Electrocatalysis of CO_2 in nanoconfinement

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Understanding the fundamentals underlying electrocatalytic cells for their optimization requires multiscale modeling to explore microscopic phenomena and their implications on the experimental scale. On the microscopic scale, nanoporous materials, such as graphene slits, enhance CO_2 solubility in the electrocatalytic leading to what is often referred to as oversolubility. To quantify the oversolubility of CO_2 in confinement, we perform molecular dynamics (MD) simulations of solutions of CO_2 in water. Firstly, we identify the optimal combination of force fields for these compounds by mapping the phase diagram of pure systems and the free energy dissolution of mixtures using Grand Canonical Monte Carlo and Free Energy Perturbation methods, respectively. Later, we validate the force fields by computing the experimental solubility for CO_2 in bulk water in terms of CO_2 chemical potentials. These are used in the Wang-Landau sampling method to procure the grand canonical potential (Ω) of solutions in confinement as a function of pore-separation and solution compositions, and to determine the corresponding CO_2 concentration. We present some preliminary results on carbon dioxide oversolubility in graphene slits. On a larger scale and in close contact with the experiments, we develop a continuous model of the electrocatalytic cell under continuous operation for the production of formic acid. Employing the Poisson-Nernst-Plank system of equations, we model the reaction-advection-diffusion process taking place inside the pores, in order to determine the concentration profiles of the relevant species, for example, CO_2, formic acid, and pH. The model allows for the inclusion of the confinement effects such as confined diffusion and oversolubility.