Direct Solar CO$_2$ for Formic Acid Conversion Using a Biological/Organic Photochemical Half-Cell

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Direct Reduction of Carbon Dioxide

\[ \text{CO}_2 + 2 \text{e}^- + 2\text{H}^+ \leftrightarrow \text{CH}_2\text{O}_2 \quad \text{Formic Acid} \]

\[ \text{CH}_2\text{O}_2 + 2 \text{e}^- + 2\text{H}^+ \leftrightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} \quad \text{Formaldehyde} \]

\[ \text{CH}_2\text{O} + 2 \text{e}^- + 2\text{H}^+ \leftrightarrow \text{CH}_3\text{OH} \quad \text{Methanol} \]

\[ \text{CH}_3\text{OH} + 2 \text{e}^- + 2\text{H}^+ \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \text{Methane} \]
Light-induced Generation Of Formic Acid from Carbon Dioxide

$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{CO}_2$

Formic Acid As A Storage Medium

$\text{H}_2\text{CO}_2 \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- + \text{light}$

Generation of Electricity From Direct Formic Acid Fuel Cell

Formic Acid as Fuel
Formic Acid

Standard Enthalpy of Combustion, formic acid \(-255\) kJ/mol
Standard Enthalpy of Combustion, methanol \(-715\) kJ/mol

Standard Biochemical Midpoint Potential

\[
\begin{align*}
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \leftrightarrow \text{CH}_2\text{O}_2 & -420 \text{ mV} \\
2\text{H}^+ + 2\text{e}^- & \leftrightarrow \text{H}_2 & -420 \text{ mV}
\end{align*}
\]

Fig. 5. Cell voltage and power density were plotted as a function of the current density using 5, 10 and 15 M formic acids. The formic acids and air were fed to the anode at a flow rate of 1 ml min\(^{-1}\) and 400 sccm, respectively, at 30 °C. The dry air was used without applying any backpressure.
Reversible interconversion of carbon dioxide and formate by an electroactive enzyme

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Fig. 1. Schematic representation of the electrocatalytic interconversion of CO₂ and formate by a formate dehydrogenase adsorbed on an electrode surface. Two electrons are transferred from the electrode to the active site (buried inside the insulating protein interior) by the iron-sulfur clusters, to reduce CO₂ to formate, forming a C-H bond. Conversely, when formate is oxidized, the two electrons are transferred from the active site to the electrode. The structure of FDH1 (which contains at least nine iron-sulfur clusters) is not known, so the structure shown is that of the tungsten-containing formate dehydrogenase from Desulfovibrio gigas [PDB ID code 1H0H (12)].

Fig. 2. Electrocatalytic voltammograms showing CO₂ reduction and formate oxidation by FDH1. Shown are the reduction of 10 mM CO₂ (pH 5.9) (A); electrocatalysis in 10 mM CO₂ and 10 mM formate (pH 6.4) (B), showing the points of intersection (marked with crosses) that define the reduction potential for the interconversion of CO₂ and formate; and the oxidation of 10 mM formate (pH 7.8) (C). The first voltammetric cycles are shown in black, subsequent cycles are in gray; background cycles recorded in the absence of substrate are also shown (gray). Note that the background cycle in B is offset slightly from the catalytic scans because of variation in the electrode capacitance. Substrates were added as sodium formate or sodium carbonate. For A and C, 25 mV s⁻¹, for B, 100 mV s⁻¹; 37°C, electrode rotation 1,000 rpm.
Project Goal

To use sunlight to drive the formation of H$_2$CO$_2$ from CO$_2$ by tethering FDH to Photosystem I using a molecular wire.
**Light-Driven Electrolysis**

Overall Reaction:

\[
2\text{H}_2\text{O} + 8\text{hv} \rightarrow 2\text{H}_2 + \text{O}_2
\]

Anodic half reaction:

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

Cathodic half reaction:

\[
2(2\text{H}^+ + 2\text{e}^- + 2\text{hv}) \rightarrow \text{H}_2
\]
The Sensitizer: Photosystem I

The Catalyst: Formic Acid Dehydrogenase

The Coupler: A Molecular Wire
Photosystem I

- 96 Chl $\alpha$
- 22 $\beta$-carotene
- 3 [4Fe-4S]
- 2 Phylloquinones
Photosystem I Cofactors
Properties of Photosystem I

The charge-separated state is stable for ~60 ms, which is sufficient time to remove the low potential electron to perform useful work.

The $F_B$ cluster has a pH-independent redox potential of -580 mV.

Nearly every photon that is absorbed by PS I antenna is processed into the charge separated state $P_{700}^+ F_B^-$.

The 1.01 V in the charge-separated state $P_{700}^+ F_B^-$ represents a 59% conversion efficiency for a red photon, and a 38% conversion efficiency for a blue photon.

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Coupling PS I to the Catalyst

- Time: 1 ns, 1 µs, 1 ms, 1 s, 1 h, 1 yr, 1 century
- Distance: < 20 Å

Moser & Dutton

< 20 Å
Solution: Molecular Wire

![Molecular Wire Diagram](image-url)
Reconstitution of Dicluster Ferredoxin
C14G Variant of PsaC

- $\text{S-CH}_2\text{-CH}_2\text{-OH}$

2 $[4\text{Fe-4S}]$  \quad S = 1/2, 3/2
Evidence for Rescue Ligand

$p$-fluorothiophenol
Tether Substituted 4,4’-Dipyridinium
Construct PS I-wire
Construct PS I-wire

PsaD → P700-Fx Core → PS I-Molecular Wire

Graph: Time (m) vs. construct concentration
PS I-wire-Pt

PsaD → P700-Fe₃ Core

PS I-Molecular Wire

Pt Nanoparticle

50 nm
Light-Induced $\text{H}_2$ Production

$\text{Pt NP}$

$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

Rate = 377 μmol $\text{H}_2$ mg Chl$^{-1}$ h$^{-1}$
# Length and Identity of the Molecular Wire

<table>
<thead>
<tr>
<th>Tether</th>
<th>H₂ evolution rate (μmol H₂ mg Chl⁻¹ h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-propanedithiol</td>
<td>2.2</td>
</tr>
<tr>
<td>1,6-hexanedithiol</td>
<td>57.7</td>
</tr>
<tr>
<td>1,8-octanedithiol</td>
<td>40.8</td>
</tr>
<tr>
<td>1,10-decanedithiol</td>
<td>13.6</td>
</tr>
<tr>
<td>1,4-benzenedithiol</td>
<td>159.4</td>
</tr>
</tbody>
</table>
Desulfovibrio desulfuricans Fe-Fe H$_2$ase
Purification of HydA and Cys\textsubscript{98}\textrightarrow{Gly} Mutant

HydA

Cys\textsubscript{98}\textrightarrow{Gly} Mutant

Graphs showing absorbance (Abs) against wavelength for both HydA and Cys\textsubscript{98}\textrightarrow{Gly} Mutant.
PS I-wire-H$_2$ase
PS I-Molecular Wire-H$_2$ase

30.3 μmol H$_2$ mg Chl$^{-1}$ hr$^{-1}$

Carolyn Lubner
Escherichia coli Formate Dehydrogenase
PS I-wire-FDH

PsaD \rightarrow P700-F_x Core

PS I-Molecular Wire

Mutant Formic Acid Dehydrogenase
PS I-wire-FDH

In Progress
Biological/Organic Hybrid Half-Cell

Anode

Cathode

$2e^- ightarrow Au electrode$


**High Density Liquid Fuel**

\[
\text{CO}_2 + 2\text{H}^+ \rightarrow \text{CO} + \text{H}_2 \text{O} \\
(2n+1)\text{H}_2 + n\text{CO} \rightarrow C_nH_{(2n+2)} + n\text{H}_2\text{O} \\
\text{C}_n\text{H}_{(2n+2)} + n\text{H}_2\text{O} \rightarrow \text{C}_n\text{H}_{(2n+2)} + n\text{H}_2\text{O}
\]

**Fischer-Tropsch**

\[
2\text{e}^- \rightarrow \text{Au electrode} \\
2\text{hv} \\
2\text{H}^+ \\
\text{CO} \rightarrow \text{H}_2
\]

**Water Gas Shift**

\[
\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}
\]
Cobalt Difluoroboryl Diglyoximate Catalyst

(1) $M=\text{Co}, R=\text{CH}_3$
(2) $M=\text{Co}, R=\text{C}_6\text{H}_5$
(3) $M=\text{Ni}, R=\text{CH}_3$
(4) $M=\text{Ni}, R=\text{C}_6\text{H}_5$

Richard Eisenberg, University of Rochester
Project Participants

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