Temperature Dependent Surface Electrochemistry on Noble Metal Single Crystals in Alkaline Electrolyte

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Despite many studies on the surface processes and electrochemistry on noble metal single crystal electrodes, *viz*., Pt(hkl), Au(hkl), Ag(hkl) in acid electrolyte, relatively little is known about the electrochemical and electrocatalytical properties of these electrode materials in alkaline electrolyte. Therefore, we decided to study the surface processes during fuel cell relevant reactions, *e.g.*, oxygen reduction, hydrogen oxidation, CO oxidation, on Pt, Au, and Ag single crystal electrodes, respectively. In order to gain further insight into the individual properties of the electrode materials, our measurements are carried out in a temperature range between 275 K and 333 K. By using a combination of the rotating ring-disk electrode technique and in-situ surface x-ray scattering we try to create a link between the microscopic level of understanding of surface processes and the macroscopic measurement of the kinetic rates of the aforementioned electrochemical reactions.

In order to get insight the basic surface processes on Pt(hkl), *i.e*., hydrogen underpotential deposition and OH_{ad} formation, we titrated the surfaces by CO oxidation as described recently for Pt(111) [Mar99a], which clearly shows the onset of OH_{ad} formation on the surfaces. Surprisingly, we found significant CO oxidation currents close to the reversible H_2/H^+ potential, which suggests that OH_{ad} is formed already deep in the hydrogen upd region on all Pt(hkl) surfaces. As will be shown in detail in the contribution, the consequence of this finding is that the adsorption isotherms for hydrogen upd and OH_{ad} can only be determined semi-quantitatively from the charge in the cyclic voltamogramms. It will be demonstrated that hydrogen oxidation measurements on Pt(hkl) can be used to determine the availability of free Pt sites, especially at more positive potentials, *i.e.*, in the region of interest for the oxygen reduction reaction. With the knowledge of both the results obtained from CO and hydrogen oxidation, respectively, we developed a kinetic model which describes the oxygen reduction reaction kinetics on Pt(hkl) in alkaline electrolyte at different temperatures. Finally, this model is used to explain the kinetics for the oxygen reduction reaction on other noble metals like Au(hkl) and Ag(hkl).

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References
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