IAP Seminar

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TU Wien, Institut für Angewandte Physik, E134
1040 Wien, Wiedner Hauptstraße 8-10
Yellow Tower „B“, 5th floor, SEM.R. DB gelb 05 B

Searching for the *Active Site* in Electrocatalysis: Imaging Oxidation and Oxygen Evolution on Gold *Operando*

Conventional wisdom suggests that a heterogeneous catalyst's activity and selectivity is governed by a small percentage of the total surface area: the active sites. However, particularly for electrocatalytic systems at buried interfaces, confirming this received wisdom and, once confirmed, exploring the nature of the active site(s), is extremely challenging. Perhaps the most straightforward way to address this problem is to image the electrocatalyst under *operando* conditions using approaches that provide insight into both interfacial structure and chemical speciation.

Here we address this challenge for (electro)oxidation of and oxygen evolution at a gold electrode in aqueous electrolyte over a range of length scales. Using a second harmonic generation microscope we image the oxidation and subsequent oxygen evolution at a polycrystalline Au foil over microns. We demonstrate that oxidation currents that are well defined when integrated over the entire electrode reflect several hundred mV heterogeneity on ten micron length scales. At more positive potentials we show that oxygen evolution is dominated by micron scale hot spots that are stable under voltammetric cycles.

Gaining additional insight into the causes of such oxidation heterogeneity requires imaging structure and chemical speciation with (much) higher spatial resolution. We meet this challenge using a recently developed electrochemical tip-enhanced Raman (ECTERS) spectroscope. The sub-10 nm spatial resolution, and concurrent STM imaging, this approach allows makes it possible to map gold oxidation at defects/active sites on well-defined Au(111) at potentials below which terraces oxidize. We find that oxide species appear at defect terrace and protrusion sites and that these oxides are distinguished by their coordination number.

All interested colleagues are welcome to this seminar lecture (45 min. presentation followed by discussion).

Friedrich Aumayr
(LVA-Leiter)

Markus Valtiner
(Seminar Chair)