Electrochemical CO$_2$ Conversion at NETL

Douglas R. Kauffman (NETL / DOE)
Catalytic CO$_2$ conversion at NETL

\[ \text{CO}_2 \quad \text{H}_2\text{O} \quad \text{CH}_4 \]

Catalyst

Waste heat

Excess Renewables

Polymers & Plastics
Ethylene
Hydrogen
Carbon Monoxide
Methanol
Fuels
Electrochemical catalyst design

Structure-controlled product selectivity

H$_2$O → \textbf{Products}

\[
\begin{align*}
\text{CO}_2 & \rightarrow \text{Products} \\
& \quad \text{J. Mater Chem. A, 2019, 7, 27576}
\end{align*}
\]

Surface-science enabled electrocatalysis

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10 nm
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ACS Catalysis, 2019, 9, 5375
ACS Catalysis, 2020, 10, 11768
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“Atomically Precise” nanocatalysts

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JPCC, 2018, 122, 49, 27991
ACS Catalysis, 2020, 10, 12011
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3D Structured SnO$_2$ Catalysts

- Electrochemically reduce CO$_2$ to formate/formic acid (HCOO$^-$ / HCOOH).

- Formic acid has agricultural and industrial uses.
  - Currently produced via NG reforming and methanol processing.
  - Extremely carbon intensive.

- Formic acid is also an emerging energy carrier (53 g H$_2$ / L)

- Key Challenges:
  - Current density
  - Stability / durability
  - Scalable catalyst synthetic procedure.
Catalyst synthesis approach

- Sphere size is fixed at ~200 nm based on PMMA template.
- Constituent SnO$_2$ nanoparticles are controlled between 2-10 nm with calcination in air between 300-600$^\circ$C.
- Simple solution-phase synthesis and thermal processing.
• XRD, XPS and Raman showed increased calcination temperature produced larger, more crystalline SnO$_2$ NPs.
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• XRD, XPS, EXAFS and Raman all confirmed SnO$_2$ oxidation state.
Characterization Results and Echem Details

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- SnO$_2$ catalysts mixed w/ 10 wt% carbon black, Nafion binder and deposited onto PTFE-coated carbon paper electrodes at 5.4 mg$_{SnO_2}/cm^2_{geo}$.

- All electrochemical experiments conducted in H-Cell reactor with CO$_2$ saturated 0.1M KHCO$_3$
All catalyst synthesis temperatures selectively produced formate with 60-80% FE between -0.7V to -1.3V.

500 C calcination temperature produced highest overall formate FE.

CO and H₂ were the only other products detected.
Catalyst Activity vs Calcination Temperature

Balance between crystallinity and particle size

- Below 500 °C the SnO$_2$ formed smaller and less crystalline NPs.
- Above 500 °C larger SnO$_2$ particle sizes formed: reduced catalyst surface area.
- 500 °C was the optimum calcination temperature.
Benchmarking Catalyst Performance

- Benchmarked against commercially available SnO₂ catalyst particles (Sigma Aldrich; ~28 nm diameter NPs)
- Substantially higher formate current density at all potentials.
- Approximately 3 times larger electrochemical surface area and number of electrochemically active Sn atoms at equivalent catalyst loading.
3D morphology Boosts Surface Area and Performance

SnO2 Nanospheres also outperformed non-templated SnO2 NPs of identical size.

<table>
<thead>
<tr>
<th>Electrochemical Surface Area (cm²/ mg₅SnO₂)</th>
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<td>NETL SnO₂ NPs</td>
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<td>Comm. SnO₂ NPs</td>
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Long-Term Performance at -1.2V vs. RHE

- NETL SnO$_2$ Nanospheres demonstrated ≥2x performance increase over SnO$_2$ NPs.
- All catalysts demonstrated ~70% Formate FE during long-term runs.
- Currently being translated into high-performance electrolyzer.
Post-Reaction Morphology

NETL SnO\textsubscript{2} Nanospheres

Before CO\textsubscript{2} Reduction

After CO\textsubscript{2} Reduction

NETL SnO\textsubscript{2} NPs

Commercial SnO\textsubscript{2}
Time Dependent synchrotron X-Ray Diffraction shows:

- Rapid formation of ~25 nm metallic Sn nanoparticles with β-Sn crystallographic orientation.
- No further particle growth after initial reduction.
- In situ Raman spectroscopy confirms SnO$_2$ transforms into metallic Sn at operating voltages.
SnO² Nanosphere Conclusions

1. NETL SnO² Nanospheres out-perform SnO² NPs and commercially available SnO².
   - Unique shape with extremely high surface area
   - Optimized synthetic process to maximize formate current density
   - High formate FE and selectivity
   - Stable ~25 nm nanoparticle size under steady state operation

2. In situ Raman and time dependent XRD show SnO² is quickly reduced to metallic Sn

3. Ongoing work: Collaboration with NREL to evaluate NETL SnO² Nanospheres in recently reported formate electrolyzer
   - Reach industrially relevant current densities (100s mA/cm²).
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**Synchrotron XAS**: Brookhaven NSLS-II, beamline 8-ID (ISS); Eli Stavitski.

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We have an open post-doc / early career position for electrolyzer testing

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In situ Raman Data

![Graph showing Raman data with labels for different modes and time points.]

- **Intensity / a.u.**
- **Raman shift / cm⁻¹**
- **Dry electrode**
- **Open circuit**
- **Time points:**
  - 4 min
  - 8 min
  - 12 min
  - 16 min
  - 20 min
  - 24 min
  - 28 min
  - 32 min
  - 36 min

- Modes:
  - $A_{1g}$
  - $A_{2g}$
  - $E_g$
  - $A_{2u}$
  - $B_{2g}$
Temp Dependent O1s XPS and Raman data

![Graph showing the relative area ratio of O1/O1 with calcination temperature](image-url)
Temp Dependent Sn K-Edge EXAFS data

FT magnitude / a.u.

R / Å

Sn foil
bulk SnO$_2$
SnO$_2$ sph-600
SnO$_2$ sph-500
SnO$_2$ sph-400
SnO$_2$ sph-300

Sn-O
Sn-Sn (in oxide)
Sn-Sn (in metal)
Potential Dependent Product FE

(A) \(\text{Formate FE} \%\) vs. Potential / V vs. RHE

(B) \(\text{CO FE} \%\) vs. Potential / V vs. RHE

(C) \(\text{H}_2 \text{ FE} \%\) vs. Potential / V vs. RHE

SnO\(_2\) sphere-300
SnO\(_2\) sphere-400
SnO\(_2\) sphere-500
SnO\(_2\) sphere-600
Current normalized to Electrochemical Surface Area

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