Opportunities and challenges in the electrocatalysis of CO₂ and CO reduction using bifunctional surfaces: A theoretical and experimental study of Au-Cd alloys

Electrolysis could enable the large-scale conversion of CO₂ to fuels and small molecules. This perspective discusses the state-of-the-art understanding of CO₂ and CO reduction electrocatalysis and provides an overview of the most promising approaches undertaken thus far. We set to explore "bifunctional" catalysts using Au-Cd based alloys inspired by theoretical modelling. Density functional theory calculations suggest more favourable thermodynamics for CO₂ reduction to CO and methanol on mixed Au-Cd sites on Au₃Cd relative to similar values on Au. We use various tools to test the bulk and surface alloys experimentally. We find that Au₃Cd in neutral media exhibits lower CO evolution activity than Au, and Au-Cd alloys also show negligible activity for CO reduction in alkaline media. This indicates that the mixed Cd-Au sites predicted to be catalytically active are not present in the sample. The catalytic performance is most consistent with Au-terminated step surface on a bulk alloy, possibly formed through adsorbate-induced restructuring. We highlight that future bimetallic catalysts must consider potential-dependent surface restructuring effects caused by reaction intermediates.