

Elementary Reaction Steps in Electrocatalysis: Theory meets Experiment

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Recent years have witnessed a renewed interest in electrochemical and electrocatalytic processes. They are not only interesting from a fundamental point of view, but have become increasingly important in the context of energy conversion and storage [1,2], in particular as far as fuel cell and battery technologies are concerned. Still, in spite of their importance, it is fair to say that the understanding of electrocatalytic processes at the microscopic, atomistic level requires new theoretical developments and experimental strategies.

In the related field of surface science, in which processes at the solid-vacuum interface are studied, there has been tremendous progress in the last decades [3]. This is not only due to the development of experimental probes with atomistic resolution, but currently it is also caused to a large extent by advances in theoretical surface science [4]. Consequently, theoretical studies are no longer limited to explanatory purposes but have gained predictive power.

As far as electrochemistry in general and electrocatalysis in particular are concerned, the situation is still different. In spite of the development of an electrochemical surface science [5], some of the experimental tools with microscopic resolution that can be used at the solid-vacuum interface are not available for the solid-liquid interface. Hence experiments often do not yield a detailed atomistic information but rather integrated quantities such as, e.g., the current. Secondly, the presence of ions, solvent molecules and an electric field in the electrical double-layer makes the theoretical description much more complex and challenging. Periodic DFT codes have been enormously successful in the description of surface science systems within the so-called supercell approach. However, it is not trivial to model electrochemical systems, in particular charged systems, within this computational approach. In spite of this obstacles, there is a growing *theoretical* interest in problems related

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to electrochemistry leading to significant advances as far as our microscopic understanding of elementary processes in electrocatalysis is concerned [6, 7].

Motivated by this progress, the Research Unit *Elementary reaction steps in electrocatalysis: Theory meets experiment* funded by the German Science Foundation (DFG) was initiated in 2010. The fundamental approach of the joint theoretical and experimental research effort was to apply the rigor of microscopic *surface science* studies to structures and processes relevant in electrocatalysis in the spirit of an *electrochemical surface science* [5, 8].

The first step in the understanding of electrocatalytic processes is the determination of the structure of electrode/electrolyte interfaces at which the catalytic reactions take place. Hence an important focus of the research unit was the elucidation of the atomic structure of electrochemical solid/liquid interfaces [9, 10]. Charge transfer processes are at the heart of any electrocatalytic process. Theoretical studies have been performed to address the proton discharge at electrode surfaces [11, 12] and the electron transfer in oxygen reduction [13]. In order to create electrodes with desired electrocatalytic properties, a rational approach to design of bimetallic surface alloys has been applied [14–16]. Last but not least, elementary reaction steps in C1 electrooxidation have been addressed both experimentally [17, 18] as well as theoretically [19]. This special issue contains reports about these projects performed within the Research Unit which ended in 2016. In addition, international colleagues in the field of electrocatalysis who presented invited talks at the workshops of the Research Unit also contributed to this issue. Hence it is meant to provide an overview over the current state of the art in the study of elementary reaction steps in electrocatalysis.

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