O 30: Mini-Symposium: Electrified solid-liquid interfaces I

Time: Tuesday 10:30–12:30 Location: R1

Introduction by Symposium Organizers

Invited Talk O 30.1 Tue 10:35 R1

A Theoretical Framework for Investigating Electrochemical Reactions — •Wolfgang Schmickler — Institut für Theoretische Chemie, Universität Ulm, Deutschland

Electrochemical reactions take place at the interface between an electronic and an ionic conductor. Here we consider the most important case, a metal in contact with an electrolyte solution. The challenge is to treat electrocatalytic reaction, in which either the initial of the final state of the reaction is adsorbed on the electrode surface.

Consider the deposition of a silver ion on a silver electrode as an example. In the initial state, the 4s orbital is empty and the ion has a solvation energy of -5.1 eV. To get deposited, the ion has to approach the electrode, losing a part of its solvation energy. A thermal fluctuation takes the valence orbital, which is broadened by the interaction with the electrode, to the Fermi level. The ion takes up an electron, loses the solvation energy, and gains the energy of ionization, and the sublimation energy of silver; the potential drop between the solution and the electrode surface enters into the energy required to approach the electrode. Obviously, a good theory must treat all components of the interface, metal and solution, with the same atomic detail.

For this purpose we have developed a framework based on a model Hamiltonian, which combines ideas from Marcus theory, Anderson-Newns theory, Green's function techniques with our own ideas. The detailed form of the Hamiltonian depends on the reaction under consideration. We consider a few examples, and will how to obtain the parameters from DFT and molecular dynamics.

Invited Talk O 30.2 Tue 11:10 R1

Dynamic Evolution of CO_2 Electroreduction Catalysts — •Beatriz Roldan Cuenya — Department of Interface Science, Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Tailoring the chemical reactivity of nanomaterials at the atomic level is one of the most important challenges in catalysis research. In order to achieve this elusive goal, we must first obtain a fundamental understanding of the structural and chemical properties of these complex systems. In addition, the dynamic nature of the nanostructured films and nanoparticle (NP) catalysts and their response to the environment must be taken into consideration. To address the complexity of real-world electrocatalysts, a synergistic approach taking advantage of a variety of cutting-edge experimental methods (EC-AFM, LC-TEM, XPS, XAFS, Raman Spect., GC) has been undertaken.

This talk will provide insight into the electrocatalytic reduction of CO_2 and will feature the parameters that determine the reaction's selectivity. Important aspects that will be discussed are: (i) the design of size- and shape-controlled catalytically active nanoparticles (Cu, Zn, Cu-Zn, Cu-Ag) (ii) the role of the NP size and shape on the catalytic activity and selectivity, (iii) the evolution of the structure and composition of the electrocatalysts under operando reaction conditions and their influence on the catalytic performance, (iv) the possibility of using pulsed-electrolysis to tune the reaction selectivity. These findings are expected to open up new routes for the reutilization of CO_2 through its direct conversion into valuable chemicals and fuels such as ethylene and ethanol.

O 30.3 Tue 11:45 R1

Tuning the Stability of Platinum by means of Scan Rate — •Jon Bjarke Valbaek Mygind[1], Francesc Valls Mascaro[1], Marc T.M. Koper[1], and Marcel J. Rost[2] — [1]Leiden Institute of Chemistry, Leiden University — [2]Huygens-Kamerlingh Onnes Laboratory, Leiden Institute of Physics, Leiden University

Platinum is widely used as an electrocatalyst in several applications like fuel cells and electrolysers, due to its high catalytic activity. However, platinum is scarce and its industrial feasibility is limited by its degradation under oxidizing conditions. Repeated oxidation and reduction of a platinum electrode leads to the roughening of the surface, caused by the nucleation and growth of nano-islands, which first grow laterally (2D) and then in height (3D) [1]. The nucleation and growth of these islands is promoted by the creation of adatom vacancy pairs [2,3]. Unfortunately, the precise mechanism responsible for this process is still not fully understood. Here, we examine the growth rate of the roughness on a Pt(111) surface by analysing cyclic voltammograms at different sweep rates. From our understanding of surface growth, we have indications that the mechanism responsible for the creation of adatom-vacancy pairs is kinetically (surface diffusion) limited. At faster sweep rate, less roughening is observed, which could be explained by fewer adatoms and vacancies being created on the surface, supporting our hypothesis.

[1] Jacobse L. et al., ACS Cent. Sci. 5 (12), 1920 (2019)
[2] Rost, M.J. et al., M.T.M., Nat. Commun. 10, 5233 (2019)
[3] Ruge, M. et al., J. Am. Chem. Soc., 139, 4532-4539 (2017)

O 30.4 Tue 12:00 R1

Observing the oxidation of platinum under operando electrochemical conditions — •Leon Jacobse[1], Ralf Schuster[2], Xin Deng[1], Silvan Dolling[1], Tim Weber[3], Herbert Over[3], Jörg Libuda[2], Vedran Vonk[1], and Andreas Stierle[1] — [1]DESY NanoLab, Deutsches Elektronen-Synchrotron, Hamburg — [2]Interface Research and Catalysis, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen — [3]Physikalisch-Chemisches Institut and Zentrum für Materialforschung, Justus Liebig University, Giessen

Platinum electrocatalyst degradation forms a large barrier for the widespread application of electrolysers and fuel cells, which are crucial for a sustainable energy society. A detailed understanding of the catalyst surface structure during the chemical reaction is required to design more stable catalysts. We have developed a Rotating Disk Electrode (RDE) setup that enables a structural characterization by synchrotron High-Energy Surface X-Ray Diffraction (HE-SXRD) experiments while maintaining well-defined diffusion conditions and high catalytic reaction rates (current densities). With this setup we followed the oxidation of Pt(111) and Pt(100) model electrodes; starting from the Place-Exchange surface oxidation occurring around 1.1V until the formation of a (bulk) oxide at potentials relevant for the oxygen evolution reaction. In contrast with heterogenous oxidation experiments, no ordered oxide structures are observed.

O 30.5 Tue 12:15 R1

Electrochemical interfaces: applications to batteries — •Jean-sebastien Filhol[1], Arthur Hagopian[1], and Anja Kopac-Lautar[2] — [1]Institut Charles Gerhardt Montpellier/ENSCM/CNRS/Université de Montpellier — [2]National Institute of Chemistry, Ljubljana, Slovenia

Electrochemical interfaces are fundamental to understand electrochemical reactions either for energy storage in devices such as Li-ion batteries. Nevertheless, these interfaces are extremely complex to model not only because of the occurring electrochemical effects, but also because of the complexity of the electrode-solvent interactions.

We will present an approach allowing the modeling of realistic electrochemical interfaces at a limited cost and demonstrate the predictive capabilities of these calculations. We will first discuss electrochemical effects on interface using implicit solvent approach in order to investigate how interfaces morphology is changed with the applied potential in particular to investigate dendritic growth Then, we will use a mixed implicit/explicit solvent approach (exemplified by Li/Ethylene carbonate (EC) and Mg/Dimethoxyéthane (DME) interfaces) that allows investigating electrochemical reactivity at a limited cost. We will show that the interfacial species can be very different from the ones of the electrolyte given some new insights the specific double layer rectivity. To rationalize this reactivity, specific tools within conceptual DFT framework were developed. This allows obtaining quantitative and predictive index of the interfacial electrochemical reactivity in order to improve the electrochemical devices development, in particular in link with batteries.