CHEAC Highlights 2024

Publication: Monitoring the Structural Changes in Iridium Nanoparticles during Oxygen Evolution Electrocatalysis with Operando X-ray Total Scattering
RK Pittkowski, S Punke, AS Anker, A Bornet, NPL Magnard, N Schlegel, LG Graversen, J Quinson, A Dworzak, M Oezaslan, JJK Kirkensgaard, M Mirolo, J Drnec, **M Arenz, KMØ Jensen**. JACS 146 (40), 27517-27527 https://doi.org/10.1021/jacs.4c08149

In this work we investigate the active catalyst structure of iridium nanoparticles across different length scales by combining a set of advanced synchrotron X-ray techniques. Iridium is the most widely used catalyst for electrolysis, to split water into oxygen and hydrogen. We found that the iridium particles were decahedral in their metallic state. When oxidized to the active catalysts for oxygen evolution, the particles lost their crystallinity and shape, and a disordered iridium oxide structure was found to be the active catalyst.

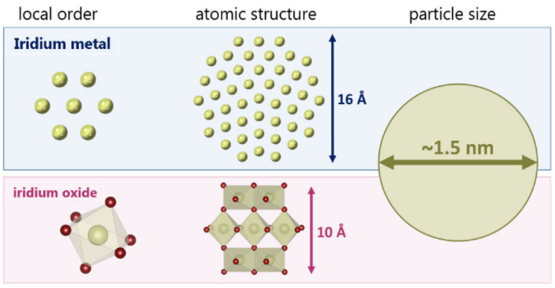
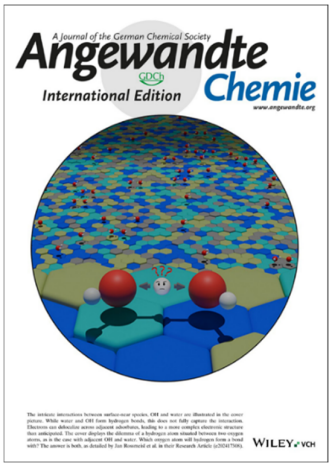


Illustration showing the order and structure of Iridium before and during oxidation.

These extensive structural characterizations at different lengths are crucial to clarify structure-property relationships. The study was featured as a research highlight in Nature Catalysis, showing a high scientific interest in our newly established toolbox of characterization techniques to study active catalysts.



Back cover illustration by Marcus F Nygaard and Martin LS Nielsen

Publication: Adsorbate resonance induces water-metal bonds in electrochemical interfaces.
MF Nygaard, MLS Nielsen, J Rossmeisl, Angewandte Chemie Int. Edt., 64 (7), e202417308 https://doi.org/10.1002/anie.202417308

This work demonstrates an unexpected effect that we did not initially anticipate. Theoretical catalysis and most quantum mechanical simulations for catalysts have primarily focused on uniform surfaces. As a result, the theories we often apply tend to rely on the mean field approximation, where effects are treated as averages. In contrast, the surface of a high entropy alloy is highly diverse, far from uniform. This opens opportunities to explore effects that are present on any surface but only emerge statistically when examining a wide range of different surface sites.

In our study, we investigated the co-adsorption of water and OH on HEA surfaces. We initially expected the co-adsorbed molecules would be described by a covalent bond between the OH group and the surface atom it is attached to, along with a hydrogen bond between the water molecule and the OH group. However, after conducting a statistical investigation of thousands of calculations, we found that water forms a fraction of a covalent bond to the surface, whereas the bond order of co-adsorbed water and OH remains one.

This effect can be understood through resonance between two electronic configurations: one where water behaves like OH and OH behaves like water, and vice versa. While this phenomenon also occurs on uniform surfaces, it is much more difficult to observe when water and OH are adsorbed on the same type of atoms. Our statistical analysis of the simulations reveals that the electronic ground state is a superposition of these two configurations. What's particularly interesting is that the quantum mechanical nature of the adsorption is clearly visible through the statistical analysis. We speculate that many of the characteristics of hydrogen-bonded networks on surfaces may result from such resonance effects.