

# Multiscale-modelling of COF-electrode systems

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Covalent organic frameworks (COFs) have emerged as a new generation of single-site heterogeneous catalysts used as molecularly precise cavities to study CO<sub>2</sub> electroreduction in confinement. A high density of pore-confined catalytic sites and local environments which can be designed with atomic precision are a toolbox to tailor products for the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR). As an electronically non-trivial material, advanced electrochemical characterization and theoretical modelling need to go hand in hand for developing a fundamental understanding of the electrochemical reactivity under confinement. Theory-guided design of geometric, electrochemical and dielectric confinement effects is expected to further the development of these novel materials.

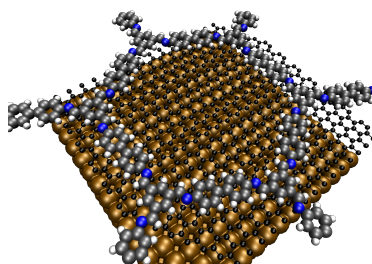


Figure 1: Atomistic model of a TFB-Bz-COF structure on a graphene-gold film. The system is inspired by successful film synthesis.

The electrostatic potential distribution and the details of the electric double layer at interfaces are of particular relevance to understand the electrocatalytic processes and require to explicitly model all molecular details and electronic details. In particular, the concentration differences, dielectric confinement effects and the potential drop in the electric double layer greatly impact the catalytic performance and selectivity and require a multiscale treatment. Also, the imperfect metallic nature of electrode materials strongly impacts the thermodynamic phase behavior and wetting [2][3]. To derive reliable concentration profiles and electric double layer properties, the electron distribution both in the supporting electrode and in the COF have to be considered at a given electrode potential, which requires ab-initio modelling of electrochemical interfaces [4]. To overcome the strong time- and length-scale limitations imposed by first-principles molecular dynamics (FPMD) we employ a two-scale strategy: we employ gaussian and plane wave density functional theory calculations that allow for accurate determination of electron and solute density profiles and also explicitly address local

dissociation effects. However, (first principle) molecular dynamics simulations at controlled electrode potential with fluctuating number of electron remains challenging. Combining first principle calculations with force field molecular simulations opens up length- and time-scales to allow the description of dynamics of confined electrode systems with high accuracy. Existing schemes [1] will be benchmarked and if necessary, novel approaches will be developed. At the same time, we are refining classical simulation approaches for imperfect electrodes - i.e. where the concept of perfect electronic screening does not hold - at applied potentials that will allow us to study solvent composition and dynamics.

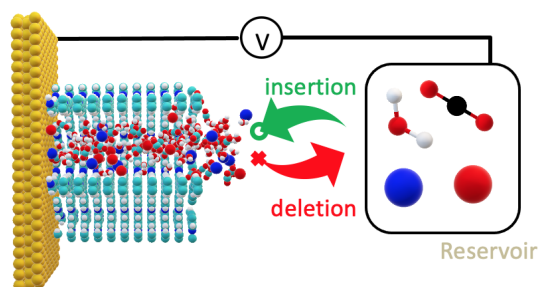


Figure 2: Schematic of a full-scale model of a COF/Electrode system at constant electron and particle potentials.

The sheer volume of scientific data sets produced in the course of a project today has brought the issue of research data management to the forefront of many organizational considerations. Strangely, the field of physical and chemical simulations, which is predestined for this, is not exactly a pioneer in the implementation of the widely accepted FAIR principles for scientific data management and stewardship. Machine learning on the other hand created lots of useful ways to deal with masses of (meta-)data out of sheer necessity. We try here to apply some of the concepts from the machine learning world to computer experiments to make them better and FAIRer.

## References

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