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A Versatile Approach to Electrochemical In Situ Ambient Pressure X-ray Photoelectron Spectroscopy: Application to a Complex Model Catalyst

Over the last decades, model catalytic studies using complex but atomically defined surfaces prepared by surface science methods have led to a profound mechanistic understanding in the field of heterogeneous catalysis. We aim to transfer this approach to electrocatalytic systems [1, 2]. However, this transfer poses new challenges: First, suitable model systems are needed (materials challenge). Second, these systems must be stable under the applied electrochemical conditions (stability challenge). Finally, new techniques are needed to study these systems in situ (methods challenge).

To analyze the surface oxidation states, X-ray photoelectron spectroscopy (XPS) is commonly used. However, XPS is a vacuum-based technique, which limits the number of approaches to investigate the potential dependent oxidation and reduction of planar electrodes. Established approaches are the ex situ emersion approach [3] and the “dip and pull” method [4]. In the ex situ emersion approach, the electrode is emersed at a given potential, transferred to ultra-high vacuum (UHV), and measured in UHV by conventional XPS. The disadvantage of this approach is that the active state may decompose after the removal from the electrolyte. In the “dip and pull” method, a thin film of electrolyte (tens of nanometers) is formed, which allows to measure in situ using “tender” x-rays. This approach requires, however, ambient pressure (AP) XPS and sample sizes of several centimeters to prepare the liquid film. The later boundary condition is not compatible with standard noble metal single crystals ($\phi \leq 10$ mm) used in surface science experiments.

Here, we present a new approach to study model electrocatalysts in situ with sample sizes typically used in surface science [5]. We have developed a custom-designed miniature capillary cell operating in a three-electrode configuration (**Figure 1a**) that is compatible with typical AP-XPS systems. This cell enables AP-XPS measurements of the electrochemical solid liquid interface in a thin-layer of electrolyte using “tender” X-ray synchrotron radiation. We demonstrate the potential of this versatile method by studying a complex UHV-prepared model electrocatalyst. It consists of palladium nanoparticles supported on a well-ordered $\text{Co}_3\text{O}_4(111)$ film on Ir(100) (**Figure 1b**).

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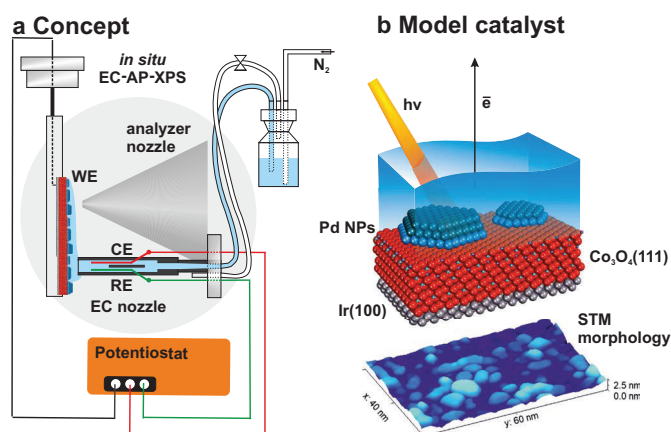


Fig. 1: Schematic representation of the new electrochemical in situ AP-XPS cell designed for small single crystal-based samples. Adapted with permission from Ref. [5], Copyright 2022, American Chemical Society.

We monitored the electrolyte and the oxidation state of the electrocatalyst in alkaline conditions at two given potentials, one below ($0.9 V_{\text{RHE}}$) and one above ($1.6 V_{\text{RHE}}$) the oxidation potential of Pd. We compared the spectra with different reference conditions: (i) hydrated conditions, without externally applied potential, (ii) spectra measured using the ex situ emersion approach, and (iii) AP-XPS under reducing (as-prepared; UHV) and oxidizing (1 mbar O_2 ; 500 K) conditions. By switching the potential from 0.9 to $1.6 V_{\text{RHE}}$ in the in situ experiment, we observe the oxidation of the Pd nanoparticles. Furthermore, we observe consistent peak shifts from the species in solution ($\text{H}_2\text{O}/\text{OH}^-/\text{CO}_3^{2-}/\text{carboxylates}/\text{potassium}$) to lower binding energies with increasing potential. At the same time, the binding energies of the signals from the electrode material (Pd) are unaffected by the applied potential, due to the common ground between the sample and the analyzer. These observations are very characteristic of the applied potential and confirm the in situ conditions [4].

Finally, the comparison of the binding energy shift between the contributions from palladium oxide and metallic palladium Pd^0 in the in situ, ex situ emersion, and AP-XPS measurements shows distinct differences (**Figure 2**). The binding energy shift between the contributions from palladium oxide and metallic Pd^0 is much larger (2.4 eV) for the in situ measurement than for the ex situ emersion (1.4 eV) and the AP-XPS measurement in 1 mbar oxygen at 500 K (1.1 eV). We propose that a labile and highly oxidized Pd oxide/hydroxide species is formed in situ, which decomposes spontaneously after the removal from the electrolyte. Our experiment demonstrates the potential of

our approach and the importance of electrochemical in situ AP-XPS for studying complex electrocatalytic interfaces.

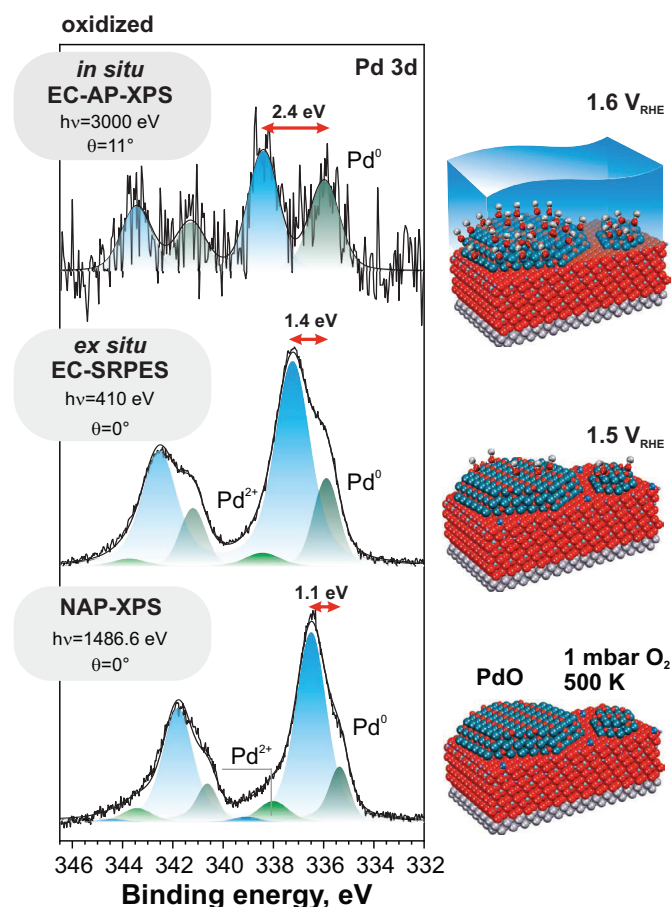


Fig. 2: The Pd 3d spectra obtained from the Pd/Co₃O₄(111) model catalyst under oxidizing conditions established during AP XPS (bottom spectra), ex situ emission EC-SRPES (middle spectra), and electrochemical in situ AP-XPS (top spectra). Adapted with permission from Ref. [5], Copyright 2022, American Chemical Society.

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Dr. Olaf Brummel studied chemistry and received his PhD at the Friedrich-Alexander-Universität (FAU) Erlangen-Nürnberg. He did his PhD in the group of Prof. Dr. Jörg Libuda. During that time, he visited the groups of Prof. Dr. Marc Koper (Leiden University, Netherlands), Prof. Dr. Jacek Lipkowski (University of Guelph, Canada), and Prof. Dr. Ulrike Diebold and Dr. Stejin Mertens (Technical University Vienna, Austria) for research stays. He finished his PhD with distinction and received for his PhD thesis the Gerda Weller award. After his PhD, he became workgroup leader for "Model Electrocatalysis" at the Chair of Interface Research and Catalysis of the FAU Erlangen-Nürnberg and visited the group of Prof. Dr. Junfa Zhu (University of Science and Technology of China, China) for a research stay. Between 2016 and 2022, he was coordinator of the DFG Research Unit "funCOS – Functional Molecular Structures on Complex Oxide Surfaces FOR 1878". He received a permanent position at the Department Chemistry and Pharmacy at FAU 2020.

The expertise of Dr. Olaf Brummel is centered around model electrocatalysis in energy conversion with a special focus on reaction mechanisms and kinetics at electrified solid/liquid interfaces. His group employs model systems with different levels of complexity including simple single crystalline surfaces, real electrocatalysts, and complex, well-defined nanostructured model electrocatalysts prepared by surface science methods. His group uses a variety of electrochemical in situ methods for mechanistic studies with a special emphasis on electrochemical infrared spectroscopy.