional cathode that combines multiple active sites, functional coatings, 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 - focus on OER (– biphasic cobalt oxide)

Prototyping: device architectures for EC and PEC CO$_2$RR