

Electrocatalysis

Greater than the sum of its parts

The performance of electrocatalysts depends on material properties that may differ spatially even within a single particle. Now, a combination of operando microscopy techniques is used to correlate morphology and metal oxidation state with local activity of an oxygen evolution catalyst, which may help to guide future catalyst design.

Marcel Risch

A sustainable energy supply is one of the grand societal challenges of the century.¹ One crucial target is to increase supply of renewable energy, which necessitates storage to buffer the intermittency of renewable sources. Electrolysers allow storage of electrical energy in chemical form; a key reaction in their operation is the electrochemical oxidation of hydroxide ($\text{pH} \gtrsim 10$)² or water ($\text{pH} \lesssim 10$)² to form oxygen, electrons and protons. These protons are the beginning of the value chain to make green hydrogen or carbon- and nitrogen-based fuels and chemicals. As the route to the most important precursor for future sustainable chemistry, a deeper understanding of this reaction is thus urgently required.

Ideal catalyst materials to facilitate hydroxide/water oxidation (or, the oxygen evolution reaction, OER) need high stability and high activity per active site, as well as a high density of active sites. Moreover, they should be based on cost-effective earth-abundant elements. Transition metal (oxy)hydroxides have thus emerged as particularly promising OER catalysts. However, improving such catalysts calls for fundamental materials research to reveal detailed atomistic insight into the location and chemical nature of the active sites. Now, writing in *Nature*, J. Tyler Mefford, William C. Chueh and colleagues across the USA and UK interrogate the local material properties of the active region of cobalt hydroxide platelets during electrocatalytic water oxidation using multimodal microscopy experiments.³

The researchers achieve these much-needed insights using correlative microscopy to probe the local activity, morphology, and cobalt oxidation state in relation to applied potential, by scanning electrochemical cell microscopy, atomic force microscopy and scanning transmission X-ray microscopy, respectively (Fig. 1). They find that morphology and oxidation state respond to the applied potential with considerable spatial heterogeneity; the as-synthesized material is

chemically and structurally different and less complex than the active catalyst. Specifically, the cobalt in the fresh electrocatalyst oxidizes from $\beta\text{-Co}^{2+}(\text{OH})_2$, via a previously elusive, pre-catalytic phase of $\alpha\text{-Co}^{2.5+}\text{O}_2\text{H}_{1.5}\cdot 0.5\text{H}_2\text{O}$, to $\beta\text{-Co}^{3+}\text{OOH}$ under applied potential. The pre-catalytic $\text{Co}^{2.5+}$ phase nucleates from sites near the platelet center; that is, the pre-catalyst does not originate from the surface where catalysis takes place.

These observations suggest that, in principle, the nuclei for the pre-catalyst could be designed independently from the surface properties, which opens up new ways to construct electrocatalysts. For example, chemical or structural defects could be placed deliberately to control the location and density of nucleation sites. Furthermore, structural differences between the pre-catalytic and catalytic phases, such as strain, could be used to develop in situ core-shell structures. Strain has been shown to affect covalence and charge transfer and thus the activity for the OER in model systems.⁴

The scanning electrochemical cell microscopy performed by Mefford, Chueh and colleagues indicates that the region at the platelet edge has the highest local activity. Thus, it either contains the most active sites, the highest density of active sites, or both. The researchers assign the active sites to cobalt with an electronic hole on oxygen ($\text{Co}^{3+}\text{-O}^\cdot$), which suggests that in alkaline electrolyte, oxygen redox⁵ may be enabled in addition to Co redox.

Having two redox centers at the active site like this offers an attractive degree of freedom to weaken the scaling relationships between reaction intermediates,⁶ which currently limit the activity of catalysts for multi-electron reactions such as the OER. Introducing two redox centers at the catalytic surface could be an important approach to optimize the activity per active site.

Furthermore, elucidating that the edges of the platelets are active could aid the design of catalysts with optimal particle size and shape to increase the density of active sites. In other work, a smaller platelet size has been shown to increase the number of active sites in the limit of molecular platelets in electrodeposited cobalt oxide.⁷ More complicated particle shapes with maximized density of the active facet have led to significant improvements in electrocatalytic activity, for example, in the hydrogen evolution reaction on molybdenum sulfides.⁸

The work by Mefford, Chueh and colleagues also adds further evidence that high energy sites with unsaturated bonds (such as surface edges on layered crystal structures³; kinks and steps

on surfaces⁹; or ad-atoms¹⁰) are likely the most active parts of catalyst materials. However, this high activity usually comes at the cost of poor stability, with high-energy sites rapidly degrading to low-energy, low-activity sites. Preserving these highly active high-energy sites is perhaps the greatest challenge for translation of fundamental proof-of-concept studies into new robust electrocatalysts for use in devices, as activity and stability are closely intertwined.

High performance electrocatalysts are materials with either complex chemistry or morphology or both. Thus, no single experimental method can resolve all relevant materials properties and differing operation parameters need to be considered. Mefford, Chueh and colleagues performed their multimodal characterisation sequentially by linking the experiments via measurement parameters in overlapping ranges on selected particles. Additional control experiments were performed to ensure comparability. Ideally, multimodal experiments would be performed simultaneously under identical conditions and on the same sample, but this is a great future challenge in terms of experimental design and implementation.

Chueh, Mefford and colleagues' work reveals the morphology and electronic structure, namely the metal valence, of their catalyst. In general, these properties have a strong impact on the OER as well as on electrocatalytic reactions involving hydrogen, carbon and nitrogen. In the future, similarly well-chosen combinations of in situ experiments could give unprecedented nanoscale insight into these important energy reactions on a wide variety of catalyst particles. To design improved electrolyser technologies, the discovery of surprising new pre-catalytic or catalytic phases and disruptive novel mechanisms is needed. Multimodal in situ experiments will be instrumental in finding and understanding them.

Address: Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Nachwuchsgruppe
Gestaltung des Sauerstoffentwicklungsmechanismus, Hahn-Meitner-Platz 1
Berlin, 14109, Germany

Email: marcel.risch@helmholtz-berlin.de

Competing interests

The author declares no competing interests.

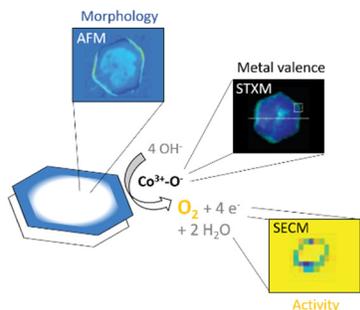


Figure 1. Mapping activity. Nanoscale insight by combination of atomic force microscopy (AFM), scanning transmission X-ray microscopy (STXM) and scanning electrochemical cell microscopy (SECM) to elucidate morphology, Co valence and activity locally, respectively. Images reproduced from ref. 3.

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