Platinum electrochemistry through a magnifying glass

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Summary and Outlook

Heterogeneous catalysis plays an important role in many industrial processes. Most of these processes use energy generated by the combustion of fossil fuels and can only be applied efficiently on a large scale. Using electrochemistry, it is possible to use electricity, preferably from a sustainable source, to directly drive chemical reactions. Additionally, as these processes run at low temperatures and pressures, they can easily be applied at various scales.

In most applications, the electrocatalysts will exhibit a large surface area to volume ratio, for example using nanoparticles. To fully understand fundamental electrochemical processes at the length scale of these nanoparticles, it is necessary to use specialized experimental techniques. In this thesis, the stability and activity of platinum electrode surfaces are studied at the nano- and micrometer scale using Electrochemical Scanning Probe Microscopy (EC-SPM) techniques.

Chapters 2 and 3 describe the roughening of an atomically flat Pt(111) electrode upon repetitive oxidation and reduction using Electrochemical Scanning Tunneling Microscopy (EC-STM). This potential cycling is similar to switching on and off an electrochemical device, during which significant electrode degradation is known to occur particularly at the positively charged electrode. Previous studies already showed that the roughening process leads to the formation of nanoislands on the electrode surface. However, it remained unclear how these nanoparticles nucleate and evolve during prolonged potential cycling. Also, the data available from literature was unable to explain the relationship between the changing surface structure and its electrochemical features.

In our EC-STM experiments, the overall electrochemical reactivity was measured while monitoring the evolution of the surface structure of a single (111) terrace. In Chapter 2, the total charge related to electrochemical hydrogen adsorption was correlated to the roughness of the imaged terrace. With this analysis, we demonstrated that the roughening process can be separated into two different regimes. Initially, we mainly observed the nucleation and slight lateral growth of nanoislands ('nucleation and early growth' regime). Once we could no longer distinguish the unaffected terrace between the nanoislands, the existing islands continued to grow mainly in height ('late growth' regime). In the 'late growth' regime, each newly formed surface site contributes equally to both the surface roughness and the integrated hydrogen adsorption signal, as we found a strong correlation between these two signals.

However, the overall correlation between electrochemical reactivity and surface structure, could not yet explain the complex evolution of the different hydrogen adsorption features, especially in the beginning of the roughening process. As this signal is known to be sensitive to the (local) surface structure, one would expect to be able to disentangle the different contributions. This is the topic of Chapter 3, where we show that we can extract the average atomic island structures from the EC-STM images. In these island structures, we determined the densities of various surface site geometries and correlated these to the charge belonging to the different hydrogen adsorption features. This analysis provided us with the electrochemical fingerprint of 'defect'-, facet-, and vacancy-sites which form during the roughening process. Thus, we could pinpoint the individual peaks in the electrochemical hydrogen adsorption signal to the presence of specific surface sites. Furthermore, it also gave an insight into the stability of such sites under potential cycling conditions.

Chapter 4 zooms out a bit from the atomic level to the micrometer scale. This chapter focuses on the relationship between the grain orientation of a polycrystalline platinum electrode and its local electrochemical reactivity towards hydrazine oxidation. To study this very active catalytic system, we employed a new mode of Scanning Electrochemical Scanning Cell Microscopy (SECCM). In this mode, voltammetric SECCM, it is possible to perform a full electrochemical experiment at every position at the surface. This enabled us to visualize differences in electrochemical reactivity that would remain unnoticed in traditional, fixed-potential, electrochemical imaging.

One of the strengths of (voltammetric) SECCM is that it is easily combined with other (*ex situ*) experimental techniques or SECCM experiments. Using Electron Backscatter Diffraction, we found that the differences in electrochemical reactivity are correlated to the orientation of the grains in the sample. Furthermore, we performed the same experiment, at the same part of the sample, without a protective gas atmosphere. These experiments showed that the presence of oxygen dramatically decreases the reactivity, again in a grain-dependent manner.

With increasingly specialized experimental techniques, there is also an increased risk of introducing contaminations that strongly affect the measurement. For example, the EC-STM results presented in Chapters 2 and 3 would not have had the same value if the electrochemical signal would not have shown the features of a clean system. Unfortunately, many studies do not present their results in such a complete way. Instead, spatially resolved data is often presented in combination with electrochemical data measured in a different experiment, using a different cell, and sometimes even using a different sample.

Similar issues play a role in many studies using ultramicroelectrodes (UMEs), as is described in Chapter 5. UMEs are very useful to overcome diffusion limitations and electrolyte resistances, e.g. in case of a highly active catalytic system and/or a weakly conducting electrolyte. However, Pt UMEs cannot be cleaned in the same way as large electrodes (by flame-annealing), which might result in a contaminated electrode surface. Moreover, they are typically characterized by measuring their reactivity using reactions that are insensitive to the surface structure or even its composition. In Chapter 5 we have shown that it is not at all trivial to obtain a sufficiently clean UME. All the commonly used cleaning methods led to blank voltammograms that are inferior to those measured on flame-annealed electrodes. As a result, UMEs showed a decreased reactivity towards surface sensitive reactions. Nonetheless, results obtained with the commonly used characterization methods were not affected at all.

Outlook

The work in this thesis resolves several phenomena that would not be visible relying on only standard electrochemical techniques. These results are of particular interest for the communities studying fundamental platinum electrochemistry, improved fuel cell and electrolyser catalysts, and electrochemical sensors.

However, beyond the direct results presented here, it is worthwhile to also have a look at the future possibilities using these EC-SPM techniques. Although the EC-STM results were already extensively analyzed in Chapters 2 and 3, there is still much to learn from these data. Considering the roughening of the (111) terrace, it is interesting to analyze the nucleation site locations and the overall mass transport. Such analyses give insight in how and how much the electrode surface is restructured during each potential cycle.[1] It is expected that these phenomena are strongly influenced by the structure of the oxidized surface, which for now, still remains unresolved. In our experiments, we have not only captured the roughening of the atomically flat terrace, but also that of the step edges. As a ‘real’ electrocatalyst will contain many of such sites, it would be very interesting to have a more in-depth look at the nanoislands that form at the step edges. Thus, these topics are indeed the focus of current data analyses.

In a broader perspective, there is a wide variety of possible studies to perform using EC-STM. Obviously, it would be interesting to follow the surface structure while studying catalytic conversions, instead of the surface reactions studied here. Another approach would be to analyze the tip current in more detail. Although one always makes an effort to minimize the faradaic contribution to this signal, there is always a small contribution left. However, the origin of this signal is not fully understood, especially under tunneling conditions. In any case, the interaction (in terms of both current and potential) between the tip and the sample when their double layers are (almost) overlapping deserves more attention. Such studies should be able to provide insight in the possibilities to perform spatially resolved electrochemical experiments while also imaging the surface structure. The first steps in this direction are already available in the literature[2] and are also a topic in our own ongoing studies.

Some insights on possibilities to extract more data from the voltammetric SECCM experiments were provided in Appendix E. There, it was described that the correlation between surface topography and activity can be quantified much better by a more sophisticated analysis of the different types of available data. The (future) challenges for SECCM, and for electrochemical imaging in general, are both the resolution (both spatial and current) and imaging speed. The development of specialized probes and imaging modes have led to significant progress in recent years.[3,4] As an example, recent results report the activity of a single MoS_2 edge plain towards hydrogen evolution.[5] Furthermore, using fast-scanning protocols, electrochemical reactivity can be visualized during a potential sweep with a total imaging time approaching 4 s per frame.[6]

Finally, considering that EC-STM is most powerful for smooth, homogeneous samples and SECCM can handle rough, heterogeneous samples, these approaches complement one another. It is therefore interesting to observe that both sides are making significant progress in studying structure-activity relationships at the nanoscale. Combining the expertise on fast, high-resolution topographical imaging and handling sensitive electrochemical systems is most definitely going to help both communities push forward.

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