

Summary

Electrochemistry is concerned with using electricity to directly drive chemical reaction, and generating electricity by having a chemical reaction occur. These reactions involve several elementary electrochemical steps and the electrocatalysts which can reduce the overall activation barrier height of these reactions are required. In most applications, the electrocatalysts are required to 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 and gives rise to theoretical approaches, i.e. density functional theory (DFT), deduce a detailed microscopic understanding.

The focus throughout this thesis will be on gathering fundamental studies of the detailed structure and composition of the electrode/electrolyte interface effect 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 platinum surface. The research described in the second part (Chapter 4-6) shifts to well-defined palladium surfaces. Chapter 4 starts 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 catalysts surface structure on formic acid oxidation reaction, which offer valuable insights to design is 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 (H-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, and 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 alkaline metal cation co-adsorbed along the 110-step sites, weakening the hydroxyl adsorption. As the electrolyte pH increased, the hydrogen and hydroxyl adsorption shift to lower absolute potentials into the region where alkaline metal cation specific adsorption along the 110-step sites starts favorable. The 110-step related peak exhibits the non-Nernstian shift, illustrating an apparent pH effect as well as an effect of alkaline metal cation identity and concentration. As the electrolyte pH further increased, the 110-step related voltammetric peak shifts further into the region where alkaline metal cation specific adsorption becomes more favorable, leading to an increased coverage of alkaline 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, here 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 our prior work 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 work of 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.

Renewable electricity stored in chemical bonds of formic acid is acknowledged to play an important role since the current energy infrastructure is optimized as liquid fuels, which is easier to handle and to store compared to gaseous fuels. It is widely believed that palladium-based materials show only the presence of the dehydrogenation pathway (free of CO poisoning) of formic acid oxidation which results CO₂ as the product. In this respect, an additional advantage for direct formic acid fuel cell is the reproduction of commodity chemicals/liquid products from CO₂ to decarbonize the energy system.

Palladium-based materials show higher activity and free of CO poisoning towards formic acid oxidation and also emerged as the best catalysts for the reverse reaction, i.e. carbon dioxide electroreduction towards formic acid. The mechanistic studies for these reactions are rarely reported due to the difficulty to prepare well-defined Pd surfaces. The remaining chapters are related to well-defined Pd surfaces, which open a way to precisely elucidate the reason for ‘Why palladium does not poison during formic acid oxidation’, and the products distribution during CO₂ reduction.

In Chapter 4, we first give a detailed study of anions adsorption on a well-defined Pd monolayer deposited Pt(111) surface. Specific adsorption of anion is an extremely important aspect for its influence on reaction kinetics in either a promoted or inhibited fashion. Perchlorate anion has been considered as ideal electrolyte for investigating reactions due to its minimum to non-specific adsorption on several metal electrodes. However, we find a very strong preference for anion adsorption on Pd_{ML}Pt(111) surface at low potential window, both for hydroxyl, as well as for perchlorate anion in perchloric acid. The results of the experimental study are confirmed by theoretical study, in which we find the exchange between *H/*OH+*H₂O and *ClO₄ in the low potential peak. 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 studies of the well-defined Pd_{ML}Pt(111) surface have been outlined in Chapter 4, the work can stimulate more interesting applications, thereby driving the first work on mechanism study of formic acid oxidation on Pd_{ML}Pt(111) in Chapter 5. We try to elucidate the still unexplained ‘Why palladium does not poison during formic acid oxidation’. We use Pd_{ML}Pt(111) and Pt(111) single crystal electrode simplify the experimental response controlling the surface structure of the electrode and allows unveiling an unprecedented relationship between surface structure, adsorbed intermediates, and reactivity during formic acid oxidation. Previous

studied showed that the dehydration path requires the presence of platinum atom ensembles, continuous neighbouring atomic sites, whereas the dehydrogenation path does not. This was further confirmed by the study of the breach of platinum ensembles using bulk platinum with adatoms on the surface to inhibit CO poisoning effect on Pt. In Chapter 5, a higher coverage of 1/3 ML of formate anion adsorption on Pd_{ML}Pt(111) electrode compared to that Pt(111) of 1/4 ML during formic acid oxidation has been elucidated by means of fast-scan cyclic voltammetry. We conclude the superior formic acid oxidation performance can be ascribed to the higher coverage of formate anion on Pd_{ML}Pt(111) electrode, which breach the continuous neighbouring atomic sites for the dehydration path. On the other hand, CO₂ can be reduced to formic acid on Pd_{ML}Pt(111) surface at considerably low overpotential of -0.29 V_{RHE} although passivated by the CO production when applying more overpotentials. The insights obtained here, can be used to explore bifunctional electrocatalysts for both the CO₂ reduction and formic acid oxidation.

In Chapter 6, we continue with the study of electrocatalytic formic acid oxidation process on an epitaxially grown Pd monolayer on a Pt(100) single crystal. Herein, together with Chapter 5, we investigate the influence of the nature of surface structure of electrocatalyst and extrinsic factors, especially the ionic species in solution, during formic acid oxidation. The Pd_{ML}Pt(100) electrode is found to be the most active, reach a mass-transport-limited process, towards formic acid oxidation in perchloric acid. The excellent catalytic properties shed light on the successful catalyst preparation for direct formic acid fuel cells.