Fundamentals of the Oxygen Reduction Reaction

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Compared to surface science experiments under UHV conditions, electrochemical systems (such as fuel cells) combine a whole variety of additional effects. These range from the nanostructure of the highly disperse catalyst particles over the presence of the electrolyte and the multi-component environment to the reaction conditions of finite temperature, pressure, and electrode potential. Due to this complexity our knowledge about the ongoing processes is mostly limited to the macroscopic regime. However, nowadays theoretical methods are able to provide a deeper insight into structures and processes at the atomistic level, which together with experiments could lead to a better understanding.

Within this talk I will first present theoretical studies on the oxygen reduction reaction (ORR) occurring at Pt(111) electrodes. Starting with the gas-phase system, effects from the reactive surrounding as well as environmental parameters are successively included, finally providing a more realistic description [1]. We find that while usual density functional theory calculations, which mimic the system to be in vacuum and at T=0 K, support the ORR via formation of hydrogen-peroxide (H_2O_2-Formation pathway), considering the water surrounding leads to a preference along the O_2-Dissociation pathway [2]. In order to describe the electrochemical interfaces developing in these systems we formulated the extended *ab initio* atomistic thermodynamics method, which allows calculating (p,T,ϕ)-phase diagrams of electrode/electrolyte-interfaces from first principles [3]. It turned out that the model of a pure and perfect catalyst surface, which is often used to study this reaction, is clearly incomplete. Instead, structure and composition of the catalyst are significantly modified.

Afterwards theoretical investigations on the morphology of the electrode are discussed [4−7]. In fuel cells usually highly disperse nanoparticles are employed to catalyze the electrochemical reactions. Unfortunately not all nanoparticles have the same size and shape, but rather show a relatively large distribution, that is why experimental measurements represent the averaged behavior of (almost) the entire ensemble of particles. Motivated by UHV-experiments on adsorbate-induced surface faceting performed in the group of Ted Madey at Rutgers University, I will discuss theoretical studies on the adsorption of oxygen and nitrogen at the different surface faces, which are involved in the nanostructuring of Ir(210) and Re(11-21). These energies are then used to construct the corresponding surface phase diagrams. We find that at high temperatures the planar surfaces are stable, while lowering the temperature stabilizes those nanofacets found experimentally. Therefore, by choosing appropriate adsorbate and electrode potential conditions it is possible to manually tailor the surface morphology, which in turn provides model systems to study structural sensitivity in electrocatalytic reactions as well as potential templates to grow nanostructures electrochemically.

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