An overview of NETL's in-house CO_2 conversion efforts

FWP-1022426 (Carbon Conversion FWP)

Douglas Kauffman
Research Chemist; NETL/DOE-FECM

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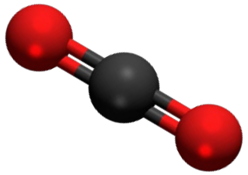
The FWP supports multiple in-house efforts.

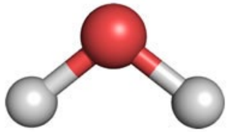
- **Catalytic conversion of CO_2 to industrially-relevant chemicals** (Douglas.Kauffman@netl.doe.gov)
  - Electrocatalyst development, electrolyzer validation, and computational modeling.
  - Microwave-assisted catalysis.
  - Surface science studies.
- **Biological conversion of CO_2 and CO_2-derived intermediates** (Djuna.Gulliver@netl.doe.gov)
- **Strategic systems analysis and engineering** (Gregory.Hackett@netl.doe.gov & Timothy.Skone@netl.doe.gov)
  - TEA/LCA and guidance documents for in-house and extramural projects.
- **Scale-up efforts for microwave-assisted CO_2 catalysis** (Christina.Wildfire@netl.doe.gov).
- **Microwave-assisted reactive CO_2 capture and conversion** (Douglas.Kauffman@netl.doe.gov)
- **Conversion of CO_2 into polycarbonates** (Daniel.Haynes@netl.doe.gov)

Catalytic CO_2 Conversion

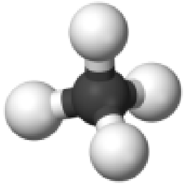
CO_2



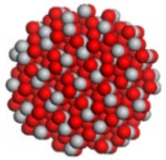
H_2O



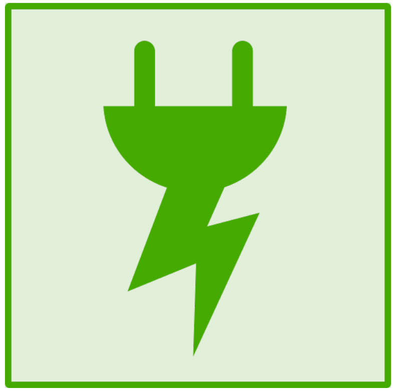
CH_4



Catalyst



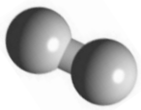
Decarbonized Electrons



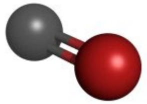
Electrochemistry

Microwave chemistry

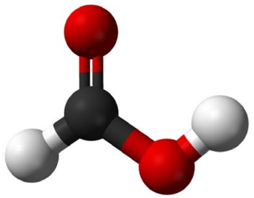
Polymers & Plastics



Hydrogen



Carbon Monoxide



Formic Acid

Alcohols / Fuels

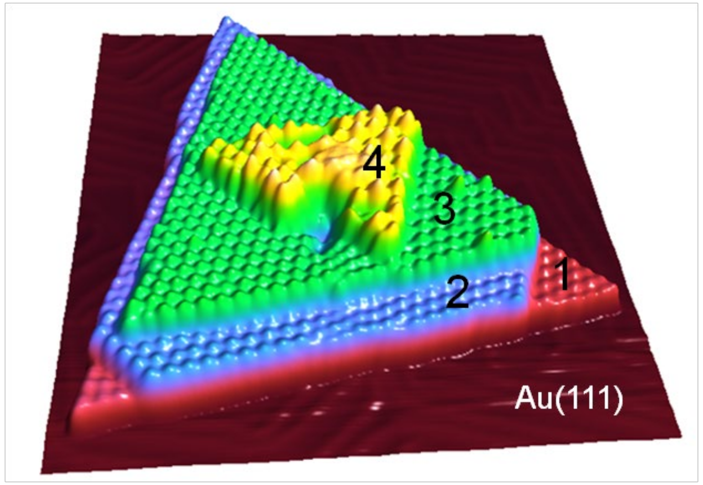
Efforts Span Technology Readiness Levels (TRLs) 1-3/4

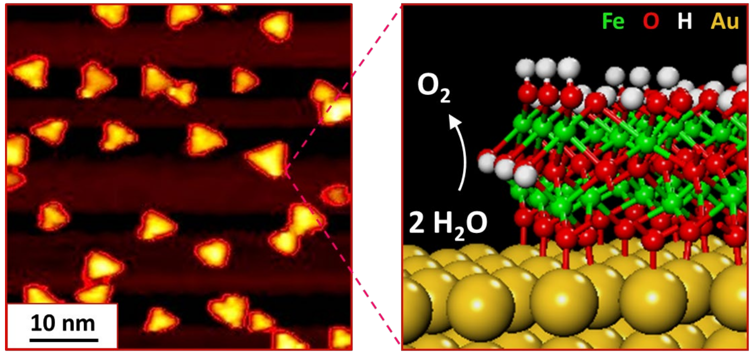
NATIONAL ENERGY TECHNOLOGY LABORATORY

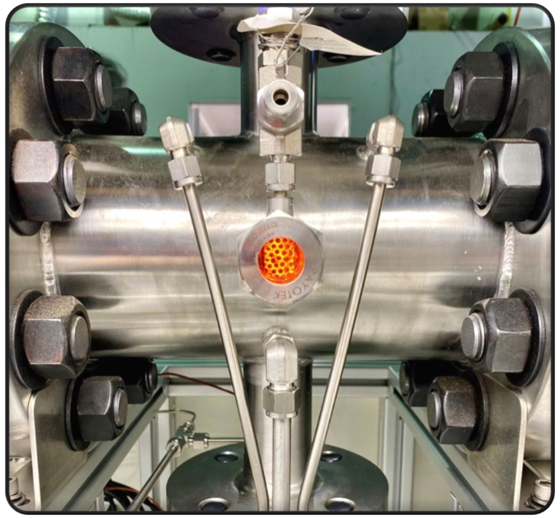
Materials Design and Advanced Characterization

Experiment and Theory to Understand and Control Chemistry

Lab-scale validation in prototype reactors, LCA/TEA







Identify which parts make the catalyst "work" to optimize performance

Fundamental Understanding → **Lab-Scale Validation**

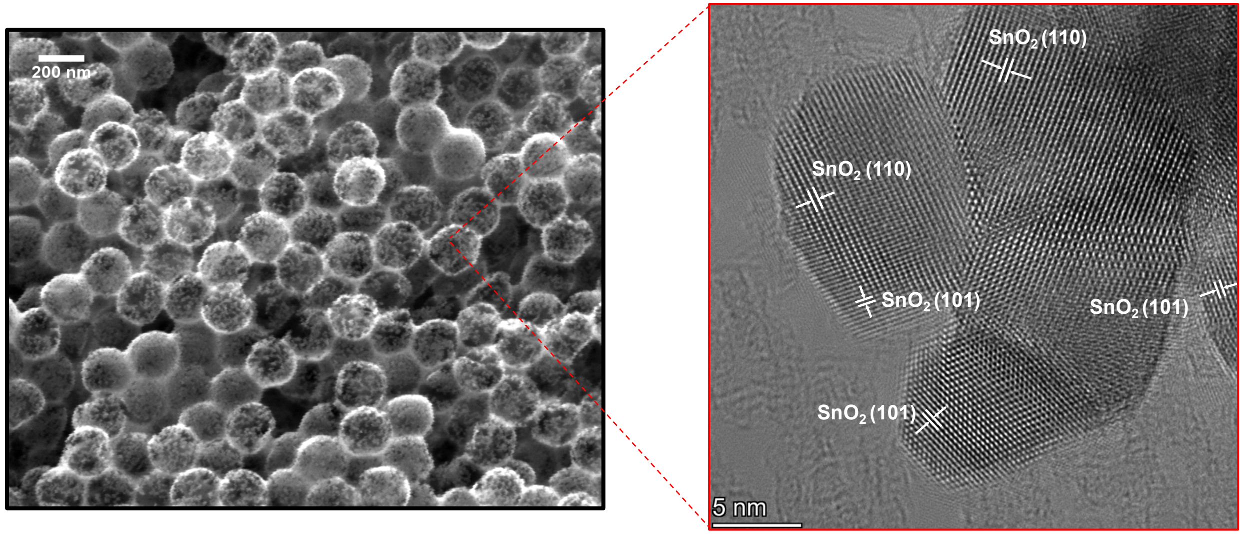
Electrocatalyst Development

Recent efforts have focused on Sn-based catalysts for formate production.

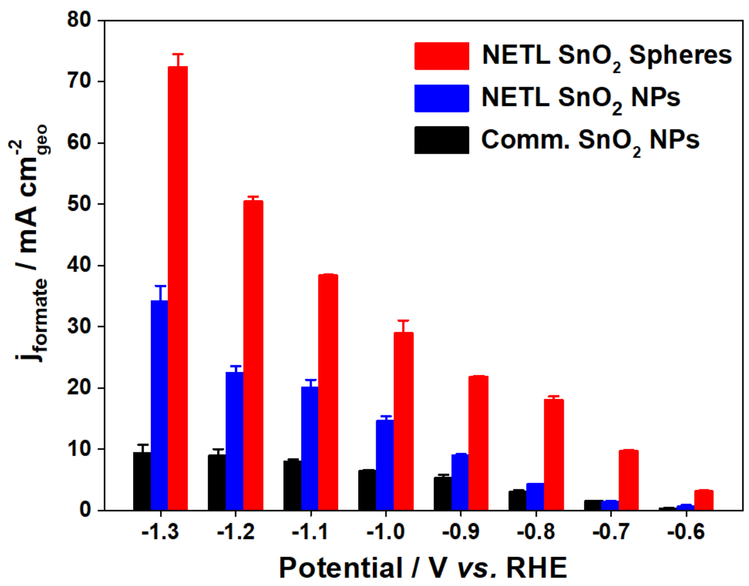
Key approaches include:

1. Controlling 3D structure to increase electrochemically active surface area.
2. Controlling composition (doping) to reduce overpotential.

High Surface Area SnO_2



Electrochemical Performance



Scientific Reports, **2022**, volume 12, Article number: 8420 (article link) & US patent appl. # 17/668061

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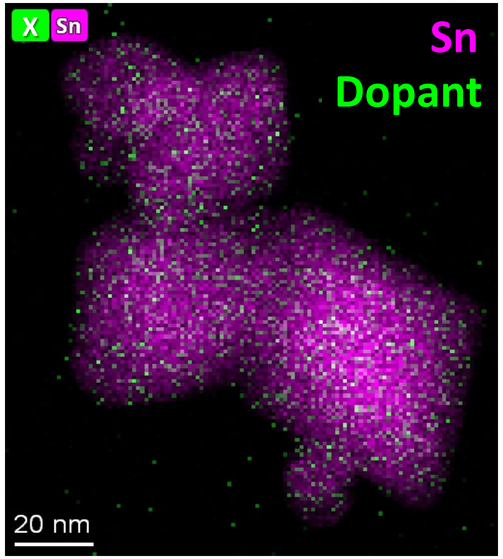
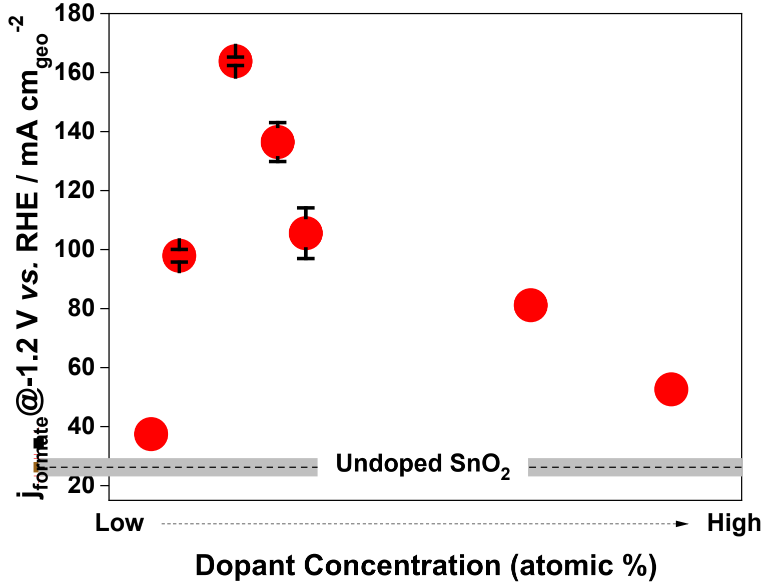
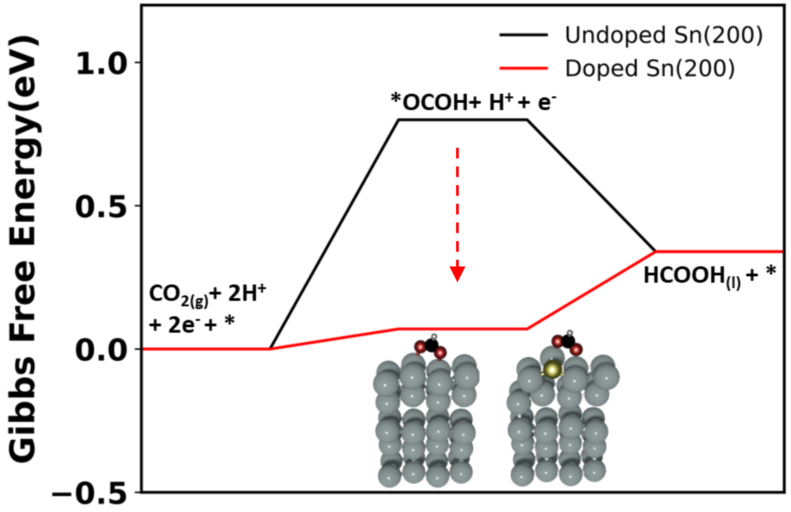
TEM



H-Cell Screening



Computational E-chem



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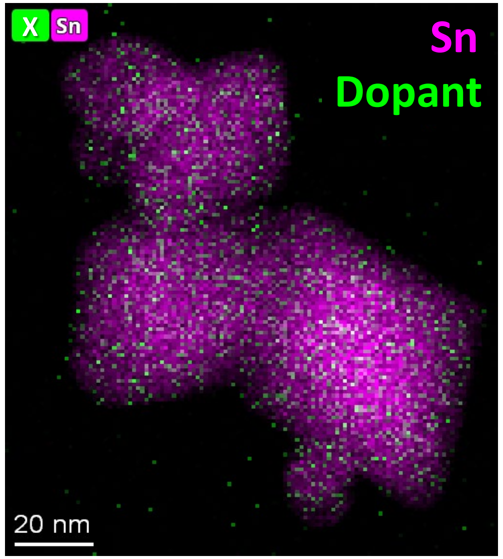
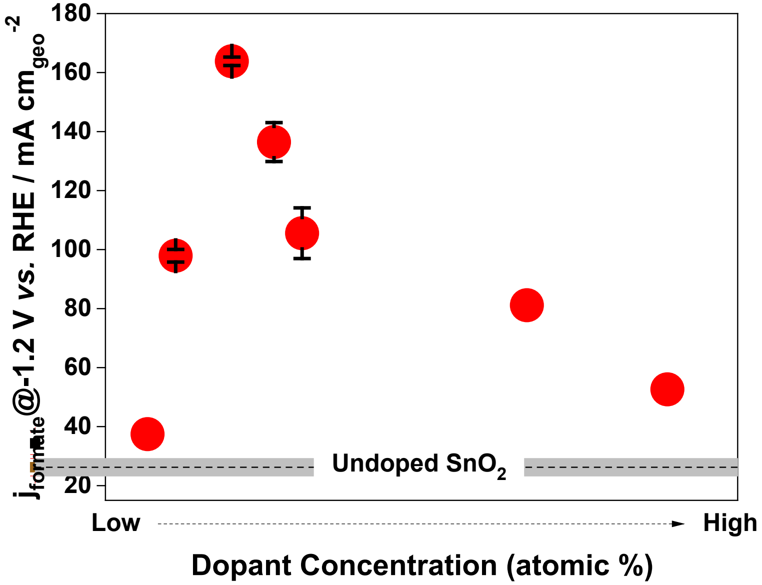
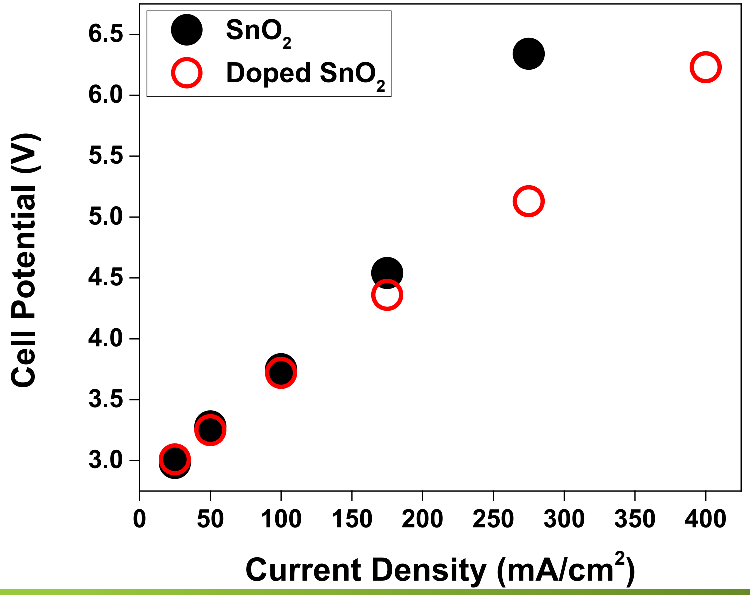


H-Cell Screening



Electrolyzer Performance



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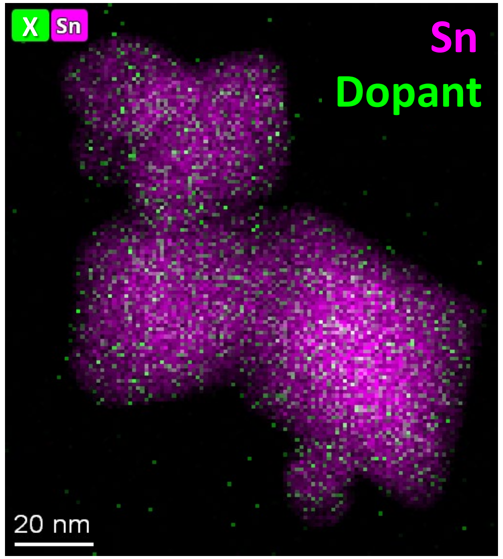
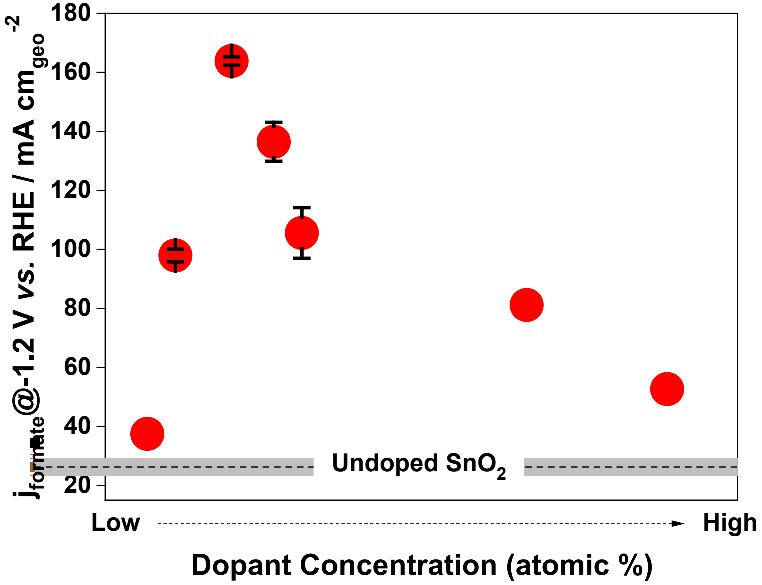


H-Cell Screening



Electrolyzer Performance

- Currently comparing long-term performance.
- Post-reaction characterization to quantify morphology/surface changes & confirm dopant retention.
- TEA/LCA

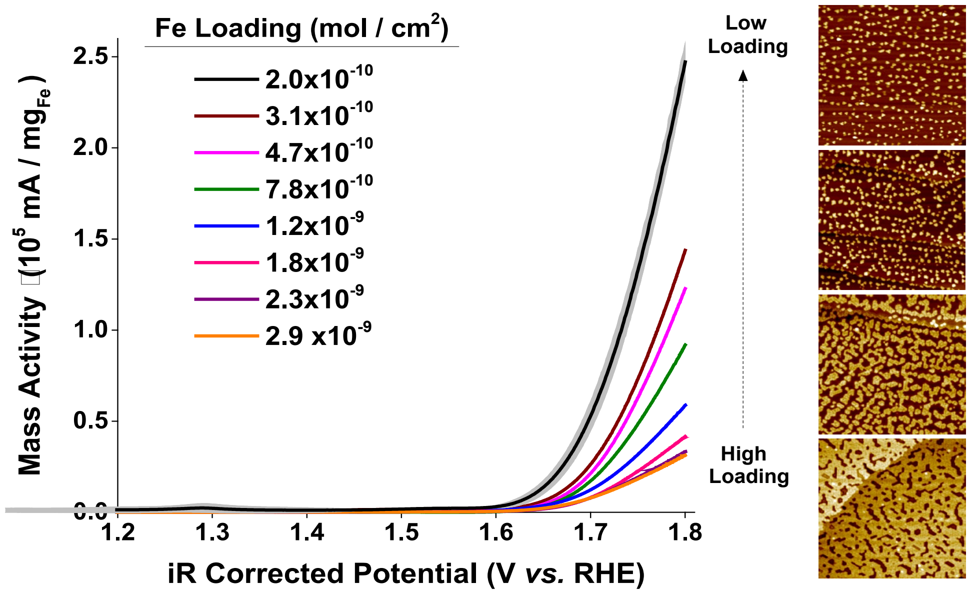
Electrocatalyst Development

Surface Science Studies.

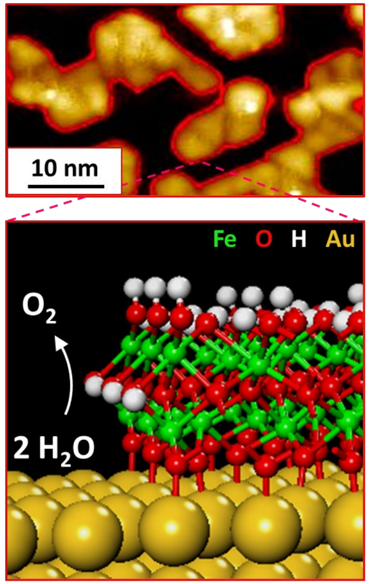
Key approaches include:

1. Probing active sites in PGM-free anode OER catalysts (Fe_2O_3 and $NiFeO_x$).
2. Mapping the size-dependent CO_2RR vs HER selectivity of Ag nanocatalysts.

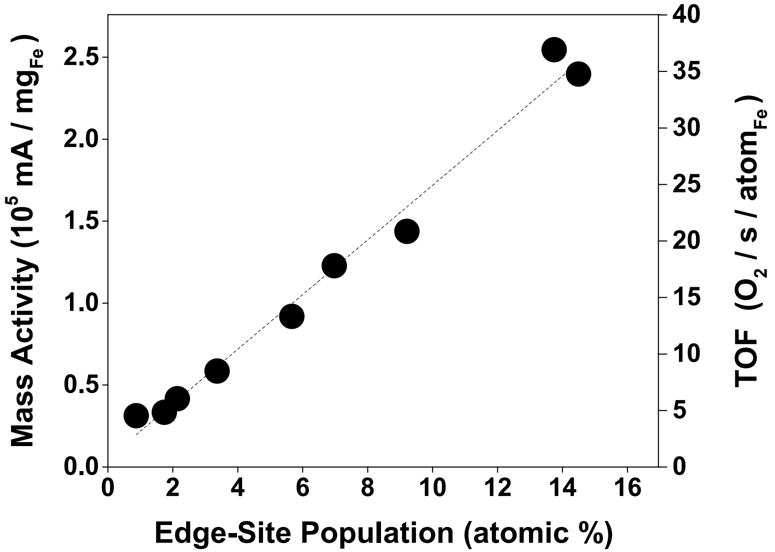
Loading and size-dependent OER activity



Experiment + DFT



Structure/Property Relationship



ACS Catal. **2019**, *9*, 5375 (article link) and *ACS Catal.* **2020**, *10*, 11768 (article link).

Electrocatalyst Development

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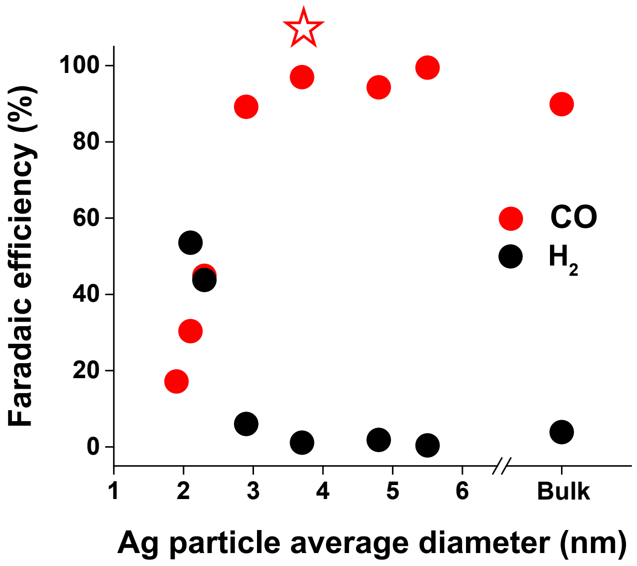
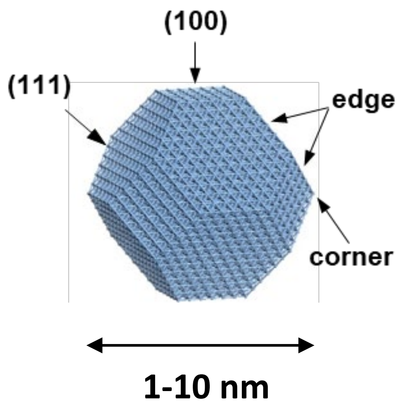
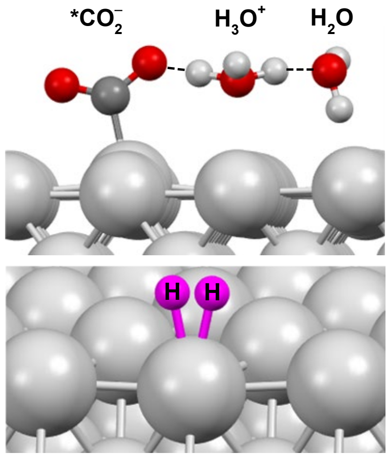
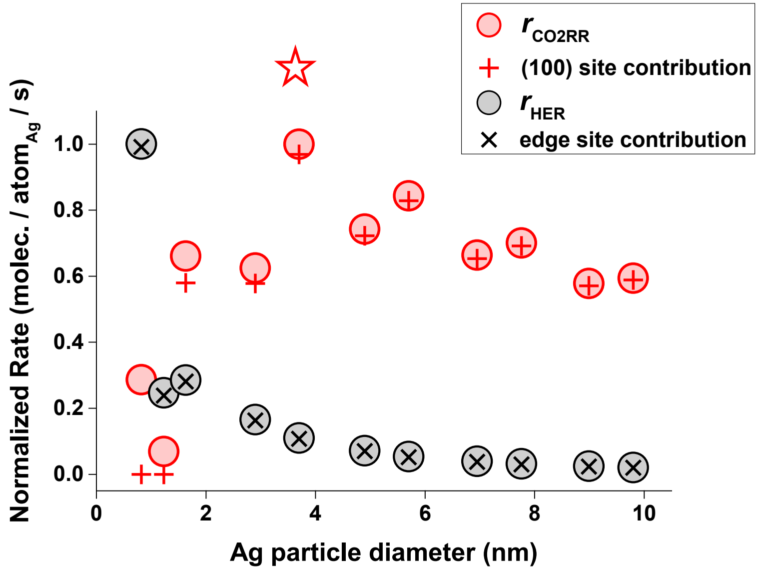
Experimental Data for Ag Catalysts





DFT, Transition State Theory, and Microkinetic Modeling





ACS Catal. **2022**, *12*, 5921 (article link).

Microwave Catalyst Development

Dry Reforming of Methane (DRM) converts CO_2 + CH_4 to syngas:
$CO_2 + CH_4 \rightarrow 2CO + 2H_2$

- High temps required for good kinetics and minimal coking (>800 C).
- Economically unappealing with traditional thermal reactors.

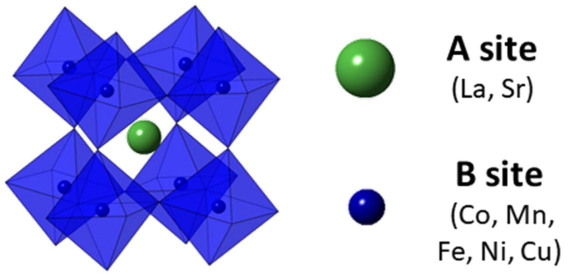
Microwave reactors are electrically driven and selectively heat the catalyst bed to ~1000C.

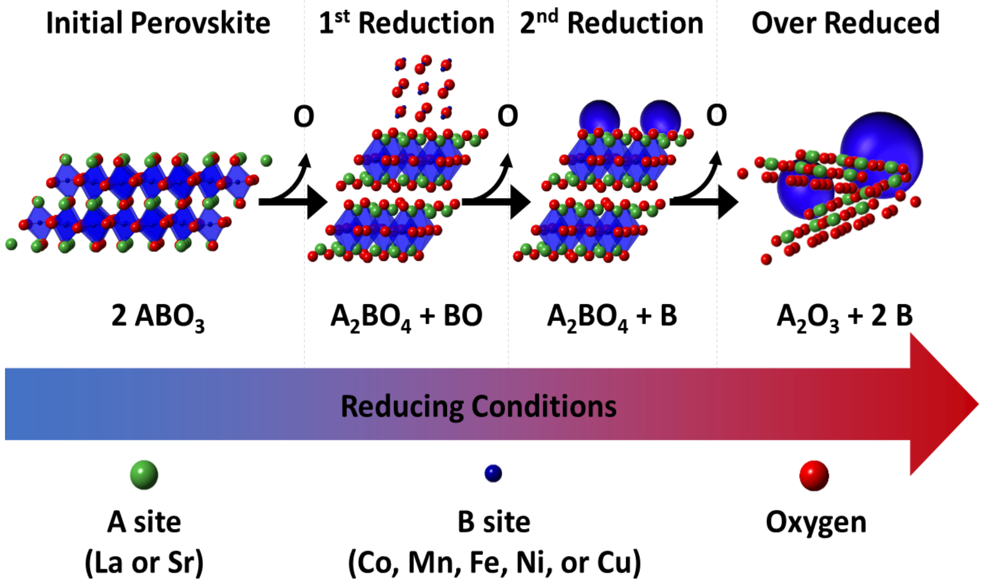
- Selectively heats the catalyst bed, not entire reactor volume.
- Rapid on/off cycling to reaction temperatures.
- Excellent energy efficiency.

Catalyst design considerations:

- Oxides must be conductive and thermal stability.
- Retain MW-absorbing active oxide phase and sustain small metallic nanoparticle active sites.
- B-site dopants control stability and overall catalytic activity.

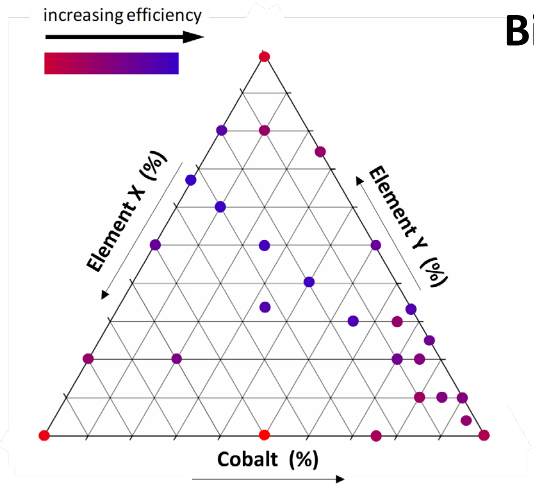
Doped LSC-X Catalyst (ABO_3 general structure)



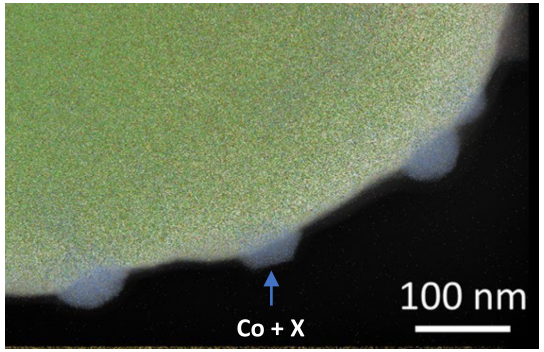


Applied Catalysis B **2021**, *284*, 119711 (article link) & US Patent Application #17/079,924 .

Microwave Catalyst Development



Bi-doped LSC-X/Y catalyst (X,Y = B site cations)



Create bimetallic active sites

- **Probed large composition space of bi-doped LSC-X/Y (~30 formulations).**
- **Sustained multi-day, 80-90% single-pass conversion of pure gases at 1 LPM with several start/stop cycles** (7 g catalyst powder).
  - **WHSV:** ~10 $L_{gas}/g_{catalyst}$/hr
  - **GHSV:** ~20,000 $L_{gas}/L_{catalyst}$/hr
- **Kg-scale synthesis achieved, creating *industrial form* for pre-pilot scale.**
- **Tuning product distribution to achieve 2:1 H_2:CO ratio for MeOH synthesis.**

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2$$

CO Production Energy Requirements:
- MW: ~3 kWh/kg_{CO}
- Echem: 5-7 kWh/kg_{CO}

H_2 Production Energy Requirements:
- MW: ~48 kWh/kg_{H2}
- Echem: 46-70 kWh/kg_{H2}

★ **5 times *lower* energy than thermally driven reaction!**

★ **TEA: microwave syngas to MeOH at $1-2/gallon with 2:1 H_2:CO ratio**

Unpublished results; US Patent Application #17/079,924 & manuscript in preparation.

Team Members

Electrochemistry: Thuy-Duong Nguyen-Phan & James Ellis

Microwave Catalysis: Chris Marin, Biswanath Dutta, and Christina Wildfire.

Computational Electrochemistry: Dominic Alfonso, Dan Sorescu, Anantha Nagarajan (U. Pitt), and Prof. Giannis Mpourmpakis (U. Pitt).

Applied Surface Science Studies: Xingyi Deng and Junseok Lee

Keep an eye out for open positions through NETL's RSS contractor: Leidos & Battelle!

Questions or Comments?

Thank you for your attention!

Douglas.Kauffman@NETL.DOE.GOV

Acknowledgement: This work was performed in support of the U.S. Department of Energy's Fossil Energy and Carbon Management's Carbon Conversion Program and executed through the National Energy Technology Laboratory (NETL) Research & Innovation Center's Carbon Conversion FWP.

Synthesis of Value-Added Organic Products

Technology Performance Data

Electrochemical reduction of CO_2 into formate / formic acid

	Units	Measured/Current Performance	Projected/Target Performance
Synthesis Pathway Steps[1]			
Step 1 (based on CO_2)	mol^{-1}	$CO_2 + 2e^- + 2H^+ \rightarrow HCOOH$	
Step 2	mol^{-1}	Balanced chemical equation	
Step n	mol^{-1}	Balanced chemical equation	
Source of external intermediate 1		Renewable energy (electrons)	
Source of external intermediate 2		(e.g., natural gas, oil, renewable energy, etc)	
Source of external intermediate n		(e.g., natural gas, oil, renewable energy, etc)	
Reaction Thermodynamics[2,3]			
Reaction[4]		Electrochemical; formal potential E0 = -0.12V *vs.* RHE)	
ΔH^o_{Rxn}	KJ/mol	378.6 (from: 10.1021/acs.chemrev.8b00705)	
ΔG^o_{Rxn}	KJ/mol	350.9 (from: 10.1021/acs.chemrev.8b00705)	
Conditions		(range)	(range)
CO_2 Source[5]		25-100%	<25%
Catalyst[6]		Doped SnO_2	Doped SnO_2
Pressure	bar	1	1
CO_2 Partial Pressure	bar	0.25-1	<0.25
Temperature	oC	20	20
Performance		(range)	(minimum)
Nominal Residence Time[7]	sec	seconds	TBD
Selectivity to Desired Product[8]	%	60-90	>90
Product Composition[9]		(range)	(optimal)
Desired Product	mol%	30% single-pass conversion	TBD; must optimize single-pass conversion and flow rates to sustain selective CO_2 conversion without HER.
Desirable Co-Products	mol%		
" "	mol%		
Unwanted By-Products	mol%	<10	0
" "	mol%		
Grand Total	**mol%**	**40%**	**TBD**

Synthesis of Value-Added Organic Products

Technology Performance Data

Microwave dry reforming

	Units	Measured/Current Performance	Projected/Target Performance
Synthesis Pathway Steps[1]			
Step 1 (based on CO_2)	mol^{-1}	$CO_2 + CH_4 \rightarrow 2CO + 2H_2$	
Step 2	mol^{-1}		
Step n	mol^{-1}		
Source of external intermediate 1		Renewable energy (electrons)	
Source of external intermediate 2			
Source of external intermediate n			
Reaction Thermodynamics[2,3]			
Reaction[4]		Microwave	
ΔH^o_{Rxn}	KJ/mol	247 (from: https://doi.org/10.1002/ente.202100106)	
ΔG^o_{Rxn}	KJ/mol	170.5	
Conditions		(range)	(range)
CO_2 Source[5]		Concentrated $CO_2 + CH_4$ (1:1)	Concentrated $CO_2 + CH_4$ (1:1)
Catalyst[6]		NETL-developed conductive oxide (PGM-free)	NETL-developed conductive oxide (PGM-free)
Pressure	bar	1	1
CO_2 Partial Pressure	bar	0.5	0.5
Temperature	^oC	800-900C (localized MW heating)	800-900C (localized MW heating)
Performance		(range)	(minimum)
Nominal Residence Time[7]	sec	seconds	TBD
Selectivity to Desired Product[8]	%	80-90	>90
Product Composition[9]	1:1 syngas	80-90%	>90%
Desired Product	mol%	80-90% single-pass conversion	>90% single-pass conversion
Desirable Co-Products	mol%		
" "	mol%		
Unwanted By-Products	mol%	Coke (solid carbon); very minor	none
" "	mol%	Unreacted $CO_2 + CH_4$; 10-20%; minor solid carbon (coke).	
Grand Total	**mol%**	**80-90%**	**>90%**