Operando Spectro-electrochemical investigations of Pt and Pt-alloys as fuel cell catalysts

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D Summary & Outlook

Summary:

Operando Spectro-electrochemical investigations of Pt and Pt-alloys as Fuel Cell Catalysts

Platinum and platinum alloys are considered the current state-of-the-art catalysts in fuel cells. However, although these materials have enabled the commercial use of fuel cells, they are still the limiting factor in the efficiency and lifetime of the fuel cell. Understanding the molecular mechanisms that lead to these limitations is essential to ensure optimal catalytic activity in the long term. In line with this, the oxygen reduction reaction at the fuel cell cathode, where the main degradation and efficiency losses occur, has been the focus of intensive research in the past decades. The developments in the past 20 years show that despite the considerable number of H2 fuel cell vehicles on the road, there is still much room for improvement in catalyst design.

During the course of this thesis, we have focused on probing the electrode-electrolyte interface under fuel cell operation conditions to develop a better understanding of the structure-activity-degradation dynamics at the atomic scale. To enable this, we commissioned a modular NAP-XPS system in our own lab as discussed in *Chapter 2*, facilitating *operando* electrochemical studies on nano-structured electrocatalysts in any aqueous electrolyte, including those with dissolved gases. In the context of fuel cell studies, this enables operando studies on the electrode-electrolyte interface structure in oxygen-saturated electrolytes, deconvoluting the behaviors of the electrode, adsorbates, oxides and the electrolyte species during electrocatalysis.

In *Chapter 3*, we develop a deeper understanding of the Pt nanoparticle degradation during fuel cell start-up conditions, where rapid Pt catalyst degradation occurs during transient oxidation and reduction of the electrode surface. In our studies on Pt oxidation behavior under simulated start-up conditions, we show that a mixture of the $Pt^{\delta+}$, Pt^{2+} and Pt^{4+} oxidation states are present on the catalyst from the onset of the oxidation. This structure is formed and equilibrated in a matter of seconds, i.e. within the time-scale of transient oxidation during fuel cell start-up. We also show that the oxides formed during initial transient startup/shutdown stages of the fuel cell may not fully reduce at operation conditions, which likely has negative impact on the catalytic activity.

In *Chapter 4*, we shift focus to Pt_3Ni catalysts, which are used in modern fuel cells due to their higher activity and stability compared to pure Pt. It has been shown in the literature that Pt-Ni alloys form a multi-atom thick Pt skin under electrochemical conditions. Here, we investigated dynamics of the subsurface Ni beneath this Pt skin as a function of applied potential, and its role in the catalytic properties of the alloy. We show that the Ni in the particle core is highly mobile, moving closer to the surface at high potential and further from the surface at low potential. This affects their electron transfer properties to the catalytic intermediates on the catalyst surface, leading to potential-dependent catalytic properties.

The conclusions made in this thesis shed light on the dynamically changing electrocatalyst structure under fuel cell operating conditions. We have shown that the surface chemistry of Pt and Pt alloys is rich, with a variety of involved oxidation states and subtle structural rearrangements. These structural changes have profound effects on the activity and long-term stability of the catalyst. Thus, our work provides a stepping stone towards understanding the atomic-level mechanisms that govern activity and stability in Pt and Pt alloy catalysts, paving the way towards better catalyst design and efficient fuel cells.