MULTISCALE MODELLING

Taming cation effects

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The electrode–electrolyte interface has a major impact in the outcome of electrocatalytic reactions, in particular, the electric double layer that forms in the electrolyte at the immediate contact with the electrode surface. The activity and/or selectivity of various electrochemical reactions can be drastically influenced by simply changing the identity of the cations in the electrolyte. One reaction where these cation effects are significant is the electrochemical reduction of carbon dioxide (CO₂RR). On Cu electrodes, the current density and Faradaic efficiency to multi-carbon products of CO₂RR increase notably with the alkali metal cation size. While a number of works have focused on evaluating this effect, its precise origin remains elusive and has been attributed to various factors.

Now, Karen Chan, Stefan Ringe and colleagues, in a joint computational and experimental effort, present a multiscale

approach to model cation effects under CO₂RR conditions. The model assumes a mean-field continuum description of the electrolyte, which is a function of the hydrated cation size. The resulting surface charge density is coupled with the charge-dependent density functional theory calculation of the rate-determining step species. Overall, they show that cations with a smaller solvation shell (such as hydrated Cs⁺) increase the surface charge density because of their higher concentration at the electrode's vicinity, as compared with, for example, hydrated Li⁺.

The researchers demonstrate the accuracy of their approach by comparing it to experimental results on Ag and Cu electrodes. They obtain quantitative agreement for the enhancement factor in the partial current density of CO on Ag or C₂ (ethylene and ethanol) on Cu upon increasing the cation size from Li⁺ to Cs⁺, for epitaxial thin films exposing different facets, as well as polycrystalline Ag. Cation effects on the vibrational Stark effect of CO on Pt and Cu and on the double layer capacitance on Au are also described and are in excellent agreement with the experimental trends. The researchers conclude by arguing that some multivalent inorganic cations are predicted to exhibit higher activity than Cs⁺ on a Ag(111) electrode.

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