

HER Suppression on Ag Electrodes via Molecular Films for Highly Selective CO₂ to CO Reduction

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

Abstract:

The carbon dioxide reduction reaction (CO₂RR) 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 CO₂ utilization. Herein, we report the selective conversion of CO₂ 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 CO₂ mass transport.

Introduction

The mechanistic landscape of CO₂RR 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 CO₂RR.¹⁻³

Team

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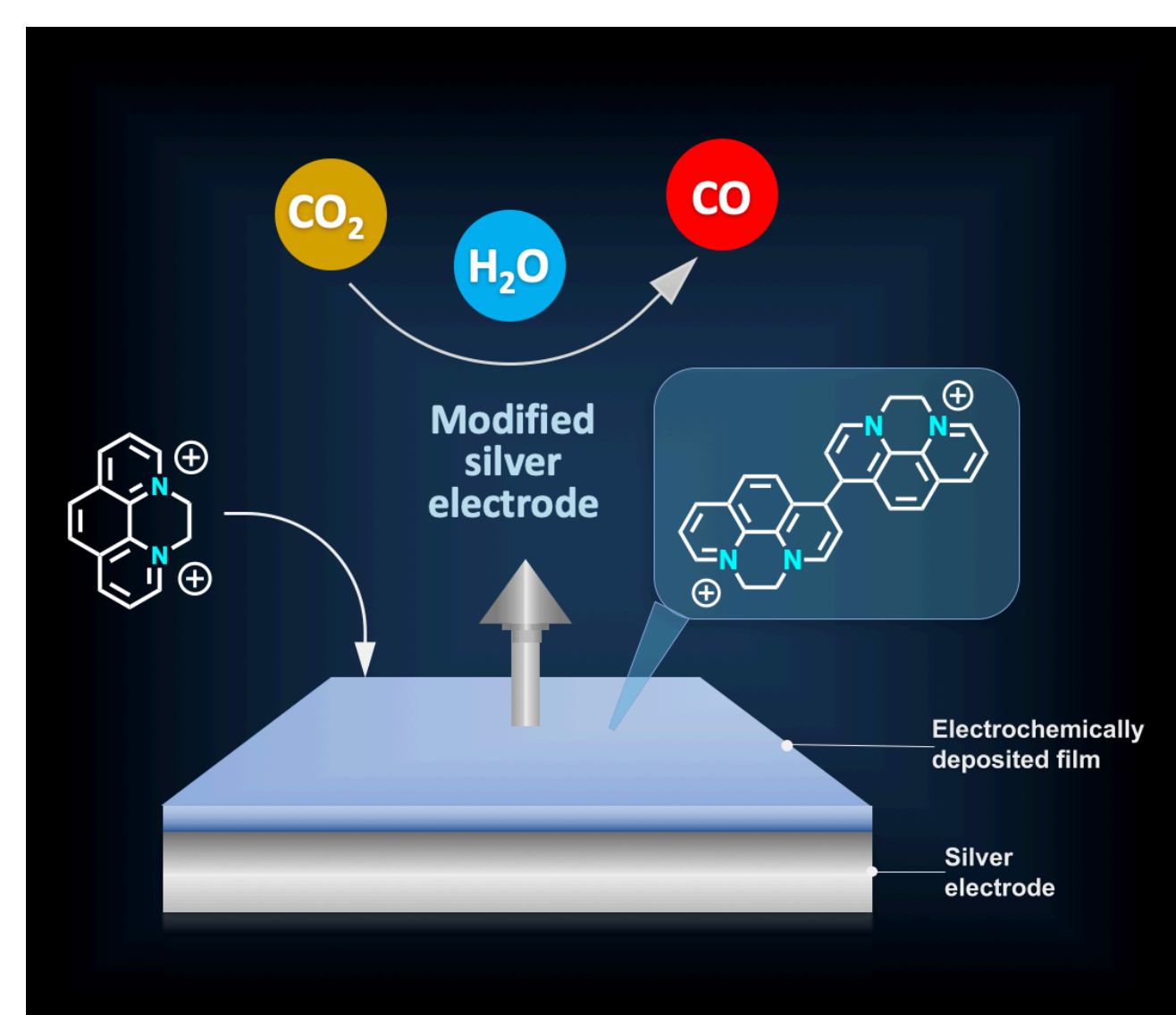
Outlook

A molecular tuning strategy opens promising opportunities for improving CO₂RR through the interaction of organic additives and metal electrodes. More importantly, this approach can be used beyond copper electrodes. This allows us to tune the selectivity and activity of other metallic surfaces for CO₂RR which have been previously overlooked because of their preferential reduction of protons over CO₂.

Acknowledgments

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Results, Highlights, and Accomplishments

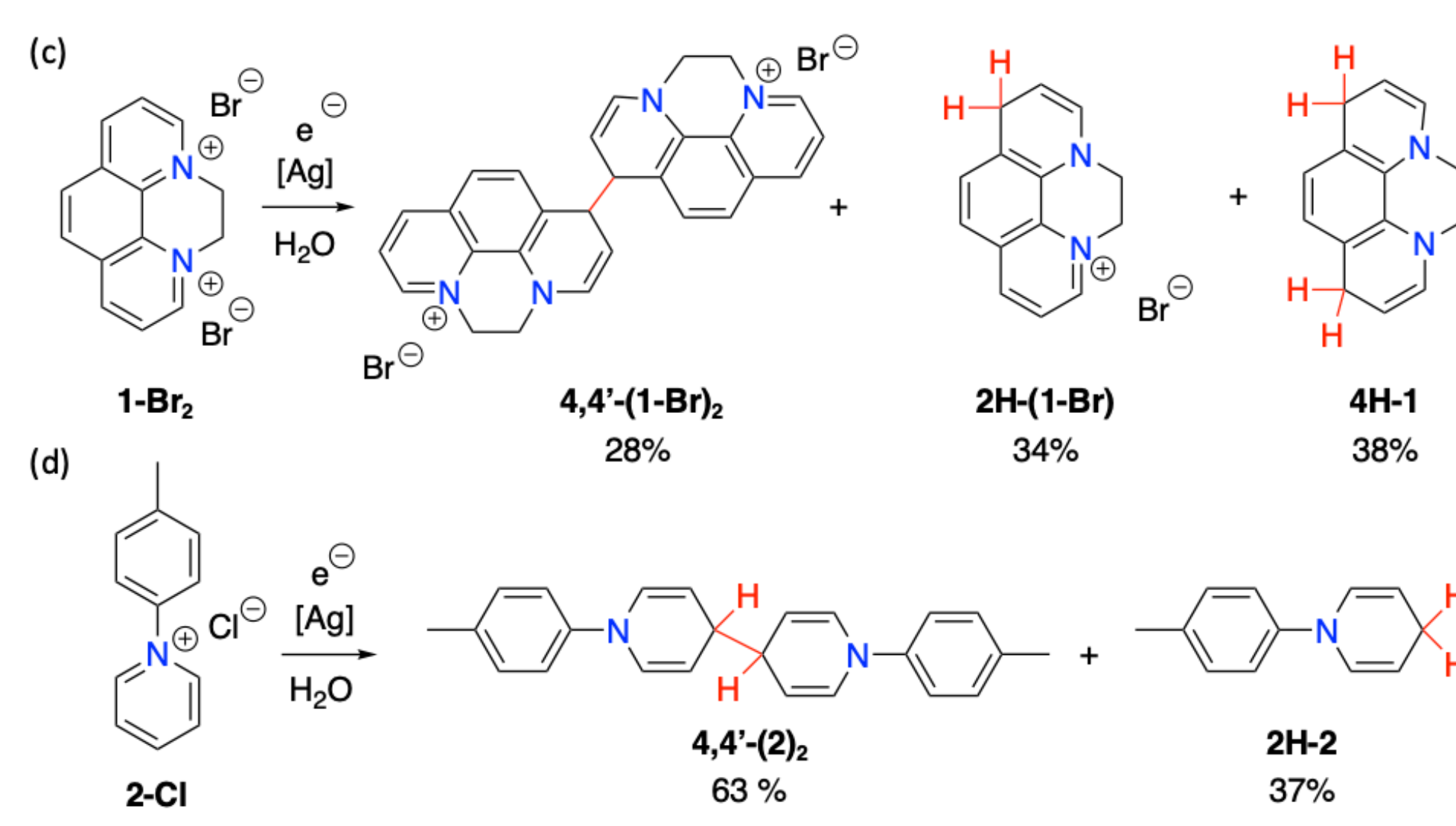
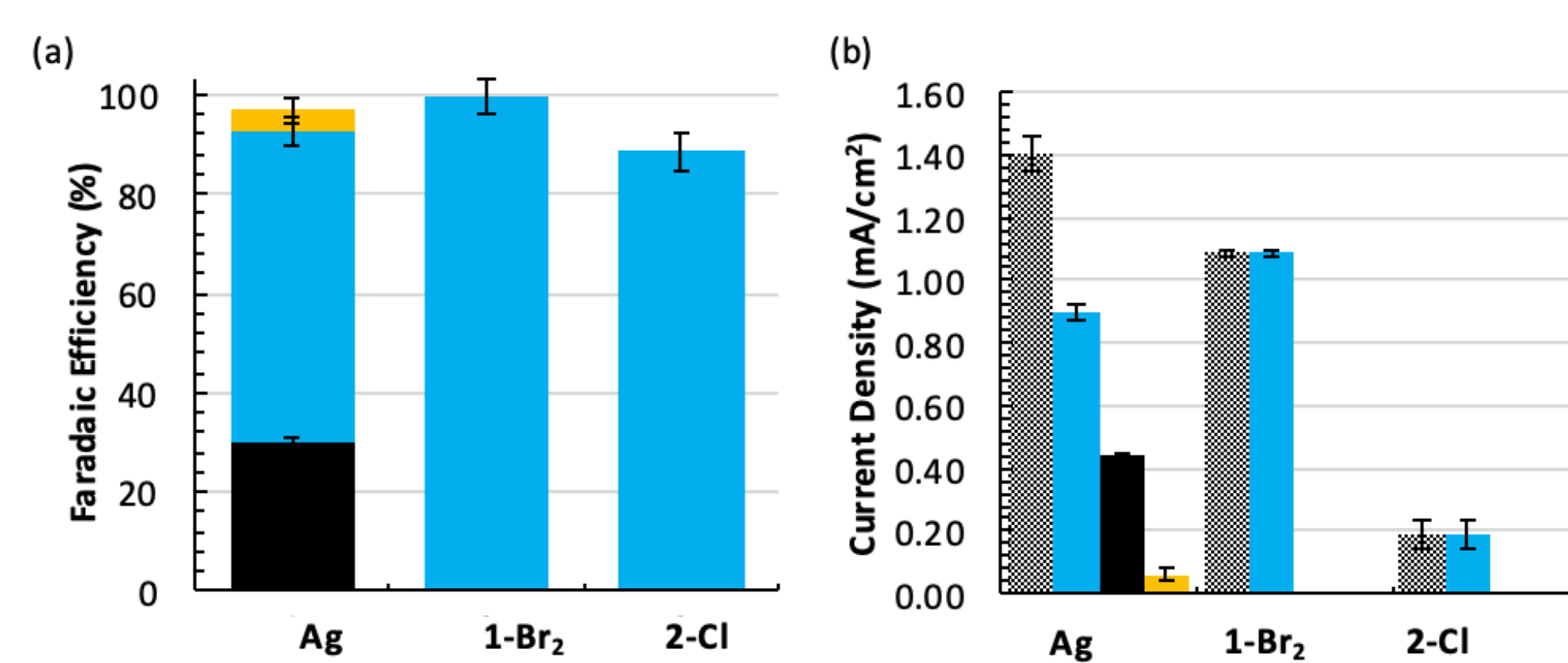


Approach:

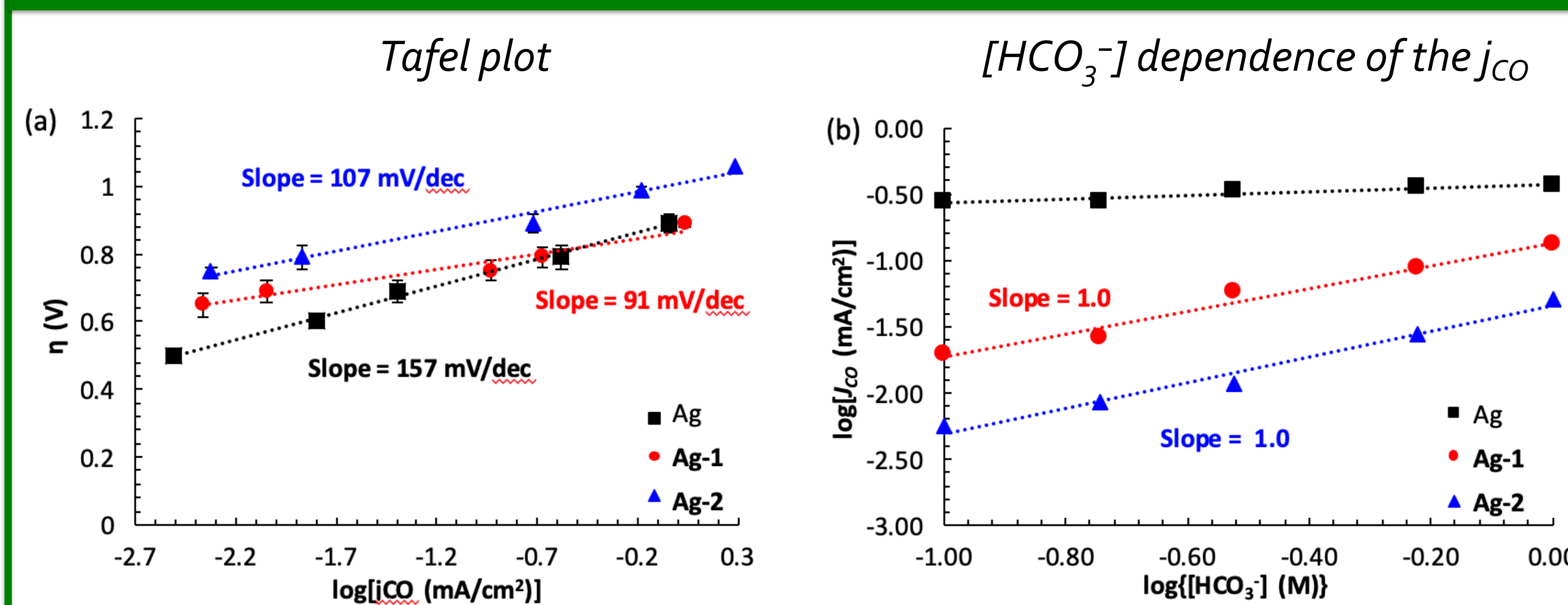
The electrocatalytic performance of polycrystalline Ag foils was evaluated in the presence of molecular additives using a 10 mM solution of either 1-Br₂ or 2-Cl.

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

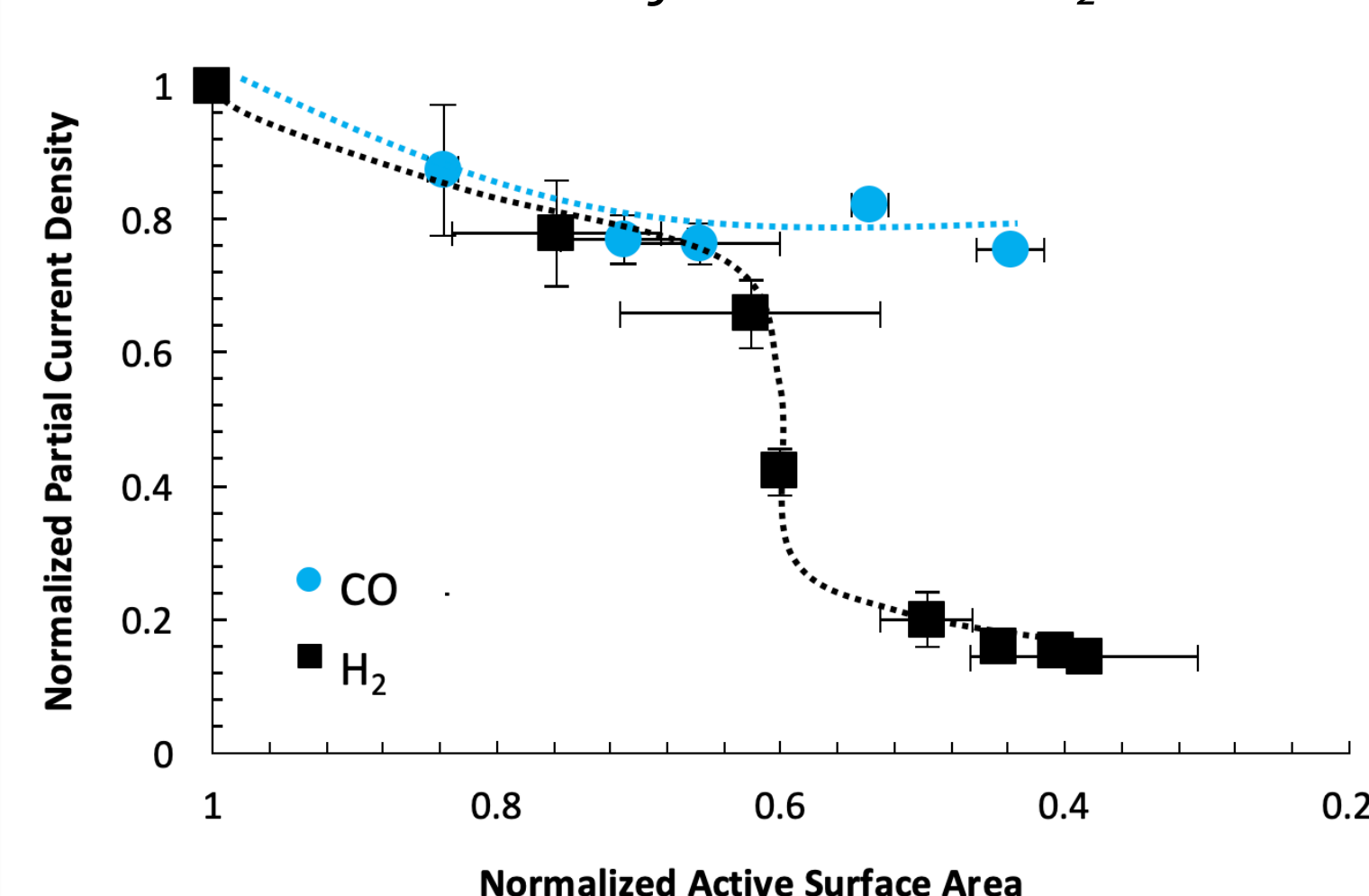
Electrocatalytic Screening



Electrochemical Kinetic Experiments



Active sites for HER and CO₂RR



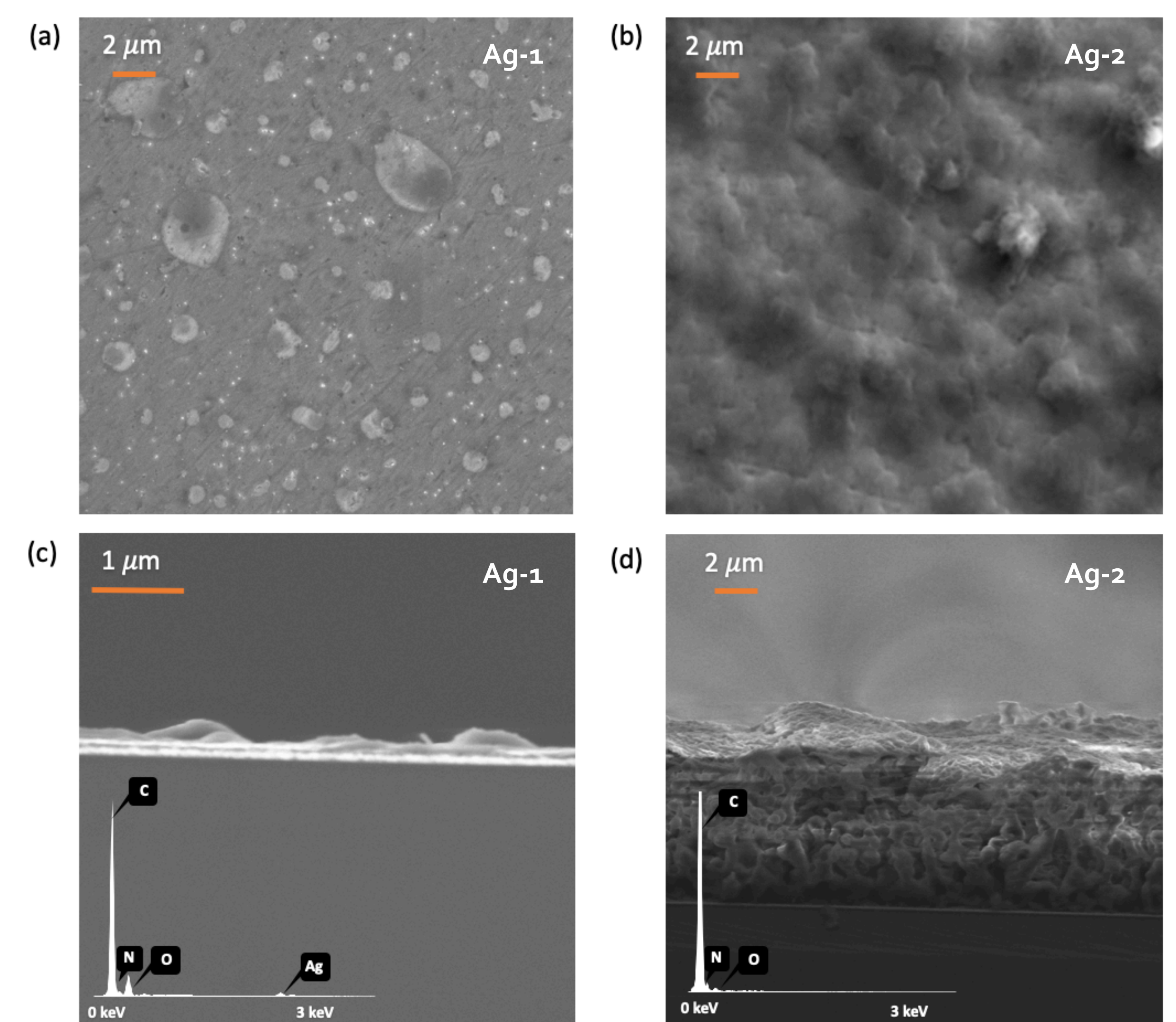
Tafel analysis:

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

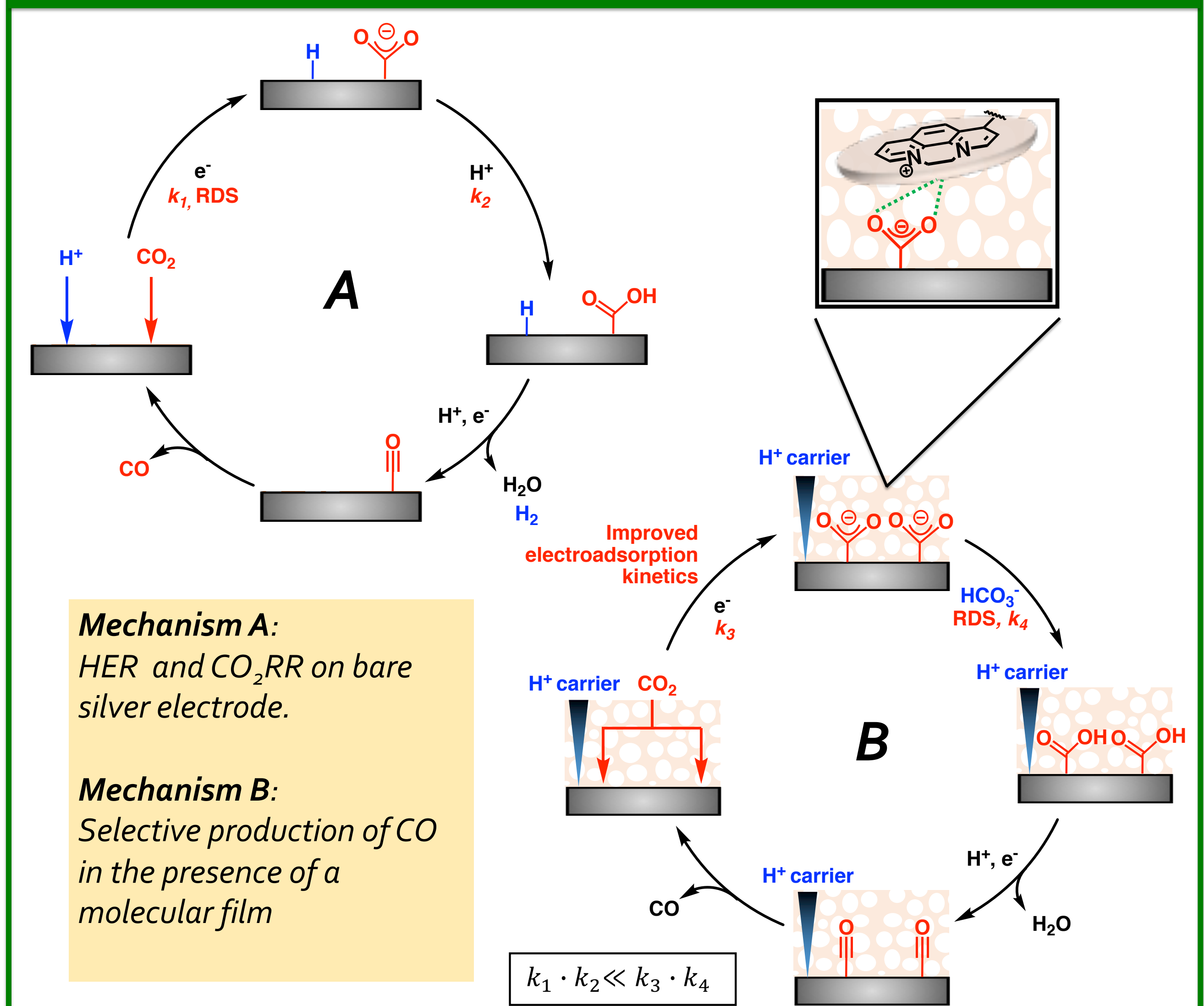
Order in [HCO₃⁻]:

- Bare Ag: zeroth order.
- Ag-1 and Ag-2: first order. R.D.S. involving a PT from HCO₃⁻

SEM and EDS Characterization



Working Hypothesis Mechanism



Conclusions

Electrokinetic studies demonstrate the impact of the film on the mechanism of CO₂RR: a proton transfer from HCO₃⁻ 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.

1) Z. Han, R. Kortlever, H.-Y. Chen, J. C. Peters, T. Agapie, *ACS Cent. Sci.* **2017**, *3*, 853. 2) A. Thevenon, A. Rosas-Hernandez, J. C. Peters, T. Agapie, *Angew. Chem. Int. Ed.* **2019**, *58*, 16952. 3) F. Li, A. Thevenon, A. Rosas-Hernandez, Z. Wang, Y. Li, et al. *Nature*, **2020**, *577*, 509.