HER Suppression on Ag Electrodes via Molecular Films for Highly Selective CO\textsubscript{2} to CO Reduction

Alonso Rosas-Hernández, Arnaud Thevenon, Alex Fontani, Theodor Agapie, and Jonas C. Peters

Abstract:
The carbon dioxide reduction reaction (CO\textsubscript{2}RR) in aqueous electrolytes suffers from efficiency loss due to the competitive hydrogen evolution reaction (HER). Developing efficient methods to suppress HER is a crucial step toward sustainable CO\textsubscript{2} utilization. Herein, we report the selective conversion of CO\textsubscript{2} to CO on planar silver electrodes with faradaic efficiencies >99\% using simple pyridinium-based molecular additives. The formation of an organic film was detected on the surface of the Ag electrode. Electrochemical kinetic data suggest that HER is selectively inhibited by the growth of such hydrophobic organic layer that limits proton but not CO\textsubscript{2} mass transport.

Introduction
The mechanistic landscape of CO\textsubscript{2}RR is complex and competing proton-coupled electron transfer (PCET) pathways can be operative; thus, the control of product selectivity remains a central issue. Molecular modifications of electrode surfaces provide an attractive approach to easily tailor the selectivity of electrocatalytic systems for the generation of desired products in CO\textsubscript{2}RR.\textsuperscript{1,2}

Team
Alonso Rosas, Arnaud Thevenon, Nick Watkins, Gavin Heim, Alex Fontani, Theo Agapie and Jonas Peters.

Outlook
A molecular tuning strategy opens promising opportunities for improving CO\textsubscript{2}RR through the interaction of organic additives and metal electrodes. More importantly, this approach can used beyond copper electrodes. This allow us to tune the selectivity and activity of other metallic surfaces for CO\textsubscript{2}RR which have been previously overlooked because of their preferably reduction of protons over CO\textsubscript{2}.

Acknowledgments
This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0009493.

Results, Highlights, and Accomplishments

Approach:
The electrocatalytic performance of polycrystalline Ag foils was evaluated in the presence of molecular additives using a 10 mM solution of either 1-Br, or 2-Cl.

A noticeable organic film was electrodeposited in situ during catalysis onto the surface of the silver electrodes.

Electrocatalytic Screening

Electrochemical Kinetics

Tafel analysis:
- Bare Ag: ET as R.D.S.
- Ag-1 and Ag-2: improved kinetics.

Order in [HCO\textsubscript{3}\textsuperscript{-}]:
- Bare Ag: zeroth order.
- Ag-1 and Ag-2: first order. R.D.S. involving a Pt form HCO\textsubscript{3}\textsuperscript{-}.


Conclusions
Electrokinetic studies demonstrate the impact of the film on the mechanism of CO\textsubscript{2}RR: a proton transfer from HCO\textsubscript{3}\textsuperscript{-} is in the R.D.S., in contrast to an ET or PCET step as has more typically been observed for bare Ag surfaces. Moreover, slow diffusion of proton carriers through the hydrophobic layer is responsible for a dramatic decrease in HER.