Understanding the Competition between Two-Electron Reduction Products for Carbon Dioxide Electrocatalysis

D. Bohra, Materials for Energy Conversion and Storage, Department of Chemical Engineering, Delft University of Technology
G. Li, E.A. Pidko, Inorganic Systems Engineering, Department of Chemical Engineering, Delft University of Technology
I. Ledezma-Yanez, Large-Scale Energy Storage, Department of Process and Energy, Delft University of Technology
W.A. Smith, Materials for Energy Conversion and Storage, Department of Chemical Engineering, Delft University of Technology

The electrochemical reduction of carbon dioxide (CO₂ER) is a highly promising technological solution providing a means to manage renewable electricity production by converting it to a chemically valuable form while recycling harmful anthropogenic CO₂ emissions. High achievable current density and relatively lower cost have led to several recent performance studies for silver (Ag) CO₂ER catalysts showing promising results for CO production. It is widely accepted that the formation of CO from CO₂ goes via a surface species *COOH whereas the formation of formate (HCOO⁻) proceeds via a O-bound bi-dentate surface species *OCHO. Consideration of only the binding energies of reaction intermediates dictates that the formation of HCOO⁻ is thermodynamically more feasible on Ag surfaces than CO. This conclusion does not reconcile with the experimental observations which have clearly shown that at intermediate potentials, Ag produces CO as the major product, H₂ as a by-product with only trace quantities of HCOO⁻. The reasons for this discrepancy and the role of the stable specie *OCHO in the catalytic performance of Ag are not well understood.

We investigate the competition between the reaction pathways for formation of CO, HCOO⁻, and H₂ on Ag(110) surface for CO₂ER. We address the mechanistic differences in the formation of *OCHO and *COOH and their respective interactions with the H₂ production pathways. We use Bader charge analysis to motivate the mechanistic study and demonstrate that it is fundamentally easier to control the selectivity between H₂ and CO than it is for H₂ and HCOO⁻. We perform climbing image nudged elastic band (CI-NEB) calculations to estimate reaction barriers for the formation of *OCHO and *COOH to show that *OCHO is not only thermodynamically more favorable than *COOH on Ag but also has a significantly lower kinetic barrier for formation and that solvation by the surrounding water plays a critical role in determining this barrier. Further, we demonstrate that lateral adsorbate interactions in the presence of *OCHO have a significant influence on the surface coverage of *H resulting in the inhibition of HCOO⁻ and H₂ production and a higher selectivity towards CO on Ag. Finally, we provide experimental evidence using surface enhanced Raman spectroscopy (SERS) of the presence of O-bound bi-dentate species on polycrystalline Ag catalyst during CO₂ER to validate our theoretical findings. Developing an understanding of the competition and interaction between the various reacting species can provide the necessary handles to design highly selective, and therefore efficient CO₂ER catalysts.

Lateral adsorbate interactions inhibit formate while promoting carbon monoxide selectivity for carbon dioxide electrocatalysis on Ag.

E-mail: D.Bohra@tudelft.nl