Adsorption and catalysis on Pt and Pd monolayer-modified Pt single crystal electrodes

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Summary and Outlook

Summary

Electrochemistry is concerned with using electricity to directly drive chemical reactions, and generating electricity by having a chemical reaction occur. These reactions involve several elementary electrochemical steps and electrocatalysts which can reduce the overall activation barrier height of these reactions are required. In most applications, the electrocatalysts exhibit a large surface area to volume ratio, especially using nanoparticles. To fully understand the fundamental electrocatalytic processes at the length scale of these nanoparticles, it is necessary to use high symmetry facets of the catalytic metal as model systems. The well-defined nature of these facets helps significantly in the elucidation of the chemical processes happening on the surface. In addition, theoretical approaches based on density functional theory (DFT), help in deducing a detailed microscopic understanding.

The focus throughout this thesis has been on gathering fundamental information on the effect of the detailed structure and composition of the electrode/electrolyte interface on the rate and mechanism of electrocatalytic reactions. The thesis can be divided in two parts. The first part (Chapter 2 and 3) is about the studies of the non-Nernstian dependence on pH of the step-related voltammetric peak on the platinum surface. The research described in the second part (Chapter 4-6) shifts to well-defined palladium surfaces. Chapter 4 describes the study of anion adsorption on a Pd monolayer deposited Pt(111) surface. Chapter 5 deals with the mechanism of electrocatalytic oxidation of formic acid and reduction of carbon dioxide on this Pd monolayer deposited Pt(111) surface. In Chapter 6, we continue to explore the effects of electrolyte composition and catalyst surface structure on formic acid oxidation reaction, which offer valuable insights in the design of effective anode catalysts for the direct formic acid fuel cells.

Hydrogen oxidation and evolution reactions (HOR/HER) are of paramount importance in hydrogen proton exchange membrane fuel cells (PEMFC). However, the rate of the electrochemical HOR/HER is significantly slower in an alkaline electrolyte than acid electrolyte on many transition metal electrodes, and is 2-3 orders of magnitude slower on the most active catalyst for this reaction, Pt. The effect of pH on the rate of this reaction on platinum has been correlated with the effect of pH on the location of sharp, low-potential features in cyclic voltammograms measured on platinum electrodes.

These sharp features were previously believed to be solely due to hydrogen adsorption on step sites, but they exhibit an anomalous non-Nernstian dependence on pH.

The thesis starts in Chapter 2 with a joint cyclic voltammetry and computational study of the non-Nernstian dependence on pH of the step-related voltammetric peak of Pt(553) single crystal surfaces. We study the effect of alkali metal cations (Li^+, Na^+, K^+, and Cs^+) on the anomalous behavior of the 110-step related voltammetric peak over a wide pH window (1 to 13). The apparent pH effect actually is an effect of the presence of alkali metal cation co-adsorbed along the 110-step sites, weakening the hydroxyl adsorption. As the electrolyte pH increases, the hydrogen and hydroxyl adsorption shift to lower absolute potentials into the region where alkali metal cation specific adsorption along the 110-step sites becomes favorable. The 110-step related peak exhibits the non-Nernstian shift, illustrating an apparent pH effect as well as an effect of alkali metal cation identity and concentration. As the electrolyte pH further increases, the 110-step related voltammetric peak shifts further into the region where alkali metal cation specific adsorption becomes more favorable, leading to an increased coverage of alkali metal cation adsorbed along the 110-step sites. This causes a greater weakening of hydroxyl adsorption, yielding a greater shift in the 110-step related voltammetric peak. The results presented in chapter 2 provided the clearest evidence to date that the cation-hydroxyl co-adsorption at the 110-step sites is responsible for the apparent pH dependence of the sharp 'hydrogen peak' of Pt(553) electrode.

To demonstrate the generality of this conclusion, in Chapter 3 we examine the applicability of this model by reporting and discussing the influence of two relevant parameters on the non-Nernstian pH dependence of the step-related peak, namely the effect of step density and step orientation. Accordingly, we report a combined experimental and computational study on Pt(554) and Pt(533) electrodes in Chapter 3. The Pt(554) is a surface consisting of 10-atom wide terraces of (111) orientation and steps of (110) orientation, whereas the Pt(533) surface consists of four-atom wide terraces of (111) orientation and steps of (100) orientation, allowing us to examine the effects of step density and step orientation, resp. Consistent with the results in Chapter 2, we find that this sharp peak corresponds to competitive hydrogen and hydroxyl adsorption onto both types of step sites. Further, we show that this step-associated peak exhibits an apparent anomalous pH dependence, whereas the (111) terrace associated peak does not. These adsorbed cations retain most of their charge and disrupt hydrogen bonding between co-adsorbed hydroxyl and water along the step. This weakens hydroxyl and water adsorption and shifts the step-associated peak to more positive potentials. The effects of pH, cation concentration, and cation identity on voltammograms measured on Pt(554) and Pt(533) match that seen in Chapter 2 with Pt(553) (110-type steps with a four-atom wide terrace), suggesting that the effect is independent of step density and orientation.

In Chapter 4, we first give a detailed study of anion adsorption on a well-defined Pd monolayer-modified Pt(111) surface. Specific adsorption of anions is an extremely important aspect for its influence on reaction kinetics in either a promoted or inhibited fashion. The perchlorate anion has been considered as an ideal anion for investigating reactions due to its lack of specific adsorption on several metal electrodes. We find a strong preference for anion adsorption on the $Pd_{ML}Pt(111)$ surface at low potential window, both for hydroxyl and for perchlorate anion in perchloric acid. The results of the experimental study are confirmed by a theoretical study, in which we find the exchange between *H/ *OH + *H$_2$O and *ClO$_4$ in the low window potential. These results improve our fundamental understanding of anion, cation and OH adsorption on well-defined single crystal palladium surfaces, which will be important for interpreting and tuning the catalytic activity of palladium-based electrochemical interfaces.

After fundamental adsorption studies of the well-defined $Pd_{ML}Pt(111)$ surface were outlined in Chapter 4, we focus on a mechanistic study of formic acid oxidation on $Pd_{ML}Pt(111)$ in Chapter 5. The role of the formate intermediate on $Pd_{ML}Pt(111)$ and Pt(111) surfaces for formic acid oxidation has been studied by means of (high-scan-rate) cyclic voltammetry. Our results in Chapter 5 show that the $Pd_{ML}Pt(111)$ electrode has a four times higher activity towards formic acid oxidation than Pt(111), with a lower onset potential of 0.20 V_{RHE}, compared to 0.40 V_{RHE} on Pt(111), and is free of CO poison formation. A higher coverage of 1/3 ML of formate anion adsorption on $Pd_{ML}Pt(111)$ electrode compared to that of 1/4 ML for Pt(111) has been identified by fast voltammetry. We suggest that the high formate coverage on $Pd_{ML}Pt(111)$ blocks the ensemble site needed for the dehydration reaction of formic acid to adsorbed CO. We also show that carbon dioxide can be reduced to formic acid on the $Pd_{ML}Pt(111)$ electrode from a low potential of -0.29 V_{RHE} but becomes passivated by CO production when applying more negative overpotentials.

In Chapter 6, we study the electrocatalytic formic acid oxidation process on an epitaxially grown Pd monolayer on a Pt(100) single crystal in perchloric acid. The formic acid oxidation activity on this $Pd_{ML}Pt(100)$ electrode in perchloric acid is significantly enhanced compared to the same electrode in sulfuric acid and compared to unmodified Pt(100), with a low onset potential of around 0.14 V_{RHE}. The absence of hysteresis between the positive and negative scan during formic acid oxidation indicates the remarkable resistance to CO poisoning of the Pd monolayer surface. Most importantly, we report, for the first time, a mass-transport-limited formic acid oxidation rate on the $Pd_{ML}Pt(100)$ rotating electrode in perchloric acid, setting a catalytic benchmark for future electrocatalysts for formic acid oxidation.

Outlook

Electrochemical reduction of carbon dioxide to liquid fuels and commodity chemicals has a promising potential with respect to the decarbonization of the current energy system. The two electron transfer products, CO and formic acid, can be produced with low overpotential and high selectivity on $Pd_{ML}Pt(111)$ electrode. An important aim for the future remains the understanding of the selectivity of products on $Pd_{ML}Pt(111)$ electrode, since the activity and selectivity are very sensitive to electrolyte properties such as pH, cations, anions and mass transport conditions. It has also been suggested from recent work that either the α- or β-phases of a palladium-hydride facilitates formate production from CO_2 reduction on palladium based catalysts[1,2]. Hydrogen absorption/diffusion in metals is related to the crystal structure of the material and the possibility of trapping hydrogen atoms. The electrochemistry of well-defined Pd surfaces is not as well studied as for Pt surfaces, which arises partially from the difficulty to prepare Pd single crystals as well as from the effect that palladium absorbs substantial amounts of hydrogen below 0.2 V_{RHE}, masking other reactions taking place on its surface. Inductive heating in an argon atmosphere has proven to be a promising protocol to prepare high-quality Pd single crystal electrodes. Therefore, future research should be directed toward the fundamental understanding of palladium single crystal electrodes to eventually develop highly active and selective palladium electrocatalysts.

References

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