

Effect of the **electrode-electrolyte interface** on the activity of a heterogeneous catalyst: developing and applying new methods

Sudarshan Vijay

Department of Materials Science, University of California Berkeley

In the first seminar, we looked at the electrode surface's influence on a catalyst's CO₂ reduction (CO₂R) activity. In this second and final seminar, we will investigate how this activity is further altered by the **electrode-electrolyte interface**.

First, we discuss how interfacial water molecules alter the adsorption energy of CO on transition metal surfaces. Using *ab-initio* molecular dynamics simulations, we find that including dynamics of interfacial water causes the adsorption of CO to weaken on steps while staying roughly constant on terraces,¹ which influences IR and Raman intensities on different transition metal surfaces.² Second, we study the influence of the interfacial electric field on the reaction intermediates of CO₂R. To include these effects, we develop a computational method to determine the charge transfer coefficient of electrochemical reactions using just the atom-centred forces from a single density functional theory calculation performed at a saddle point.³

Applying all the methods we have discussed so far to CO₂R, we find that a particular group of materials, single atoms embedded in graphene, produce large surface dipole moments interacting strongly with the interfacial field. This stabilisation through the surface dipole moments of adsorbed CO₂, the first reaction intermediate of CO₂R, leads to specific chemical signatures observed within our model. One such signature is pH dependencies of current densities towards CO. Our predictions of these pH dependencies are in excellent agreement with available experiments, supporting the hypothesis that dipole-field interactions determine the reaction kinetics of CO₂R. Based on these results, we suggest a general design principle to find more active catalysts for CO₂R, by looking for materials with narrow widths of their *d*-states.⁴

I will conclude the seminar by discussing the need for data-driven methodologies to study reaction rates, especially for applications beyond electro-catalysis, such as for electrode-electrolyte interphases in Li-ion batteries.

¹Vijay, Hogg, Ehlers, Kristoffersen, Katayama, Shao-Horn, Chorkendorff, Chan, Seger. *J Phys. Chem. C* (2021)

²Chang, Vijay, Zhao, Oliveira, Chan, Xu. *Nature Comms* (2022)

³Vijay, Kastlunger, Gauthier, Patel, Chan. *J Phys. Chem. Lett.* (2022)

⁴Vijay, Ju, Brückner, Tsang, Strasser, Chan. *Nature Catal.* (2021)