Multi-scale Modeling of Electrochemical Systems and Processes

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The oxygen reduction reaction (ORR) represents the fundamental reaction in various electrochemical energy conversion and storage technologies and the development of efficient catalysts for this reaction represents one of the major challenges for a sustainable society. At present, the most commonly used ORR catalysts are still platinum-based. However, rational design of improved ORR catalysts—platinum-based or metal-free—requires a detailed atomistic understanding of the reaction that is being catalyzed at the electrode surface under operating conditions. From a theoretical point of view, the electrochemical system is too complex to be handled holistically by any individual theoretical method at the atomistic scale. Therefore, several theoretical approaches at different levels of approximation have been developed to address specific questions in the simulation of electrochemical systems. In contrast to popular DFT-based schemes for this endeavor, a multiscale approach has been developed and applied to investigate the morphological changes of a platinum model catalyst at different oxidative conditions, *i.e.* under ultra-high vacuum, near-ambient pressures and typical fuel cell operating conditions. This stepwise increase in system complexity enabled direct comparison to experimental results and to confidently make predictions. A crucial outcome of this thorough theoretical investigation was the prediction of stable platinum surface oxides under typical fuel cell operating conditions—a fact that had been neglected thus far—which might lead to the development of new strategies to overcome current ORR performance limitations.

Furthermore, the multiscale approach enabled reactive molecular dynamics simulations of the ORR at platinum model catalysts at an extended time- and length-scale. These simulations revealed elementary reaction steps, significantly extending the commonly discussed associative and dissociative reaction mechanisms.

Besides Pt-electrodes we will also discuss how this approach was used to understand self-diffusion processes on transition metal electrodes, battery-relevant materials and finally the dynamics of alloy-based electrocatalysts under operation conditions, showing the importance and urgent need for *in-operando* experimental studies.

[1] Fantauzzi, D.; Mueller, J. E.; Sabo, L.; van Duin, A. C. T.; Jacob, T., *ChemPhysChem* **2015**, 16, 2797.
[2] Fantauzzi, D.; Krick Calderón, S.; Mueller, J. E.; Grabau, M.; Papp, C.; Steinrück, H.-P.; Senftle, T. P.; van Duin, A. C. T.; Jacob, T., *Angew. Chem. Int. Ed.* **2017**, 56, 2594.
[3] Fantauzzi, D.; Jung, K. C.; Sinyavskiy, A.; Jacob T. *in preparation*.