Hybrid electro- and thermo-catalytic upgrading of CO\textsubscript{2} to fuels and C\textsubscript{2+} chemicals

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CO\textsubscript{2} Utilization

Zhenglong Li
Oak Ridge National Laboratory

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Goal Statement

• **Goal:** develop an **electrocatalytic synthesis** approach for the **reduction of CO₂ to C₂⁺ products** to achieve the target of >58% faradaic efficiency for C₂⁺ products at -1.1V vs RHE (25% increase compared to Cu/carbon nanospike -- 46% at -1.1V vs RHE)

• **Outcome:** advance the state of technology for electrochemical synthesis of C₂⁺ molecules from CO₂ over new carbon nanospike-based electrocatalysts

• **Relevance:** this project is relevant to the bioenergy industry because it provides a means to **recycle CO₂ from the biorefinery to molecules** that were traditionally fossil-based, in a manner that is synergistic with biofuels and renewable electricity generation
Project Overview

Importance of CO₂ utilization:
- Mitigate the CO₂ emission challenges
- CO₂ as a carbon-based feedstock for producing chemicals and fuels
- CO₂ reduction as a useful means to store renewable electricity in chemical energy

Hybrid electro- and thermo-catalytic CO₂ utilization approach for making hydrocarbon fuels and valuable chemicals

This SEED project seeks to electrocatalytically synthesize C₂+ products that can be tailored for further thermal catalytic upgrading to transportation fuels, chemicals and polymers.
Quad Chart Overview

**Timeline**
- 10/1/2018
- 09/30/2020

<table>
<thead>
<tr>
<th></th>
<th>FY19</th>
<th>FY20</th>
<th>Total Planned Funding</th>
</tr>
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<tbody>
<tr>
<td><strong>DOE Funding</strong></td>
<td>$200,000</td>
<td>$200,000</td>
<td>$400,000</td>
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**Barriers addressed**
Efficient catalytic upgrading of gaseous intermediates

**Project Goal**
To design electrochemical catalysts for the conversion of CO$_2$ to C$_{2+}$ oxygenates for further thermocatalytic upgrading to desired products.

**End of Project Milestone**
Develop a CO$_2$ electrocatalytic reduction pathway based on bimetallic M-Cu/CNS electrocatalysts with the target of achieving >58% Faradaic efficiency for C$_{2+}$ products at -1.1V vs RHE (25% increase compared to current Cu/CNS - 46% at -1.1V vs RHE).
Project Overview

This project builds on a technology for selective conversion of CO$_2$ to ethanol over carbon nanospikes (CNS).

**2019 R&D100 Award**
Project Overview

Cu on carbon nanospikes can catalyze cascade reaction of CO\textsubscript{2} conversion to ethanol
1 – Technical Approach

Original Product Mix over Cu/CNS

Cu/CNS serves as the baseline for further development.

Cu/CNS performance @ -1.1V vs RHE is the benchmark.

Song et al. ChemistrySelect. 2016, 1, 6055.
1 – Technical Approach

Oligomerization is controlled by metal co-catalyst

Develop bimetallic co-catalyst to enhance the oligomerization rate by tuning CO binding energy

*ChemSusChem 2018, 11, 48 – 57*
2 – Management Approach

- **Small seed-level project with 4 team members:**
  - Zhenglong Li: PI, catalyst design
  - Adam Rondinone: (prior PI*), nanomaterials science and electrochemistry
  - Dale Hensley: synthesize carbon nanospike material
  - Seonah Jin: electrochemistry, bimetallic catalyst synthesis

- **Monthly team meetings**

- **Project structure:**
  - Task 1: Bimetallic electrocatalysts synthesis and characterizations
  - Task 2: Electrocatalytic testing and electrocatalyst optimization

- **Interaction with ChemCatBio (CO₂ upgrading)**

*Currently at Los Alamos National Laboratory*
## 2 – Management Approach: Risk and Mitigation

<table>
<thead>
<tr>
<th>Risks</th>
<th>Mitigation</th>
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<tr>
<td>Bimetallic electrocatalysts could not promote the formation of C\textsubscript{2}+ products to reach the targeted faradaic efficiency</td>
<td>Advanced catalyst characterizations and electrocatalyst testing will provide useful information about the catalyst structure and performance. Alternative bimetallic co-catalysts will be studied based on evidence of this information.</td>
</tr>
<tr>
<td>Cu and the 2\textsuperscript{nd} metal do not form alloys but distribute separately on the CNS using electrochemical deposition synthesis method.</td>
<td>Wet chemical synthesis method will be employed to prepare the bimetallic nanoparticles first, and then load onto CNS.</td>
</tr>
<tr>
<td>Some of the advanced characterizations, such as XAS, may not be available at the time needed.</td>
<td>Make plans earlier and schedule the beam time beforehand via better coordination with Advanced Catalyst Synthesis and Characterizations within ChemCatBio Consortium.</td>
</tr>
</tbody>
</table>

**Milestones Associated with Risk Mitigations**

- **FY19 Q2**: Develop at least 3 carbon nanospike supported bimetallic electrocatalysts with different formulations for electrocatalytic testing
- **FY20 Q4 (delayed)**: Develop a CO\textsubscript{2} electrocatalytic reduction pathway at lab scale based on bimetallic M-Cu/CNS electrocatalysts with the target of achieving >58% faradaic efficiency for C\textsubscript{2}+ products at -1.1V vs RHE (25% increase compared to current Cu/CNS - 46% at -1.1V vs RHE)
3 – Impact: Relevance to Bioenergy Industry

Develop electrochemical catalyst for recycling CO₂ from biorefinery into useful molecules

- Generate valuable products from fermentation derived CO₂
- Electrochemical systems are tolerant of intermittency and appropriate for renewable energy storage
- Make a green process greener
3 – Impact: Relevance to Bioenergy Industry

- Transitioning R&D discovery of CO₂ utilization to bioenergy industry

ReactWell licensed ORNL technology on electrocatalytic CO₂ conversion to ethanol

March 1, 2019

OAK RIDGE, Tenn., March 1, 2019—ReactWell, LLC, has licensed a novel waste-to-fuel technology from the Department of Energy’s Oak Ridge National Laboratory to improve energy conversion methods for cleaner, more efficient oil and gas, chemical and bioenergy production.

ReactWell will bring ORNL’s electrochemical process, which converts carbon dioxide directly into ethanol, into the company’s existing conversion solution known as the ReactWell process.

- Additional research license was added to expand further collaboration with industry
Two major objectives of this project:

- Understand CO₂ activation over CNS electrocatalyst
- Demonstrate the proof-of-concept results for enhancing C₂⁺ product formation from CO₂ with bimetallic co-catalyst to achieve the target of >58% faradaic efficiency for C₂⁺ products at -1.1 V vs RHE (25% increase compared to benchmark)
4 – Progress and Outcomes

Understand the role of bicarbonate in CO₂ activation over CNS

Literature study:
- CO₂ molecules are mediated to the Cu surface via their equilibrium with bicarbonate anions instead of direct adsorption from the solution*

This study suggests:
- CO₂ reduction with bicarbonate as electrolyte is less active than with perchlorate over CNS
- Dissolved CO₂ is more likely to react, consistent with hypothesis of CNS mediated e⁻ injection

*J. Am. Chem. Soc. 2017, 139, 3774–3783
*J. Am. Chem. Soc. 2017, 139, 15664-15667
4 – Progress and Outcomes: role of CNS in activating CO₂

Sharp tips of CNS lead to enhanced electric field, enables N₂ activation via direct e⁻ injection (BES efforts)

- CO₂ polarization over CNS has higher dipole moment than N₂

Induced Dipole Stabilizes CO₂ in Stern Layer

- Enhanced CO₂ surface coverage facilitates direct activation of CO₂ over CNS via e⁻ injection.
- Neighbor C-C coupling sites are needed to further promote the formation of C₂+ products.

4 – Progress and Outcomes

Demonstrate electrochemical synthesis of bimetallic PdCu/CNS electrocatalysts

Challenge:
- How to locate metal co-catalyst close to CNS

**In situ** electrochemical deposition synthesis:
- **Simple** synthesis methodology
- **Direct formation** of metal nanoparticles at catalytically relevant locations
- **Avoid using surfactants** in metal nanoparticle synthesis

Further advantage over CNS:
- CNS unique configuration facilitates the **in situ nucleation** of metal nanoparticles
- Form **nanoparticles close to carbon nanospikes**, CO generated from nanospikes can directly react over nanoparticle surface

**In situ** electrochemical synthesis of bimetallic PdCu nanoparticles over CNS

\[ \text{CuSO}_4, \text{Na}_2\text{PdCl}_4 \]

Metal salt solution

Electrical Potential
4 – Progress and Outcomes

CO stripping experiments were leveraged to understand metal particle composition

CO-stripping results for PdCu₉/CNS

With reduction process before CO adsorption

Without reduction process before CO adsorption

Bimetallic PdCu/CNS can be electrochemically made either in separated phases or well mixed form

Catalyst images from: Ma et al. J. Am. Chem. Soc. 2017, 139, 1, 47-50  https://pubs.acs.org/doi/10.1021/jacs.6b10740
4 – Progress and Outcomes

Synthesize bimetallic PdCu with varied surface composition to control CO binding energy

Outcomes:

• Indicate formation of Pd-rich bimetallic PdCu nanoparticles for PdCu₉, PdCu₆, PdCu
• The difference of surface Cu/Pd ratio can help to tailor the CO binding energy
4 – Progress and Outcomes

Demonstrate the feasibility of producing $C_2+$ products from $CO_2$ over bimetallic PdCu$_3$/CNS

@-1.1V (RHE)

Future work:

- Identify and quantify the products in the liquid phase (delayed due to the impact of COVID)
- Qualitative mass spectrometry measurements indicate the presence of heavier products
4 – Progress and Outcomes

Bimetallic PdCu$_3$/CNS shows relatively stable performance after initial induction period

Future work:

• Improve the current density via designing gas diffusion electrode
Summary

This project builds on the success of the CO\(_2\) to ethanol technology developed at ORNL
- CO\(_2\) to ethanol technology was licensed to Reactwell
- Received 2019 R&D100 Award

Outcome
- Advance **electrocatalytic synthesis** approach for **reduction of CO\(_2\)** to C\(_{2+}\) oxygenates, as feedstocks for thermocatalytic upgrading to hydrocarbon fuels

Approach
- Developing bimetallic co-electrocatalyst to tune the CO binding energy to enhance the C\(_{2+}\) product formation

Progress and Outcomes
- Carbon nanospike electrocatalyst can directly activate CO\(_2\) to form CO, and metal co-catalyst is needed to further oligomerize CO
- **Bimetallic PdCu/CNS** can be electrochemically **synthesized in situ**
- Bimetallic PdCu/CNS electrocatalyst could **synthesize C\(_{2+}\) product from CO\(_2\)**
- Further product identification and quantification are needed
Acknowledgement

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• Bioenergy Technologies Office:
  • Ian Rowe

U.S. Department of Energy
Bioenergy Technologies Office

ChemCatBio
Chemical Catalysis for Bioenergy

Energy Materials Network
U.S. Department of Energy
Additional Slides
Publications, Patents, Presentations, Awards, and Commercialization


• “ALLOY BASED CATALYST FOR THE ELECTROCHEMICAL SYNTHESIS OF HYDROCARBONS FROM CARBON DIOXIDE” US Provisional Application Serial No. 63/085,340, filed on September 30, 2020. (This work has led to a research license.)