Water on well-defined platinum surfaces : an ultra high vacuum and electrochemical study

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Summary

The world is in need of more sustainable energy sources and devices. Methanol, ethanol, or hydrogen fuel cells are promising candidates for efficient energy convertors that can operate on renewable energy sources. In these fuel cells, platinum is often the catalyst material of choice for both cathode and anode. Therefore, the reactivity and dissociation of water at the platinum–aqueous electrolyte interface, in particular the effect of platinum surface structure, is of immense importance to electrocatalysis. In direct alcohol fuel cells water will have to dissociate in order for its oxygen atom to react with the carbon atoms, forming CO_2. The question is whether it dissociates into OH fragments or oxygen atoms before it reacts. In this thesis we have modeled the platinum fuel cell electrode under both electrochemical and ultra high vacuum (UHV) conditions to answer this question. Step and defect sites are thought to be most active in reactions involving bond breaking and making. Therefore, we have studied the influence of these sites in particular. To this end we have used stepped single crystal surfaces with (100) or (110) steps as a model for the catalyst. All UHV experiments have been described in chapters 3–9. The techniques used in these chapters are temperature programmed desorption, reflective absorption infrared spectroscopy, and low energy electron diffraction.

In chapter 3 we had a separate look at the interaction of H (D), O, and H_2O with platinum surfaces. We have shown that desorption is influenced significantly by the presence of step sites and the geometry of those sites. In general, molecules and atoms are thought to be bound more strongly to step sites than to terrace sites. Our D_2 desorption data from Pt(553) provide an anomalous counterexample to this common belief, since D atoms on this surface appear to be bound stronger by terrace sites. We also show that if an adsorbate binds stronger to step than to terrace sites, it is not possible to say *a priori* which step geometry will have a more pronounced effect. Recombinatively desorbing O atoms bind stronger to (100) than to (110) step sites, but H_2O molecules bind more strongly to the latter step site. Furthermore, the amount of ad-atoms or molecules that are affected by the presence of steps varies for the different species, as is evident from the various step : terrace ratios of $\sim 1 : 1.3$ for O_2 (O), $\sim 1 : 3$ for D_2 (D), and $\sim 1 : 1$ for H_2O. This indicates that, in contrast to deuterium, more oxygen atoms and water molecules are affected by the presence of steps than would be expected on geometrical arguments alone.

Under UHV conditions OH groups can be formed on Pt(111) by pre-covering the surface with O adatoms and let them react with water, causing water to dissociate. The formed OH-groups are incorporated in a hydrogen bonded network of OH/H_2O at the surface.[14,15] A similar tactic could lead to the formation of OH at step sites at stepped platinum surfaces. This hypothesis has been tested in chapters 4–6 for both (100) and (110) steps. We have shown that on stepped platinum surfaces OH_{ad} might not be as readily formed as one would assume based on the energetics of OH adsorption alone, which would suggest an OH affinity series of Pt(533) > Pt(553) > Pt(111). In fact we find that the amount of OH_{ad} formed follows the reverse trend. We attribute this to the fact that, although step-bonded OH by itself has a higher stability, on Pt(111) OH_{ad} can actually be incorporated in a three dimensional OH/H_2O hydrogen bonded network. This favors $OH_{terrace}$ formation over OH_{step} formation, leaving unreacted oxygen adatoms at step sites. For the electrochemical situation, this could imply that O is a more likely species to form at steps than OH. This may make atomic oxygen a more likely candidate for the step-bonded oxygen donor than OH.

Another interesting co-adsorbant from an electrochemical point of view is hydrogen. Both in the hydrogen fuel cell as well as in the often used reversible hydrogen electrode, water and hydrogen are simultaneously present at the catalyst. The co-adsorption of H_2O and D has been discussed in chapters 7–9. Even though the Pt(533) and Pt(553) surfaces have similar geometries, the hydrophobicity on the deuterated surface is surprisingly different: on D/Pt(533) the surface is hydrophobic with water clustering at steps, whereas the entire surface is wet on D/Pt(553). The destabilizing effect of D_{ad} increases with increasing deuterium pre-coverage: for both surfaces H_2O binds less strongly when more D_{ad} is present. This is in contrast to what is observed on Pt(111),[90] where the presence of D_{ad} has a stabilizing effect on adsorbed H_2O. Consequently, the reactivity of the two surfaces towards hydrogen exchange between D_{ad} and H_2O is completely different: it is much higher for the D/Pt(553) surface, where more water is in direct contact with the surface. Moreover, we observe that the presence of bare platinum patches, *i.e.* metal that is not pre-covered with D_{ad}, is beneficial to the exchange reaction.

In chapters 10 and 11 we have studied the platinum–water interface under electrochemical conditions. We have shown in chapter 10 using impedance spectroscopy that, in spite of the similar looking cyclic voltammograms, the kinetics of underpotential deposited hydrogen are significantly different in acidic and alkaline media. In alkaline media the ad- and desorption process is slow, whereas it is very fast in acidic media.

In chapter 11 we have pointed out three discrepancies in the current interpretation of the blank cyclic voltammetry of stepped platinum surfaces. First, for H adsorption both H-ter and H-step contributions are identified, whereas for OH adsorption only OH-ter has been identified. Second, different shapes (broad vs. sharp) of the H-ter and H-step peaks imply different lateral interactions between hydrogen adatoms at terraces and steps, *i.e.* repulsive vs. attractive interactions. Third, the H-step peak has a non-trivial pH-dependence of 50 mV_{NHE} per pH unit. These discrepancies can be explained by a model that assumes that the H-step peak is not due to just ad- and desorption of hydrogen, but to the replacement of H with O and/or OH. The O : OH ratio varies with step geometry, step density and medium. In alkaline media relatively more OH is adsorbed than in acidic media where more O is adsorbed.