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Platinum surface instabilities and their impact in electrochemistry

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Summary

The transition from fossil fuels to renewable energy sources necessitates efficient methods to store the energy generated in order to ensure its availability during periods of high demand and low production. The most effective way to do this is by converting the renewable electricity into chemical energy, which can be achieved by using electrochemical devices such as batteries, electrolyzers, and fuel cells. Optimal electrocatalytic materials are key for the development of these technologies, as they enhance the efficiency of the conversion process by minimizing energy losses. However, the best catalysts known to be used in fuel cells are platinum-based, and thus scarce and expensive. Moreover, platinum catalysts degrade upon prolonged usage, which leads to a decrease of their activity and the need to replace the fuel cell. Therefore, it is crucial in electrochemistry to identify those material compositions and geometries that not only satisfy the catalytic requirements, but are also stable for prolonged device longevity. In this thesis, we used an Electrochemical Scanning Tunneling Microscope (EC-STM) to study the (in)stability of platinum electrode surfaces as well as to establish structure-activity relationships at the atomic scale.

In Chapter 2 we used Density Functional Theory (DFT) and EC-STM to expand the previous knowledge on the nucleation and growth of adatom islands on Pt(111) upon oxidation-reduction cycling, a process that mimics the real operation of hydrogen fuel cells and that is linked to the catalyst degradation. Our results showed that the surface oxidation results in the formation of PtO₂-adatoms. However, their actual concentration on the surface is far from reaching their equilibrium concentration, and therefore nucleation into adatom islands is not favored. In addition, we show that at high electrode potentials the mobility of PtO₂-adatoms is severely restricted, not only because their diffusion is inherently slow, but also because these species are trapped in between the oxide rows lifted above the surface. During the cathodic (reverse) scan, the reduction of the surface oxide is followed by the reduction of the PtO₂-adatoms into Pt-adatoms. The latter not only diffuse faster, and thereby can rapidly find each other and nucleate into islands, but also have a much lower equilibrium concentration. As then the actual Pt-adatom concentration is much higher than their equilibrium concentration, the formation of adatom islands is favored.

Moreover, we show with EC-STM that these adatom islands are dendritic, and not hexagonal, as suggested in an earlier publication [1]. The origin of the dendritic shape resides in a growth instability that is caused by the Kink Ehrlich-Schwoebel Barrier, which hinders

the diffusion of step-adatoms around kink sites that are present at island edges. As dendritic islands are less compact than hexagonal islands, they also exhibit a larger ratio of step sites to terrace sites. This has consequences for the catalyst reactivity as well as for its degradation.

In Chapter 3 we study the (in)stability of flame-annealed Pt(111)-vicinal surfaces, which are widely used in fundamental electrochemistry to investigate the reactivity at platinum step sites. Our statistical analysis on the step height and the terrace width concluded that, while Pt(554) presents a regular array of single steps that are separated by the nominal terrace width, around 51% and 14% of the steps on Pt(553), a surface with higher step density, are bunched into pairs and triplets, respectively. Moreover we show, based on surface science formalism, that the step bunching instability has its origin on the highly-repulsive interaction between closely-spaced steps, which can be lowered by forming step bunches with larger separation. This occurs during the flame-annealing and cooling down of the surface, when the sample is hot and thus the surface mobility is enhanced.

We end this chapter by showing how Pt(111)-vicinal surfaces with bunched steps present an extra peak in the Hydrogen desorption fingerprint, as well as an anomalous, non-linear trend of their potential of zero total charge (E_{pztc}) and Oxygen Reduction Reaction (ORR) activity with their step density. However, we assert that step bunching also has a significant effect on other structure-sensitive electrochemical reactions that are most active at step sites, such as the Hydrogen Oxidation Reaction, the CO Oxidation, and the Nitrate Reduction. Consequently, our findings hold significant implications on the current understanding of platinum electrochemistry at step sites.

With our new insights on the step structure of Pt(111)-vicinal surfaces, in Chapter 4 we move on to quantify the adsorption of hydrogen and oxygen at step sites. Our results show that the voltammetric peak associated to hydrogen desorption from the steps involves more than one electron per unit step length, and thus more than the simple desorption of one hydrogen atom per step site. This could point out towards an exchange mechanism between hydrogen and hydroxide, as stated in recent literature [2, 3]. On the other hand, at high potentials the adsorption of oxygen leads to the formation of PtO_2 along the steps. Additionally, we identify the oxygen adsorption sites at the step edge and we relate them to the corresponding peaks in the Cyclic Voltammogram (CV). Finally, we link this chapter to the previous one by quantitatively demonstrating that step bunching results in a decrease of the hydrogen and oxygen adsorption.

References

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