

# Mechanistic insights into the electrochemical CO<sub>2</sub> reduction reaction using surface enhanced infrared spectroscopy

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The electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) is a method to convert a greenhouse gas, CO<sub>2</sub>, into chemicals and fuels using electricity generated from renewable sources. CO is an intermediate in this process which can be split into two steps. The first is the conversion of CO<sub>2</sub> to CO while the second is the further reduction of CO into hydrocarbons and oxygenates. This second step, known as the electrochemical CO reduction reaction (CORR), occurs on the surface of Cu catalysts under alkaline conditions. The CORR produces C<sub>1</sub> products like methane and the more commercially favorable C<sub>2+</sub> products such as ethylene, ethanol, acetate, and 1-propanol but suffers from competition from the undesirable hydrogen evolution reaction.

The goal of this dissertation is to elucidate selectivity trends in the CO<sub>2</sub>RR with a view to developing design principles for optimizing the production of C<sub>2+</sub> products. Effects such as Cu catalyst preparation method, reactant mass transport and nature of the electrolyte cation can all impact the reaction selectivity. However, these effects remain a topic of discussion in recent literature. In this dissertation, we employ in-situ attenuated total reflection surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) coupled with reactivity studies to probe the electrochemical interface and obtain mechanistic insights into the CO<sub>2</sub>RR pathway.

Our results show that oxide derived copper (OD-Cu) enhances the CORR activity compared to polycrystalline Cu catalysts at low overpotentials because of its ability to expose the C-C coupling active Cu(100) facet. We also show that CO mass transport limitations do not alter the C<sub>2+</sub>/C<sub>1</sub> product ratio which suggests that CO adsorbs in patches on the Cu surface. Further, hydrated electrolyte cations do not impact the CO<sub>2</sub>RR reactivity by buffering the interfacial pH but instead through their electric and nonelectric field interactions. These cation effects are not exclusive but can be obtained by changing the structure and composition of the electrochemical interface, highlighting its interdependent nature. Advances in both the temporal and spatial resolution of current in-situ spectroscopic techniques are needed to further probe how the electrochemical interface impacts electrode-mediated reactions.