

Finding efficient catalyst designs: A high-precision method to reveal active sites

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Designing efficient electrocatalytic structures requires reliable guidelines. For this purpose, experimental approaches for the characterization of model electrodes in *operando* conditions are valuable. Reporting in *Joule*, Agnoli et al. showcase the determination of site-specific reaction onset potentials and Tafel slopes by using electrochemical scanning tunneling microscopy.

Plastics, pharmaceuticals, fertilizers—all of these essential products and more require catalytic materials in their fabrication process. Moreover, with sustainable energy systems rapidly gaining momentum, the interest in electrochemical conversion and storage devices, such as hydrogen fuel cells and water electrolyzers, is growing. In line with the commercialization goals of these devices, the optimization of the respective reaction kinetics has become a pressing issue. In order to design an efficient catalyst, it is particularly important to possess knowledge about the nature of the active sites—i.e., the electronic configurations of the atoms on the electrode surface, which are beneficial for promoting the desired reaction.

Taking the oxygen reduction reaction (ORR) as an example, Figure 1 (left) summarizes the current state-of-the-art catalyst structures. The highest activities using only one element are achieved by platinum (Pt), which is applied as spherical nanoparticles on a carbon (C) support (Pt/C) as a common commercial solution. Still, as evident from the graph, even the low-index planes of an extended Pt surface can achieve higher activities than the commercial standard.¹ The enhancement becomes even more significant

when Pt is alloyed with other metals such as nickel (Ni) or cobalt. The highest ORR activity has so far been found on extended Pt₃Ni(111) surfaces.¹ The alloying of Pt leads to surface strain and electronic changes due to a ligand effect that together shift the binding of reaction intermediates to a more favorable value, thus increasing the ORR activity. An additional option to improve the activity of Pt catalysts is to take advantage of shape effects by synthesizing nanostructures with a maximum number of active sites. For example, PtNi nanoframes,² jagged Pt nanowires,³ and PtNi octahedra⁴ have shown extraordinary ORR activities.

Besides these shape effects, it is necessary to consider size effects as well. It has been demonstrated that the size of nanoparticles can influence the activity; more specifically, it has been found that there are discrete sizes at which the activity is maximized. Figure 1 (right) displays this effect for spherical Pt nanoparticles on the ORR, with mass activities obtained by density functional theory calculations.⁵ The study predicted the highest mass activities for particles with diameters around 1, 2, and 3 nm, while other sizes in the investigated range returned significantly lower activities. This trend was linked to the atomic configuration of the sur-

face and the coordination of the active sites. It turned out that at specific sizes, the particle surface consists of advantageous combinations of Pt facets, maximizing the number of active sites with optimal coordination. Following these considerations, it is clear that designing nanoparticles with optimized electronic properties is the key to efficient catalysts. Nowadays, material scientists can synthesize nanoparticles of a wide variety of shapes, sizes, and material combinations. Therefore, with the knowledge about the active sites, creating nanoparticles with a maximum number of such configurations is achievable.

But which sites are active? Answering this question can be complicated due to the complex interactions at the electrified electrode-electrolyte interface. For instance, Pt has been well known as an excellent catalyst for almost 200 years,⁶ and still, the optimal structural properties are under debate. In the past, catalyst optimization was often achieved by a trial-and-error approach, which is time consuming and ineffective. Instead, modern research has resorted to more direct routes to determine the structure-activity relation of electrode materials. For example, would it not be most straightforward to “see” where a reaction is occurring at the electrode surface while it is happening? There are *in situ* and *in operando* techniques, which are approaching this idea. For instance, the scanning tunneling microscope (STM) can comparatively easily adopt the *operando* concept. The original purpose of the STM was to resolve the electronic

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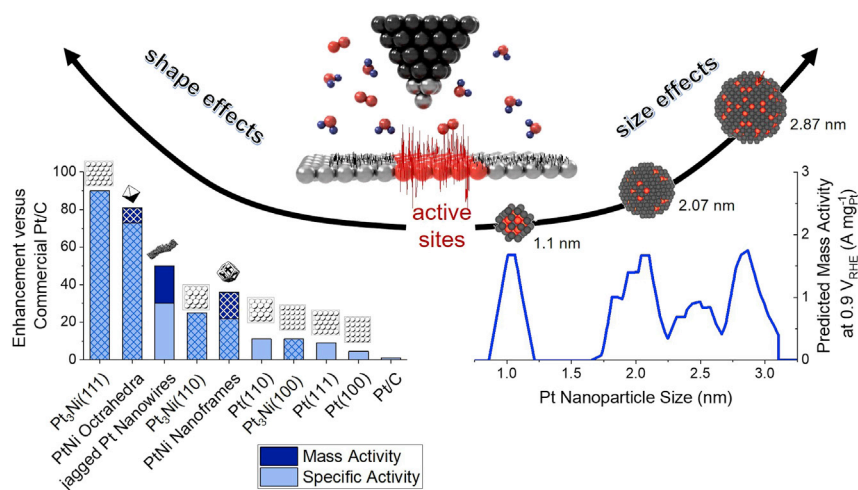


Figure 1. Exploiting shape and size effects to optimize the ORR activity of Pt-based electrocatalysts

To tailor electrocatalysts with optimal performances, it is important to know the nature of the active sites. For instance, shape effects together with strain/ligand effects (left side) can alter the ORR activity of Pt (filled bars) and Pt-Ni (patterned bars) electrodes. Since the experimental parameters were not equal in each of the literature sources, the activity of a commercial Pt/C reference catalyst was used for comparison. Extended Pt surfaces of different orientations and compositions show different activities, with Pt₃Ni(111) currently reaching the highest enhancement compared to Pt/C.¹ In addition to the composition and crystalline orientation, shape effects can be exploited to synthesize nanoparticles with exceptional performances: PtNi nanoframes,² jagged Pt nanowires,³ and PtNi octahedra.⁴ Moreover, size effects can tune the activity of Pt nanoparticles (right). The reasons for the dissimilar activities are the differences in the number of active sites, which can be identified theoretically by their coordination (modified with permission from Garlyyev et al.,⁵ copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; active sites are marked in red). A possibility to identify active sites *in situ* is the evaluation of noise features in EC-STM (top inset).

structure of a surface at an atomic level, but already in the early days, unexpected noise features were observed and related to dynamic phenomena.⁷

Reporting in *Joule*, Agnoli et al.⁸ demonstrate the application of an electrochemical STM (EC-STM) for a comprehensive *operando* characterization of catalyst surfaces during the hydrogen evolution reaction (HER). The technique builds on the principle first introduced by Pfisterer et al.⁹ of detecting electrocatalytically active areas by monitoring locally confined disturbances in the EC-STM signal (Figure 1 [top inset]). Essentially, the tunneling barrier at an electrocatalytically active site is perturbed due to the reaction dynamics. As a consequence, the participation of structural motifs such as steps, terraces, and defects can be visualized under reaction conditions. Based on the sentiment that the noise itself should

contain more information than merely qualitative disclosure of the active centers, Haid et al. recently demonstrated that a direct correlation between the intensity of the noise and the local activity exists, allowing a more quantitative analysis.¹⁰ In this so-called “noise”-EC-STM, the distribution of the signal derivatives (tunneling current versus time and/or height versus scanning direction) are exploited to compare the local activity of different surface sites in a semi-quantitative manner. Following a similar train of thought, Agnoli et al. explore an alternative route to obtain quantitative information on the electrochemical processes in their study, deriving properties such as the onset potential, the Tafel slope, and the turnover frequency. For this purpose, they assume that the electrocatalytic influence on the tunneling current takes the form of a first-order perturbation at low overpotentials. Accordingly,

the EC-STM signal consists of two components: (1) the raw electronic conductivity and (2) the influence of the Faradaic reaction events. The authors develop a mathematical model to perform a roughness analysis of the current and separate the components. During the current roughness (*cr*) analysis, the unperturbed STM signal (under reaction “off” conditions) is used as a baseline to extract the irregularities provoked by the reaction. The model accounts for influences of structural motifs in the image and differences in the analyzed surface area. Finally, to add comparability to the method, a normalization to the basal plane of the investigated system is introduced.

Equipped with this comprehensive description of the EC-STM response, the authors demonstrate its potential on a variety of model systems monitored under HER conditions. At first, the local HER onset of the Au(111) basal plane is extracted from the EC-STM data via the *cr* approach. Comparing the behavior of several structures in the images, the authors find a particularly low reaction onset and high activity at the edge sites. A particular highlight of the article is the translation of the recorded noise level at different potentials into a local Tafel slope. The accuracy of these pseudo-Tafel slopes is confirmed by macroscopic measurements of the basal and edge plane of Au(111), exhibiting remarkable accordance. With this powerful electrochemical descriptor, the authors can speculate on the rate-determining step of individual active sites. Circling back to the matter of nanoparticles, the study also includes an investigation on the catalytic activity for the HER of Pd nanoparticles deposited on a carbon support. Amongst other aspects, the effect of the size of the nanoparticles is carefully considered. By using the *cr*-EC-STM method, the authors extract Tafel plots for nanoparticles of different sizes. The local activity versus particle size follows a “volcano-like” trend with an optimum diameter of approximately 3.4 nm. Additionally, the *cr*-EC-STM method confirms

the influence of geometric properties by a detailed analysis of the noise features at an asymmetric nanoparticle. From the respective Tafel slopes, the authors conclude that the HER reaction mechanism is independent of the particle size. Lastly, Agnoli et al. demonstrate the outstanding ability of the *cr*-evaluation approach to extract the catalytic activity of a single-atom defect site on a WSe₂/Au(111) surface.

With their study, the authors impressively demonstrated the *cr*-EC-STM approach to extract the local activity and Tafel slope at an atomistic level from the *operando* noise data. As outlined in the beginning, this elemental knowledge is valuable in the design of efficient nanoparticulate catalysts.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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A photochemical interruption of the Cloke-Wilson rearrangement

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In the inaugural issue of *Tetrahedron Chem*, Liu, Wei, and Shi describe a photoredox catalyzed variant of the Cloke-Wilson rearrangement featuring the ring-opening and interrupted recyclization of cyclopropyl ketones by intramolecular nucleophilic attack with an indole moiety, thus leading to unique macrocyclic frameworks.

Visible-light mediated catalysis has made a tremendous impact on a great variety of transformations such as cross-couplings, atom transfer radical

addition reactions, or cycloadditions. Arguably, photoredox catalyzed transformations that increase molecular complexity through rearrangements

are less explored but have great potential to access novel scaffolds valuable for drug discovery. In this context, an intriguing strategy utilizing readily available cyclopropyl ketones **1** was developed by Liu, Wei and Shi¹ that does not only give rise to unique oxygen-bridged macrocyclic frameworks **2** but also challenges the current mechanistic understanding of photoredox pathways.

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