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## **O<sub>2</sub>-evolution electrocatalysis: Electronic, atomic *and* nanoscale dynamics matter**

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In *Nature*, Mefford, Chueh and colleagues describe how they investigated the oxygen evolution reaction (OER) *in situ* at sub-micrometer resolution. Nanoscale variations of current density, geometry, and oxidation states show that the currently emerging and potentially paradigm-shifting picture of redox-active, structurally dynamic catalyst materials may need to include the nanoscale.

The oxygen-evolution reaction (OER), also denoted as water splitting or water oxidation, proceeds in photosynthetic organisms: cyanobacteria, algae, and land plants. Because of its fundamental importance for life on Earth, biological OER has been a topic of intense research already for decades revealing an astounding sophistication at both, (i) the atomic level of the catalytic site, a protein-bound Mn<sub>4</sub>Ca-oxo cluster and (ii) the nanoscale level of protein complexes and lipid-bilayer membranes, the latter representing nanostructures that *inter alia* organize proton transport and pH gradients.<sup>1,2</sup>

A well-known non-biological pendant of photosynthetic water splitting is water electrolysis driven by the electric potential difference between a positive anode and a negative cathode, where oxygen (O<sub>2</sub>) is formed at the anode and hydrogen (H<sub>2</sub>) at the cathode. For many decades, water electrolysis was a subject that dutifully had found its way into textbooks, typically without sparking much excitement among students and teachers. Also in science, water electrolysis was met with limited enthusiasm only - apart from a few dedicated electrochemists. The situation changed within the last 1-2 decades when the meager scientific interest in the electrochemical OER was replaced by establishment and almost hectic growth of a high-impact research area. The reason for this growth is the pivotal role of OER in future technologies for sustainable production of non-fossil fuels. Noteworthy, the full energy content of a fuel is released in a reaction with (atmospheric) O<sub>2</sub> thereby producing, *inter alia*, H<sub>2</sub>O. Consequently, water splitting with coupled O<sub>2</sub> formation is essential in any closed cycle of technological fuel production and usage, in analogy to the biological cycle of photosynthetic water oxidation and respiratory dioxygen reduction.

In current OER research, the classical electrochemical investigation of metallic model electrodes became largely superseded by comparative investigation of new catalytic materials, where physical characterization methods reveal structural properties at the nanometer, atomic and electronic level that can be correlated with the macroscopic

electrochemical performance of catalyst-coated electrodes. Such investigation of structure-function relations – an expression borrowed from biochemical research – initially has been restricted to correlating electrocatalytic performance with the structural properties of the as-synthesized catalyst material and occasionally the post-operation (or post-mortem) catalyst. Not only the temporal evolution of corrosive processes remained unresolved. Reversible structural dynamics in response to application of electric potentials also escaped attention. Yet recently, new experimental technology has been developed that facilitate investigation catalysts materials exposed to an electrolyte and during application of well-defined electric potentials. The techniques of this rapidly developing toolbox of experimental technology are often referred to as *operando* methods, where today *operando* is used largely synonymously with *in situ*. (We note in passing that spectroscopic *operando* methods do not differ from spectroelectrochemistry applied to electrocatalytic processes.)

Mostly electrochemical *operando* investigations have been addressing structures and structural dynamics at the level of atomic structures (geometrical arrangement of nuclei) and electronic structures (orbital occupancies, oxidation states). Prominent examples are the use of *operando* X-ray absorption spectroscopy (XAS),<sup>3</sup> in the hard and soft X-ray regime, and *operando* Raman spectroscopy.<sup>4</sup> Both report on potential-dependent and time-dependent variations of atomic and electronic structure, which can be correlated with simultaneously measured electrochemical parameters. Now the connection to the nanoscale has been added, by ‘correlative *operando* microscopy’.

A smart combination of the investigated catalyst particles and only recently developed experimental methods facilitated the success of the investigation by Tyler Mefford, William Chueh and their coworkers.<sup>5</sup> The particles they deposited on a substrate electrode are hexagonal, with micrometer diameter and a typical height of 70 nm. At the atomic level, the particles are well-ordered cobalt oxyhydroxides with parallel layers of edge-sharing  $\text{CoO}_6$  octahedra, where the bridging oxygens are completely or partially protonated. The hexagonal particles reflect the atomic structure with hexagonal arrangement of cobalt and oxygen within the oxyhydroxide plane. Layered hydroxide or oxide structures are generally found in many OER catalyst materials based on transition metals and can be described, for perfectly defect-free material without intercalated ions (aside from  $\text{H}^+$ ), as  $\text{M}^{\text{II}}(\text{OH})_2$ ,  $\text{M}^{\text{III}}\text{OOH}$ , and  $\text{M}^{\text{IV}}\text{O}_2$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Mn}, \text{Ru}, \text{Ir},$  and others).<sup>6</sup> Often the OER catalyst materials are defect-rich layer fragments that comprise also corner-sharing  $\text{MO}_6$  octahedra as well as intercalated layers of water molecules and counterions. At the nanoscale, an amorphous morphology is frequently encountered, in marked contrast to the catalyst particles investigated by Mefford et al. Their choice of comparably large  $\text{Co}(\text{OH}_x)$  particles of crystalline order supports both correlative *operando* microscopy with limited spatial resolution and interpretation in terms of ideal atomic structures of crystalline materials. However, the degree of transferability of their conclusions to other catalyst materials remains an open question.

After deposition of the flat hexagonal particles on a planar substrate electrode, Mefford et al. investigated the effect of various near-catalytic and catalytic electric potentials using scanning electrochemical cell microscopy (SECCM) for simultaneous detection of current

density and particle height. In these experiments, the electrolyte meniscus of a nanopipette electrode is scanned across the planar substrate electrode. The spatial resolution of the resulting microscope images is said to be determined by the diameter of the nanopipette tip of 440 nm, but the effective spatial resolution in the pipette scanning mode appears as being by at least one order of magnitude below the tip diameter. In a separate experiment on fully electrolyte exposed hexagonal particles, Mefford et al. spatially resolved the cobalt oxidation state by measuring Co L<sub>III</sub>-edge spectra using scanning transmission X-ray microscopy (STXM) with a resolution of 50 nm in the two planar dimensions. Analysis of the three microscopy signals leads to the following conclusions:

- (i) Catalytic currents are detectable only at the particle margins implying that the basal planes of the layered oxides are catalytically inactive, as suggested before but never visualized so impressively. Caveats include the possibility of formation of hydrated amorphized regions at the particle margins. Catalytic activity in the interior of the catalyst particles also could have escaped detection by the SECCM method but is unlikely for these catalyst particles.
- (ii) Conventional electrochemistry and STXM suggest two redox transitions assigned as follows:  

$$\text{Co}^{\text{II}}(\text{OH})_2 \leftrightarrow \text{Co}^{\text{II/III}}\text{O}_{0.5}(\text{OH})_{1.5}-(\text{H}_2\text{O})_{0.5}^{\text{intercalated}} \leftrightarrow \text{Co}^{\text{III}}\text{OOH},$$
 where in the mixed-valent oxidation state, the catalyst material acquires intercalated water molecules. The particle height images determined by SECCM show swelling of the particle height by about 10% (ca. 7 nm) at electric potentials corresponding to the intermediate redox state, thereby motivating the proposed water intercalation. Interestingly also an associated lateral expansion of the particle margins was resolved, for which presently a definitive assignment cannot be made.
- (iii) Transmission X-ray spectroscopy reveals that the Co oxidation-state changes are heterogeneously distributed at the nanoscale, with the onset of the Co<sup>II</sup>→Co<sup>III</sup> oxidation at the particle margins shifted to higher potentials then compared to the particle bulk.

For decades, electrochemists discussed electrolytic water splitting as one among many other electrochemical processes taking place at structurally inert metallic or metal-oxide surfaces. Electrochemical operando investigations have started to address structural dynamics at the level of atomic structures (geometrical arrangement of nuclei) and electronic structures (orbital occupancies, oxidation states) as they are induced by variation of the electrode potential. Such operando investigations begin to shake the assumption of electrocatalysis by adsorption and desorption of molecules at structurally inert metallic or metal oxide surfaces as well as related concepts in describing the electrocatalytic reactions computationally. A paradigm change is dawning, from structurally inert to redox-active, structurally dynamic catalyst materials.<sup>2,7-10</sup> But also in potentially paradigm-changing studies, structural features and dynamics at the nanometer and micrometer level were considered as being mechanistically irrelevant and discussed merely in terms of differences in the electrochemically active surface area or corrosive material modification. The investigations

of Mefford, Chueh and their coworkers has the potential to put the nanoscale into focus. Their work reveals unexpected dynamics at the nanoscale, which are induced by application of electric potentials and explained by the interplay between metal-ion redox chemistry, atomic structure and nanoscale morphology. Their results are unlikely to be definitive, but still represent a breakthrough with possible kickstart effect: Electric potentials induce non-trivial nanoscale dynamics and they now can be investigated in operando experiments.

Mefford, Chueh and colleagues have shown that the used Co oxyhydroxide particles are a useful model system but will not promote optimal OER performance due to a limited number of reactive margin sites. The development of catalyst materials with their static and dynamic properties optimized not only at the atomic level but also on length scales ranging from nanometers to millimeters is desirable. Optimization targets are number and reactivity of OER-active sites as well as superior transport properties—water accessibility, electron transfer, proton transport, and O<sub>2</sub> release are relevant issues. Biological nanostructures and their dynamics have been evolutionarily optimized for superior functionality during billions of years. Maybe we can do faster by knowledge-based development of inorganic catalyst materials.

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