Electrochemical CO₂ Conversion at NETL

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Catalytic CO₂ Conversion at NETL

De-Carbonized Electricity

Catalyst

CO₂

H₂O

CH₄

Carbon Neutral H₂ and C₁ Chemicals

Hydrogen
Carbon Monoxide
Formic Acid
Electrochemical Catalyst Design

Structure-controlled product selectivity

H₂O → Products

CO₂ → Products

J. Mater Chem. A, 2019, 7, 27576

Surface-science enabled electrocatalysis

“Atomically Precise” nanocatalysts

JPCC, 2018, 122, 49, 27991
ACS Catalysis, 2020, 10, 12011
3D Structured SnO₂ Catalysts

• Electrochemically reduce CO₂ to formate/formic acid (HCOO⁻ / HCOOH).

• Formic acid has agricultural and industrial uses.
  • Currently produced via natural gas reforming and methanol processing.
  • Extremely carbon intensive.

• Formic acid is also an emerging energy carrier (53 g H₂ / L)

• Key Challenges:
  • Current density
  • Stability / durability
  • Scalable catalyst synthetic procedure.
Catalyst Synthesis Approach

- PMMA template produces sphere diameter at ~200 nm.
- Control the size and crystallinity of constituent SnO₂ nanoparticle by air calcination temperature (300-600°C.)
- Simple solution-phase synthesis and thermal processing

US patent application submitted and manuscript in preparation
Characterization Results

- XRD, XPS and Raman showed higher calcination temperatures produced larger, more crystalline SnO$_2$ NPs.
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• XRD, XPS, EXAFS and Raman all confirmed SnO$_2$ oxidation state.

• Performance differences stem from the size and crystallinity of constituent nanocrystals.
Electrochemical Details

- SnO$_2$ catalysts mixed w/ ~10 wt% carbon black powder to increase conductivity & Nafion binder.

- Deposited onto PTFE-coated carbon paper electrodes at 5.4 mg$_{\text{SnO}_2}$/cm$^2_{\text{geo}}$.

- Electrochemical H-Cell screening conducted in CO$_2$ saturated 0.1M KHCO$_3$
Catalyst Activity vs Calcination Temperature

Balance between crystallinity and particle size

- <500 °C the SnO₂ formed smaller, less crystalline NPs.
  - Lower formate partial current density.
  - Increased HER (~20% FE).
- >500 °C produced larger SnO₂ particles with lower activity.
  - Reduced active surface area
500 °C calcined SnO$_2$ Nanosphere

- 500 C calcination temperature produced highest activity and formate FE.
- CO and H$_2$ were the only other products detected.
In situ Raman Spectroscopy

Rapid reduction of SnO$_2$ to metallic Sn during CO$_2$RR.

Catalyst Powder

Raman shift / cm$^{-1}$

Intensity / a.u.

dry electrode
open circuit
4 min
8 min
12 min
16 min
20 min
24 min
28 min
32 min
36 min

ΔT @ -1.2V
Benchmarking Catalyst Performance

- Benchmarked against commercially available SnO$_2$ catalyst particles (Sigma Aldrich; ~28 nm diameter NPs)

- Benchmarked against identically synthesized non-templated SnO$_2$ nanoparticles (~8 nm diameter)

- Substantially higher formate partial current density at all potentials.
Estimating Active Site Density

- **SnO$_2$** has characteristic redox peaks.
- **SnO$_2$** reduced to metallic Sn during cathodic-going sweep.
  - Confirmed with *in situ* Raman
  - Overall 4 electron process.
- We can use the cathodic reduction peak to estimate active site density.
  - Integrated peak area (Coulombs; C)
  - $C / (F\times n\text{e}^-) = \text{mol Sn sites}$
- **NETL SnO$_2$** nanospheres have ~2-4 times higher active site density and ~2-3 times higher electrochemical surface area.
Long-Term Performance at -1.2V vs. RHE

- NETL SnO$_2$ Nanospheres demonstrated ≥2x performance increase over SnO$_2$ NPs.
- Average 68±8% formate FE during 36 hour electrolysis
  - Multiple start/stop cycles
Post-Reaction Morphology

NETL SnO$_2$ Nanospheres resist large-scale particle agglomeration.
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.
- Metallic Sn consistent with *in situ* Raman spectroscopy.
Electrolyzer Performance

- Collaboration with NREL
- 25 cm$^2$ electrode; 0.5 mg/cm$^2$ catalyst loading
- 0.4 M K$_2$SO$_4$ catholyte (40 mL/min)
- 1M NaOH anolyte (50 mL/min)
- Ni mesh anode

After 24 hr @ 500 mA$_{geo}$/cm$^2$

Initial

68% FE

86% FE

Electrolyzer Voltage ($V_{\text{cathode}} + V_{\text{anode}}$)

Current Density (mA / cm$_{geo}^2$)

Held at 500 mA/cm$^2$ for 24 hours.

NETL SnO\textsubscript{2} Nanosphere Conclusions

1. NETL SnO\textsubscript{2} Nanospheres out-perform SnO\textsubscript{2} NPs and commercially available SnO\textsubscript{2}.
   - Unique shape with extremely high surface area
   - Optimized synthetic process to maximize formate current density
   - High formate FE and selectivity
   - Stable under steady state H-Cell operation

2. Raman and synchrotron-XRD show SnO\textsubscript{2} was quickly reduced to metallic Sn

3. Collaboration with NREL to evaluate NETL SnO\textsubscript{2} Nanospheres in electrolyzer
   - Sustained 24 hour performance at industrially relevant current densities (~500 mA/cm\textsuperscript{2}).
   - Ongoing efforts to minimize component level losses (BPM degradation, overpotentials, etc.)
Doped SnO$_2$ for Improved Performance

- Doping Strategies to improve performance.
- Scalable synthetic strategy.
- Preliminary H-Cell data shows excellent activity and good stability.
- Initiating in-house electrolyzer testing.

*Patent application and manuscript in preparation.*
Alternative CO₂ Utilization Technology: Microwave Catalysis

- Microwave-assisted Dry Reforming of Methane: CO₂ + CH₄ → 2CO + 2H₂
- Electrically-driven process; microwaves selectively and rapidly heat catalyst bed to ~900°C.
- Ultra-efficient production of CO and H₂; >80% single pass conversion.
- Kilogram-scale catalyst production.

Typical Electrolyzer Performance

CO Production via MW-Dry Reforming

<table>
<thead>
<tr>
<th>Gas Flow Rate (mL/min)</th>
<th>Energy Input (kWh / kg CO₂ produced)</th>
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<tr>
<td>1</td>
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H₂ Production via MW-Dry Reforming

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<tr>
<th>Gas Flow Rate (mL/min)</th>
<th>Energy Input (kWh / kg H₂ produced)</th>
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Typical Electrolyzer Performance:

- (2.5-3V; >85% FE; 100-600 mA/cm²)
Key Contributors

**Catalyst Design, Characterization, and Electrochemistry:** Thuy-Duong Nguyen-Phan and Douglas Kauffman (NETL).

**Electrolyzer Validation:** Leiming Hu and K. C. Neyerlin (NREL).

**Synchrotron XRD:** Wenqian Xu; beamline 17-BM-B (ANL; APS).

**Synchrotron XAS:** Eli Stavitski; beamline 8-ID (ISS) (BNL; NSLS-II).
Acknowledgement and Disclaimer

ACKNOWLEDGMENT
This work was performed in support of the US Department of Energy’s Fossil Energy Carbon Use and Reuse Program. The Research was executed through the NETL Research and Innovation Center’s CO₂ Utilization Technology Field Work Proposal. Research performed by Leidos Research Support Team staff was conducted under the RSS contract 89243318CFE000003. This research used Beamline 17-BM of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. This research used the 8-ID (ISS) and 23-ID-2 (IOS) beamlines of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704.

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Questions or Comments?

Thank you for your attention!

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