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Ultrahigh Vacuum and Electrocatalysis – The Powers of Quantitative Surface Imaging

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Abstract

We highlight the impact of Ultrahigh Vacuum (UHV)-born surface science on modern electrocatalysis. The microscopic, atomic level picture of surface adsorption and reaction, which was developed in the surface science community in decades of systematic research on single crystals in UHV, has meanwhile become state-of-the-art also in electrochemistry. For the example of CO on Pt(111) single crystals, which has been extensively studied at the solid/gas and the solid/liquid interface using atomic resolution scanning tunnelling microscopy (STM), we highlight how both interfaces may have even more in common than often assumed. We then illustrate how planar model surfaces such as mono- and bimetallic single crystals and surface alloys, prepared and thoroughly analysed in UHV, enabled a systematic search for improved electrocatalysts. Surface alloys, thermodynamically more stable than foreign metal islands, are a particularly important subgroup of model surfaces, which so far have only been fabricated in UHV.

We also flag that model surfaces may not always assume the structure anticipated for the respective experiment, regardless of their preparation in UHV or by electrochemical methods. “Accidental” surface alloying may be more common than often assumed, leading to misinterpretations of the structure-property relationships targeted in many model studies. We highlight that controlled surface alloy formation should be a key step in any model study looking at bimetallic systems in order to get an idea what the effect of unintended alloying could possibly be, and to cross-check whether alloyed surfaces may potentially be the better electrocatalysts in the first place.

1 Introduction

Surface science under vacuum conditions pioneered the research on adsorption and reaction at solid surfaces; these phenomena are monitored by an ever increasing pool of spectroscopic, diffraction, and imaging techniques. A microscopic picture of adsorption and reaction, including the local structure and chemistry of the involved surface, was developed in that community. In

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