Understanding the reaction environment of a CO₂ electrocatalytic system using continuum modeling

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Renewable electricity-powered electrochemical reduction of CO₂ (CO₂ER) is a promising technological solution to mitigate climate change. The reaction environment of the CO₂ER catalyst is an important handle to rationally optimize the overall performance of the system. In this study, we resolve the species concentrations and potential profiles in the electrical double layer (EDL) of a CO₂ER system by self-consistently solving the migration, diffusion and reaction phenomena using the generalized modified Poisson-Nernst-Planck (GMPNP) equations which include the effect of volume exclusion due to the solvated size of solution species. We demonstrate that the presence of the electric field and the accumulation of cations in the EDL have significant consequences for CO₂ concentration, pH and the relative permittivity of the electrolyte in the immediate vicinity of the catalyst surface. Our results highlight the significance of the EDL in understanding and designing efficient CO₂ER systems.