OVERVIEW OF PHOTOELECTROCHEMICAL DEVICES FOR CONVERSION OF CO\textsubscript{2} AND WATER TO OXYGEN AND FUELS

Chengxiang ("CX") Xiang
Joint Center for Artificial Photosynthesis (JCAP)
California Institute of Technology

Addressing the Mars ISRU Challenge Workshop
Keck Institute for Space Studies
June 28 - July 1, 2016
• The Basic Operating Principles of a Photoelectrochemical (PEC) CO$_2$ Reduction Reaction (CO$_2$RR) System.
• Materials and Components.
• Device Designs and Demonstration.
WHAT IS A PHOTOELECTROCHEMICAL CO₂ REDUCTION SYSTEM

The system takes the sunlight, carbon dioxide and water and converts them into fuels and oxygen.
WHAT IS A PHOTOELECTROCHEMICAL CO₂ REDUCTION SYSTEM

The system takes the sunlight, carbon dioxide and water and converts them into fuels and oxygen.

Oxygen evolution reaction (OER)

\[
\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 \text{(g)} + 2\text{H}^+ + 2\text{e}^-
\]

\[
\text{CO}_2 \text{RR} \text{Reaction (CO}_2\text{RR)}
\]

\[
\text{CO}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{CO} + \text{H}_2\text{O}
\]

\[
\text{CO}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{HCOOH}
\]

\[
\text{CO}_2 + 6\text{e}^- + 6\text{H}^+ \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}
\]

\[
\text{CO}_2 + 8\text{e}^- + 8\text{H}^+ \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}
\]
WHAT IS A PHOTOELECTROCHEMICAL CO₂ REDUCTION SYSTEM

The system takes the sunlight, carbon dioxide and water and converts them into fuels and oxygen.

Oxygen evolution reaction (OER)

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

\[
CO_2 + 2e^- + 2 H^+ \rightarrow CO + H_2O
\]

\[
CO_2 + 2e^- + 2 H^+ \rightarrow HCOOH
\]

\[
CO_2 + 6e^- + 6 H^+ \rightarrow CH_3OH + H_2O
\]

\[
CO_2 + 8e^- + 8 H^+ \rightarrow CH_4 + 2 H_2O
\]

Key materials:

- Photoabsorber
- CO₂RR catalyst
- OER catalyst
WHAT IS A PHOTOCURRENT CHEMICAL CO₂ REDUCTION SYSTEM

The system takes the sunlight, carbon dioxide and water and converts them into fuels and oxygen.

Oxygen evolution reaction (OER)

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

CO₂ Reduction reaction (CO₂RR)

\[ \begin{align*}
                  CO_2 & + 2e^- + 2 H^+ \rightarrow CO + H_2O \\
                  CO_2 & + 2e^- + 2 H^+ \rightarrow HCOOH \\
                  CO_2 & + 6e^- + 6 H^+ \rightarrow CH_3OH + H_2O \\
                  CO_2 & + 8e^- + 8 H^+ \rightarrow CH_4 + 2 H_2O 
\end{align*} \]

Key materials:
- Photoabsorber
- CO₂RR catalyst
- OER catalyst

Key components:
- Reactant delivery
- Ionic transport
- Product separation
**WHAT IS A PHOTOELECTROCHEMICAL CO₂ REDUCTION SYSTEM**

The system takes the sunlight, carbon dioxide and water and converts them into fuels and oxygen.

![Diagram of CO₂ reduction system](image)

**Oxygen evolution reaction (OER)**

\[ \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 (\text{g}) + 2\text{H}^+ + 2\text{e}^- \]

**CO₂ Reduction reaction (CO₂RR)**

- \[ \text{CO}_2 + 2\text{e}^- + 2 \text{H}^+ \rightarrow \text{CO} + \text{H}_2\text{O} \]
- \[ \text{CO}_2 + 2\text{e}^- + 2 \text{H}^+ \rightarrow \text{HCOOH} \]
- \[ \text{CO}_2 + 6\text{e}^- + 6 \text{H}^+ \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \]
- \[ \text{CO}_2 + 8\text{e}^- + 8 \text{H}^+ \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \]

**Key materials:**
- Photoabsorber
- CO₂RR catalyst
- OER catalyst

**Key components:**
- Reactant delivery
- Ionic transport
- Product separation

**Key performance metrics:**
- Conversion efficiency
- Selectivity
- Stability
- Scalability
WHAT IS A PHOTOELECTROCHEMICAL CO₂ REDUCTION SYSTEM

The system takes the sunlight, carbon dioxide and water and converts them into fuels and oxygen.
**WHAT IS A PHOTOELECTROCHEMICAL CO₂ REDUCTION SYSTEM**

The system takes the sunlight, carbon dioxide and water and converts them into fuels and oxygen.

![Diagram showing the process of converting sunlight, carbon dioxide and water into fuels and oxygen. The diagram includes labels for Photoabsorber, CO₂ RR catalyst, Fuel, O₂, H₂O, Photoabsorber power curve, Operating point, Overall load curve, 1-dimensional analysis.]
WHAT IS A PHOTOELECTROCHEMICAL CO₂ REDUCTION SYSTEM

The system takes the sunlight, carbon dioxide and water and converts them into fuels and oxygen.

The overall load curve includes:
- Thermodynamic voltage window.
- Kinetic overpotentials for OER and CO₂RR.
- Concentration overpotentials due to reactant and product transport.
- Ionic transport losses.
**What is a Photoelectrochemical CO$_2$ Reduction System**

The system takes the sunlight, carbon dioxide and water and converts them into fuels and oxygen.

The overall load curve includes:
- Thermodynamic voltage window.
- Kinetic overpotentials for OER and CO$_2$RR.
- Concentration overpotentials due to reactant and product transport.
- Ionic transport losses.
WHAT IS A PHOTOELECTROCHEMICAL CO₂ REDUCTION SYSTEM

Modeling and simulation of multi-dimensional prototype performances
Outline

- The Basic Operating Principles of a Photoelectrochemical (PEC) CO$_2$ Reduction Reaction (CO$_2$RR) System.
- Materials and Components.
- Device Designs and Demonstration.
PHOTOABSORBERS

The “engine” of the system: provide the necessary voltage and current for the overall chemical reaction
PHOTOABSORBERS

The “engine” of the system: provide the necessary voltage and current for the overall chemical reaction.
PHOTOABSORBERS

The “engine” of the system: provide the necessary voltage and current for the overall chemical reaction.

http://www.nrel.gov/solar_radiation/

Photoabsorbers

The “engine” of the system: provide the necessary voltage and current for the overall chemical reaction.

http://www.nrel.gov/solar_radiation/
**PHOTOABSORBERS**

The “engine” of the system: provide the necessary voltage and current for the overall chemical reaction.

![Diagram of CO₂ reduction and electricity generation](image)

**Solar spectrum**

**Photoabsorber charge-separation**

**Electrochemical conversion of CO₂ to CO at 10 mA cm⁻²**

- Thermodynamic voltage window: **1.33 V**
- Kinetic overpotential for OER: **~300 mV**
- Kinetic overpotential for CO₂RR: **~200 mV**
- Concentration overpotentials: **~100 mV**
- Ionic transport losses: **~100 mV**

Total voltage needed at 10 mA cm⁻² = **~2.03 V**

---

http://www.nrel.gov/solar_radiation/

**PHOTOABSORBERS**

The “engine” of the system: provide the necessary voltage and current for the overall chemical reaction.

**Electrochemical conversion of CO$_2$ to CH$_4$ at 10 mA cm$^{-2}$**
- Thermodynamic voltage window: 1.33 V
- Kinetic overpotential for OER: $\sim$300 mV
- Kinetic overpotential for CO$_2$RR $\sim$1.4 V
- Concentration overpotentials: $\sim$100 mV
- Ionic transport losses: $\sim$100 mV

Total voltage needed at 10 mA cm$^{-2}$ = $\sim$3.23 V

For high operating voltages
- Current-voltage optimization by coupling various PV modules in series and/or in parallel and by adjusting area ratios of the catalyst to PV area.

Max Efficiency- 6.95% at optimal band-gap combination

CO₂ REDUCTION REACTION (CO2RR) CATALYST

We can perform CO₂ reduction to CO or formic acid quite well!


What about everything else?

Cu electrode for CH₄ production


CO2 REDUCTION REACTION (CO2RR) CATALYST

What about everything else?

Vojvodic, A.; Norskov, J. K., New design paradigm for heterogeneous catalysts. National Science Review 2015, 2, (2), 140-143


**Key materials:**
- Photoabsorber
- CO$_2$RR catalyst
- OER catalyst

**Key components:**
- Reactant delivery
- Ionic transport
- Product separation
CO₂ Delivery to the Electrode Surface

- Elevated pressure

<table>
<thead>
<tr>
<th>CO₂ Pressure (atm)</th>
<th>CH₄</th>
<th>C₂H₄</th>
<th>C₂H₅OH</th>
<th>CO</th>
<th>HCOO⁻</th>
<th>H₂</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9</td>
<td>0.03</td>
<td>0.2</td>
<td>N</td>
<td>N</td>
<td>96.8</td>
<td>96.0</td>
</tr>
<tr>
<td>5</td>
<td>31.2</td>
<td>0.59</td>
<td>2.9</td>
<td>3.1</td>
<td>2.8</td>
<td>60.9</td>
<td>101.8</td>
</tr>
<tr>
<td>10</td>
<td>36.3</td>
<td>0.78</td>
<td>2.8</td>
<td>2.9</td>
<td>4.4</td>
<td>45.6</td>
<td>92.9</td>
</tr>
<tr>
<td>20</td>
<td>38.8</td>
<td>0.87</td>
<td>2.6</td>
<td>3.8</td>
<td>6.3</td>
<td>42.2</td>
<td>94.4</td>
</tr>
<tr>
<td>30</td>
<td>33.4</td>
<td>0.67</td>
<td>2.3</td>
<td>3.3</td>
<td>10.3</td>
<td>28.8</td>
<td>70.1</td>
</tr>
<tr>
<td>50</td>
<td>32.3</td>
<td>0.66</td>
<td>2.2</td>
<td>N</td>
<td>6.7</td>
<td>27.9</td>
<td>65.9</td>
</tr>
</tbody>
</table>

Cathode, Pt-DGE (apparent surface area, 1 cm²); reaction temperature, 25°C; current density, 600 mA cm⁻²; passed charge, 150 C; electrolyte, 0.8 mol dm⁻³ KHCO₃.
* Corrected with an IR compensation instrument (vs. Ag/AgCl).

- Gas diffusion electrodes

- Non-aqueous solvent (imidazolium-based ionic liquids, amines, etc)

CO₂ Solubility (25°C, 1 atm):
- 0.034 M in water
- 0.28 M in acetonitrile
- ~ 1 M in imidazolium-based ionic liquids

IONIC TRANSPORT AND PRODUCT SEPARATION

**At extreme pHs**

Schematic illustration of an alkaline electrolyzer, PEM electrolyzer and a solid oxide electrolyser

At **near neutral pHs**

Re-circulation with other cations as the ionic current carriers

Bipolar membrane for sustainable electrolysis at near neutral pH.

---


OUTLINE

• The Basic Operating Principles of a Photoelectrochemical (PEC) CO$_2$ Reduction Reaction (CO$_2$RR) System.
• Materials and Components.
• Device Designs and Demonstration.
STAND-ALONE PV+MEA DESIGN

1. Series connected PV+MEA design


6.5% to CO

4.5% to CO
Some inspiration from PEC water-splitting system:

1. Series connected PV+MEA design coupled with solar concentrator

2. Integrated macroscopic planar devices


2. Integrated macroscopic planar devices coupled with solar concentrator

Optimal bandgap combination for the integrated system: 1.6 eV/1.0 eV

---

James, B. D.; Baum, G. N.; Perez, J.; Baum, K. N. Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production; Directed Technologies: 2009
WHAT A PEC CO2RR SYSTEM MIGHT LOOK LIKE?

Some inspiration from PEC water-splitting system:

3. Vapor feed cell design

Seawater vapor electrolysis at 6% STH conversion efficiency.

- Eliminate the use of strong base and strong acid as the system input feedstock.
- Mitigate the deleterious effects associated with bubble formation.
- Potential advantage in product separation for liquid fuel devices

Various water vapor device designs


Some inspiration from PEC water-splitting system:

4. Nanoparticle-based “baggie” design

James, B. D.; Baum, G. N.; Perez, J.; Baum, K. N. Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production; Directed Technologies: 2009

Some inspiration from PEC water-splitting system:

5. Integrated microwire-based PEC devices


The system takes the sunlight, carbon dioxide and water and converts them into fuels and oxygen.

**Oxygen evolution reaction (OER)**

\[
\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 (g) + 2\text{H}^+ + 2\text{e}^-
\]

**CO₂ Reduction reaction (CO₂RR)**

\[
\begin{align*}
\text{CO}_2 + 2\text{e}^- + 2 \text{ H}^+ & \rightarrow \text{CO} + \text{H}_2\text{O} \\
\text{CO}_2 + 2\text{e}^- + 2 \text{ H}^+ & \rightarrow \text{HCOOH} \\
\text{CO}_2 + 6\text{e}^- + 6 \text{ H}^+ & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \\
\text{CO}_2 + 8\text{e}^- + 8 \text{ H}^+ & \rightarrow \text{CH}_4 + 2 \text{ H}_2\text{O}
\end{align*}
\]

**Key materials:**
- Photoabsorber
- CO₂RR catalyst
- OER catalyst

**Key components:**
- Reactant delivery
- Ionic transport
- Product separation

**Key performance metrics:**
- Conversion efficiency
- Selectivity
- Stability
- Scalability
The Joint Center for Artificial Photosynthesis (JCAP) is the nation’s largest research program dedicated to the development of an artificial solar-fuel generation technology. Established in 2010 as a U.S. Department of Energy (DOE) Energy Innovation Hub, JCAP aims to find a cost-effective method to produce fuels using only sunlight, water, and carbon-dioxide as inputs. JCAP is led by a team from the California Institute of Technology (Caltech) and brings together more than 140 world-class scientists and engineers from Caltech and its lead partner, Lawrence Berkeley National Laboratory. JCAP also draws on the expertise and capabilities of key partners from the University of California campuses at Irvine (UCI) and San Diego (UCSD), and the Stanford Linear Accelerator (SLAC). In addition, JCAP serves as a central hub for other solar fuels research teams across the United States, including 20 DOE Energy Frontier Research Center.

For more information, visit http://www.solarfuelshub.org.