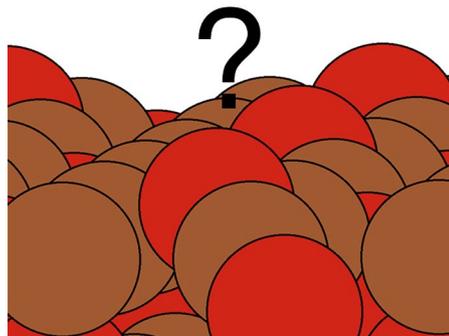


ELECTROCHEMICAL CARBON MONOXIDE REDUCTION

Probing the speciation

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The electrochemical reduction of carbon dioxide — or monoxide — is a very attractive strategy to produce valuable chemical feedstock and fuels, especially when powered with electricity obtained from renewable sources. Copper is, to date, the only catalyst capable of facilitating C–C bond formation to produce multi-carbon species. However, the actual active structure of Cu under operation remains elusive, albeit having been intensively studied.

Now, Levi Thompson, Feng Jiao, Bingjun Xu and colleagues at the University of Delaware combine in situ surface-enhanced Raman spectroscopy and CO electroreduction experiments on five relevant copper catalysts to demonstrate that multiple oxide and hydroxide species exist on all five surfaces at negative potentials, although the speciation varies among the catalysts. The experiments are performed on Cu foil, Cu microparticles, Cu nanoparticles, electrochemically deposited Cu film and oxide-derived Cu in Ar- and CO-saturated

alkaline electrolyte (pH = 11.7) at potentials ranging from the open-circuit potential (OCP) to –0.8 V versus the reversible hydrogen electrode (RHE). Isotopically labelled D₂O is used to discriminate between Cu–O and Cu–OH modes — as the shifts are smaller than expected for hydroxide modes, the researchers assign them to mixed Cu oxide and hydroxide species, CuO_x/(OH)_y.

At the OCP Cu foil exhibits a slightly reduced oxide surface (Cu₂O_{1-x}), whereas the other micro/nanostructured catalysts show features of well-defined Cu₂O. At more-negative potentials in CO-saturated electrolyte, CuO_x and CuO_x/(OH)_y species are observed on all five catalysts, but the relative abundance of the former is higher for Cu foil, whereas that of the latter is higher for the micro/nanostructured catalysts. This suggests that the surface speciation at negative potentials correlates with the initial degree of oxidation at the OCP. The assumption is confirmed by recording in situ Raman spectra with a square wave potential profile switching between a positive potential (increased after each wave) and –0.4 V versus RHE. Finally, the electrochemical CO reduction experiments show different trends in product selectivity among the catalysts. The researchers conclude that oxygen-containing species are unlikely to play a major role in facilitating multi-carbon product formation.

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