# Rational Design Platform for Transition Metal Catalyzed Electrochemical Synthesis

**WBS#2.1.10.3**
**Lawrence Livermore National Laboratory/Opus 12/TOTAL**
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# Overview

## Timeline

- Award issued May 2018
- Projected End date April 2020
- Project 5% complete

## Barriers

Electrochemical conversion of $CO_2$ to methane and other fuels requires the improvement of the energy efficiency and selectivity of electrochemical catalysts.

## Budget

| | FY 18 Costs | FY 19 Costs | FY 20 Costs | Total costs |
|---|---|---|---|---|
| DOE Funded | $208k | $500k | $292k | $1000k |
| Project Cost Share | $96 | $230k | $134k | $460k |

## Partners

**Opus 12:**
Brings in expertise in CO2RR catalyst testing under industry relevant conditions and commercial scaling

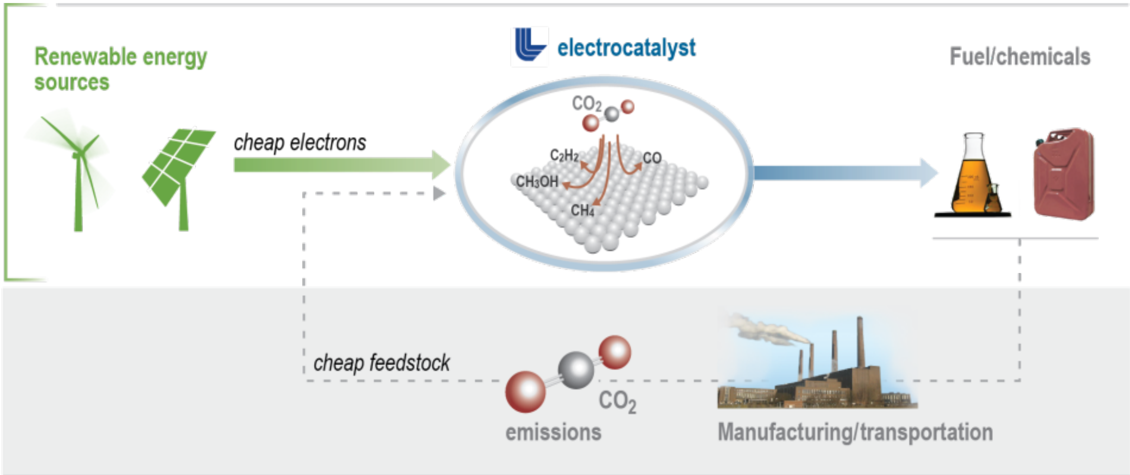
**TOTAL:**
Provides industry insight regarding electrochemical $CO_2$ reduction to target molecules.

# Rational Design Platform for Transition Metal Catalyzed Electrochemical Synthesis

Control No. 1465-1741

## Project Goal:
## Optimize Catalyst Performance

Improve the energy efficiency and selectivity of Cu-based catalysts for electrochemical $CO_2$-to-fuel conversion by engineering the potential energy landscape




## Objective 1: Morphology Control at the nano/meso/macro scale

- Increase number and accessibility of active sites.
- Control the local atomic configuration of the active sites

## Objective 2: Catalyst Composition Tuning

- Localized and selective stabilization of critical intermediates to improve catalyst reactivity and selectivity

## Objective 3: Interface Environment Control

- Control the local potential energy landscape by tuning solvent, local electric field and ionic strength

**Advanced Manufacturing Office Mission Relevance of $CO_2$-to-fuel conversion :**
Conversion of inexpensive, renewable electrical energy to chemical energy for grid energy storage, fuels, and chemicals is broadly attractive to utilities and chemical manufacturers, and contributes to reduce the life-cycle energy consumption of manufactured goods.

# Technical Innovation

**Current state-of-the-art:** Current Power-to-Gas technologies are energy and capital intensive. The largest Power-to-Gas plants are based on platinum catalyzed water electrolysis to convert (renewable) electricity into hydrogen followed by $CO_2$ methanation via the “Sabatier” reaction. The leading $CO_2$-to-CO electrochemical reduction catalysts are based on Au.

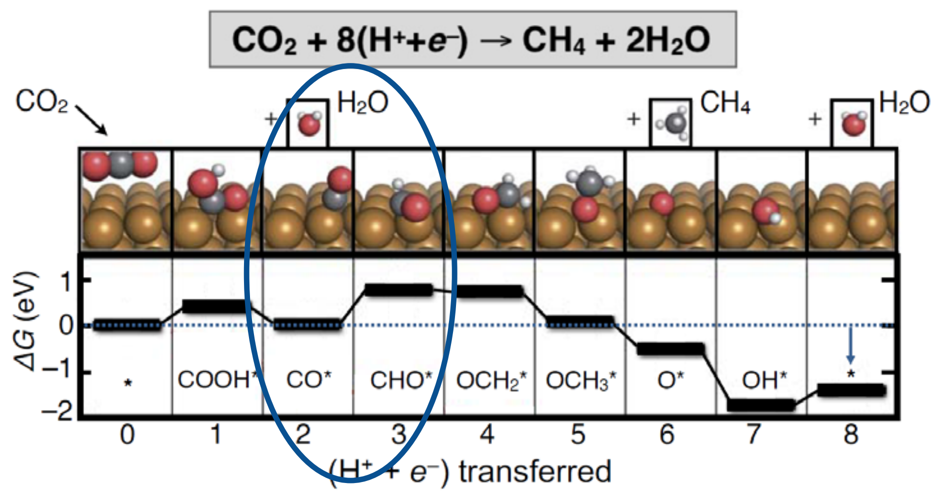
$$CO_2 + 4\,H_2 \xrightarrow[\text{pressure}]{400\,^\circ C} CH_4 + 2\,H_2O \quad \text{Sabatier process}$$

**Innovation: One-step electrochemical $CO_2$-to-fuel conversion technology:**

- Has the potential to significantly reduce capital and process costs.
- Opens the door to new selective pathways to higher value chemicals that are not accessible by thermal processes such as the “Sabatier” process.

**Our Approach:**

Improve the energy efficiency and selectivity of Cu-based catalysts by manipulating the potential energy landscape through tuning the composition, morphology, and environment of the catalyst.

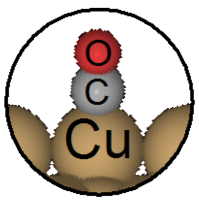


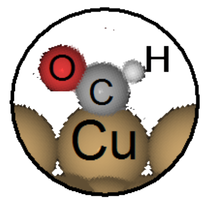

**CO and CHO are Critical Intermediates to $CH_4$**

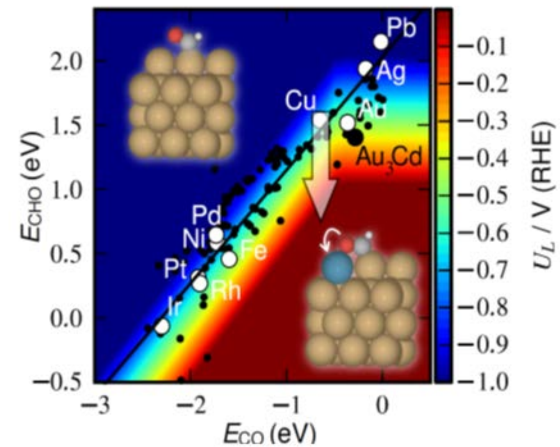
# Technical Approach

The energy efficiency and selectivity of a catalyst can be improved by engineering the binding energies of critical intermediates that typically are related through scaling relationships

CO* binding strength $\propto$ CHO* binding strength

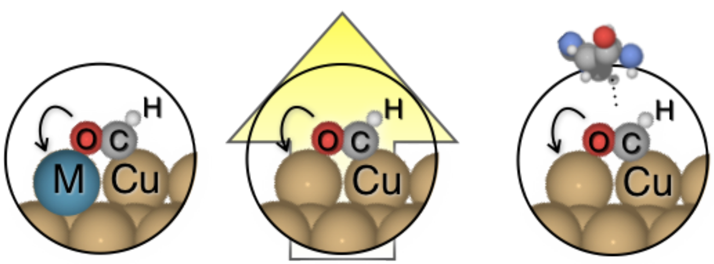


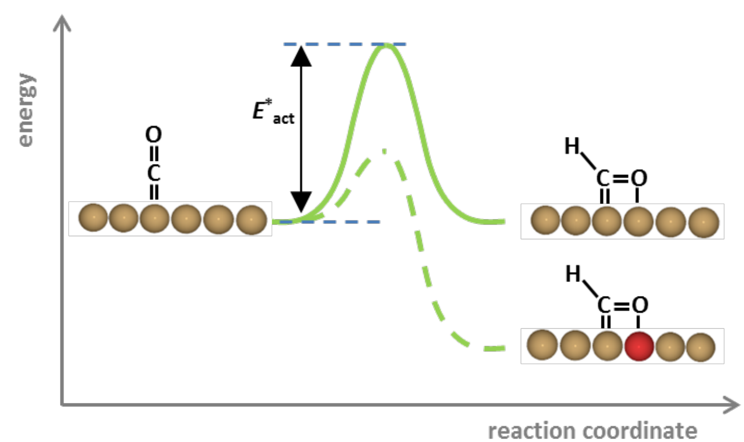




Journal of Catalysis 343 (2016) 215–231

Overcoming the energy coupling of rate limiting intermediates by selective stabilization thus decreasing the activation barrier.

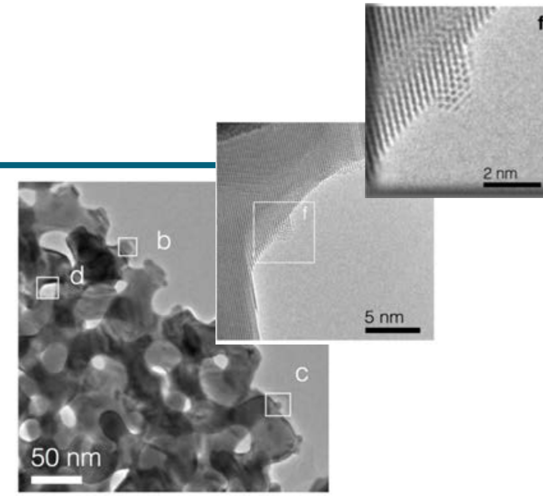



*Alloying* *Field effects* *Additives*



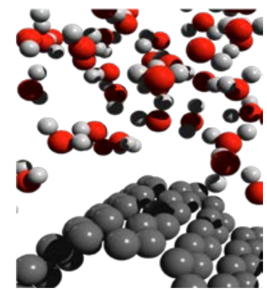
# Technical Approach

## Full integration of the team's unique expertise:



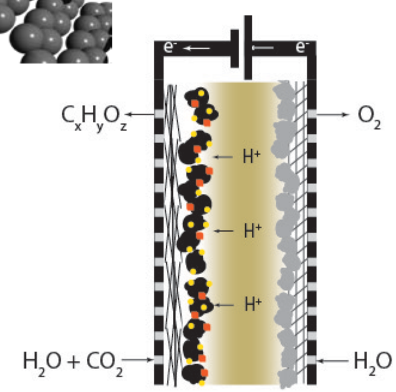

### Novel nanoporous metals and dilute alloys (LLNL)

- Synthesis and characterization of nanoporous dilute alloy catalysts
- Additive manufacturing of engineered hierarchical nanoporous metals
- Leverages catalyst development expertise and investment gained through DOE's EFRC *IMASC*.



### Large-scale quantum simulations of realistic electrochemical interfaces (LLNL)

- Takes advantage of LLNL's unique expertise in multiscale modeling of explicit electrochemical interfaces
- Leverages cutting-edge methods development under 2017 METI-DOE U.S.-Japan Agreement on Clean Energy Research
- LLNL's leadership-class computing platforms




### CO2RR catalyst testing and commercial scaling (Opus 12)

- Provides access to Opus12's advanced Proton Exchange Membrane (PEM) electrolyzer technology

### Industry insight (TOTAL)

- As one of the world's largest integrated international oil and gas companies with operations in more than 130 countries worldwide, and leading integrated producer of chemicals, TOTAL provides valuable industry insight regarding the electrochemical CO2 reduction to target molecule.

# Results and Accomplishments

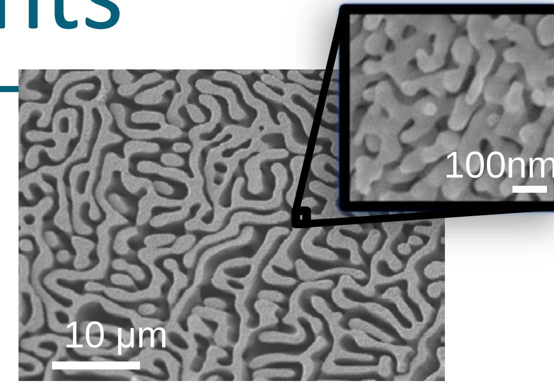
- Synthesized nanoporous Cu electrodes with monomodal and bimodalal (nano/macro) pore size distributions.

- Printed hierarchical nanoporous Cu electrodes

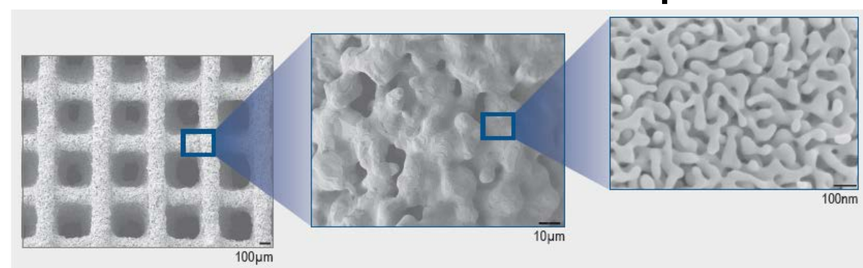
- Modified and measured the electrochemical accessible surface area of Cu electrodes by oxidation-reduction cycles (Up to 1000 times increase in the projected surface area)

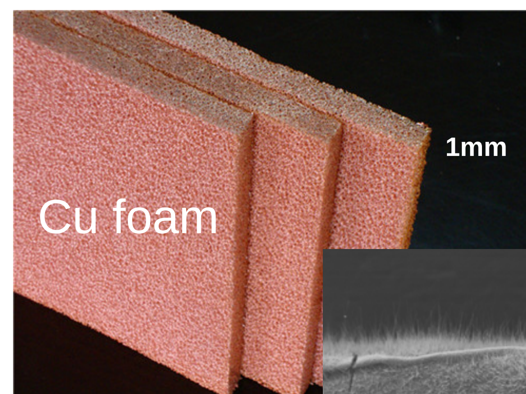
- Demonstrated that nanoporous gold electrodes exhibit 100% selectivity for $CO_2$-to-CO conversion

- Demonstrated that the presence of macropores in nanoporous Cu electrodes improves mass transport properties

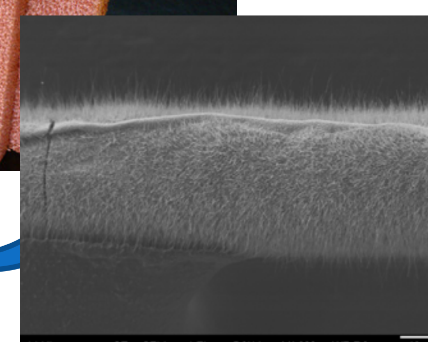



**Hierarchical nanoporous-Cu**




Engineering of the nanoscale surface morphology



# Transition

**Electrochemical CO2-to-fuel reduction has the potential to develop into a gigaton industry**

- TOTAL has imitate need to convert a 99% pure CO2 stream at a one-ton per day scale
- Scale-up of optimized reactor/catalyst design to 1 kg/day scale
- Cooperative research and development agreement (CRADA) between TOTAL, Stanford, and LLNL

# Questions?