



# Structural and electronic effects in heterogeneous electrocatalysis: Toward a rational design of electrocatalysts



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## ABSTRACT

Recent advances in the understanding of structural and electronic effects in heterogeneous electrocatalysis are summarized. Typical examples are given illustrating how the knowledge obtained from a detailed theoretical analysis of structural and electronic effects supported by model experiments can be used for the rational design of new electrocatalytic materials. Recent successes and future challenges in designing active, stable, and selective electrocatalysts are discussed.

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## 1. Introduction

Electrocatalysis is the field of catalysis that deals with the catalysis of redox reactions. Redox reactions not only play a key role in a multitude of devices, in particular electrochemical power sources such as fuel cells, batteries, and electrolyzers, but also in many naturally occurring processes, especially those related to energy conversion in living systems. There is growing awareness that the way that mankind will secure future availability of sustainable energy will depend heavily on electrochemistry, as it allows the storage and consumption of electrons in chemical bonds at ambient conditions. It is the task of electrocatalysis to make this process as efficient, reversible, robust, and cost-effective as possible.

The aim of this Anniversary Article for the Journal of Catalysis is to pull together some recent advances in the understanding of structural and electronic effects in *heterogeneous* electrocatalysis, i.e., the area of electrocatalysis which makes use of solid metal or oxide electrodes as electrocatalysts. We note that electrocatalysis is not limited to heterogeneous catalysts: molecular catalysts, either in solution or immobilized on a conductive but otherwise inert support, may also catalyze redox reactions. Redox proteins are Nature's electrocatalysts and essentially function as galvanic cells, very much like in a discharging battery. Therefore, the field of electrocatalysis bridges many areas of catalysis.

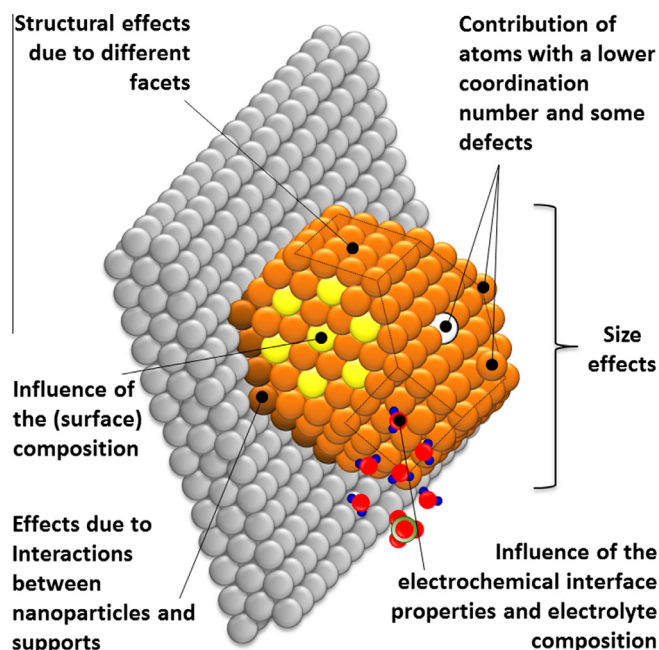
Here, we show how the study of a few selected electrocatalytic reactions on well-defined, often single-crystalline, electrode surfaces has led to a detailed insight into the atomic-level aspects that impact on electrocatalytic performance. Often, these studies have been supported by first-principles density functional theory calculations. The insight thus obtained leads to useful design rules in the development of real-world high surface-area nanoparticulate catalysts. The paper consists of three main sections. In Section 2, we provide a brief overview on electronic and structural effects in the field of electrocatalysis. In Section 3, we discuss how the atomic arrangement of the atoms at the electrode surface influences its catalytic activity, and we propose that this may be categorized into three main classes of structure sensitivity. Each of these classes is then catalyzed by differently shaped nanoparticles, as follows from the insight obtained from single-crystal studies. In Section 4, we demonstrate how the catalyst composition influences the electronic properties of the topmost atomic layer of the surface and how this can be used to design efficient electrocatalysts. In a final section, we will summarize our main conclusions and sketch the possible perspectives for future research work.

## 2. Structural vs. electronic effects in electrocatalysis

Industrial electrocatalysts are typically produced either as nanoparticles or (porous) extended layers to increase the overall useful surface [1]. If a nanoparticulate material is used, the nanoparticles are immobilized on a conducting support developed to work under conditions of catalyzed electrochemical reactions [2]. It should be noted that ready-to-use electrocatalytic materials

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**Fig. 1.** Real-world high surface-area nanoparticulate electrocatalysts are complex systems where the resultant electrocatalytic activity depends on many parameters. The figure schematically illustrates common factors and parameters that control the catalyst performance.

are complex systems where the resultant performance, i.e., activity, selectivity and stability, depends on many factors. Even a single-supported nanoparticle in contact with an electrolyte represents a multiparametric system [3]: different facets, surface defects, interactions with the support material, surface and bulk composition, size effects, specific properties of the electrochemical interface, electrolyte composition, and other parameters [4] control its catalytic properties (Fig. 1). Therefore, in order to gain deeper understanding of these systems and to be able to develop a new generation of electrocatalysts, it is essential to simplify the system and use model objects, where all these aspects are investigated separately in detail [5–11].

Apart from the complexity of electrocatalytic systems, one can broadly distinguish at least two major effects that influence the whole variety of parameters. Basically, the resultant catalytic performance of active sites at the surface essentially depends on two intrinsically interconnected effects: (i) structural effects and (ii) electronic effects. The former are important to elucidate and understand the contribution of different facets, steps, kinks, and atoms with lower coordination number to the overall electrocatalytic activity. For a given electrocatalytic material, it is critical to find the surface sites, which are responsible for the observed catalytic activity (or selectivity) and use this knowledge to design new catalysts or optimized existing catalysts. The electronic effects determine the electronic status of active sites or facets. Those effects are taken into the analysis when the active sites are identified, and their electronic properties should further be adjusted, e.g., by changing the (local) chemical composition.

The design of new efficient electrocatalysts assumes that structural and electronic effects are analyzed equally. However, in practice, there could be different situations. If the choice of the materials is very limited, pure structural effects play the dominant role, as only they provide the necessary degree of freedom to optimize the catalyst performance. It is then essential to create an abundance of the most active sites, for instance, specific facets or atoms with a lower coordination number. Alternatively, if the choice of material is wider and the most active sites are known,

further optimization of their electronic structure (e.g., by changing the composition) becomes critical. Ideally, structural and electronic effects have to be taken into account simultaneously: then, both composition and surface structure are optimized in parallel.

In practice, rational development of efficient electrocatalysts requires application of many different techniques, methods, and model objects. On the one hand, techniques of electrochemistry alone cannot provide all the necessary information about the surface and the electrochemical interface [12,13]. The whole arsenal of ultra-high vacuum surface science techniques [14] and in situ spectro-electrochemical approaches [12,15–19] is also required to characterize and tailor [20,21] the surface. Additionally, modern quantum chemical methods can give valuable insight when the necessary information is not directly available from the experiments [22]. On the other hand, model objects help in better understanding of electrocatalyst performance, including low- and high-index single-crystal surfaces [6,23], well-defined (for instance, size-selected or shape-controlled) nanoparticles, thin films (often with a monolayer thickness), and some other specific objects to investigate different aspects influencing the catalytic performance separately. In the following sections, we show how the knowledge obtained from a thorough theoretical analysis of *structural* and *electronic* effects supported by model experiments can be used for the rational design of new electrocatalytic materials.

### 3. Structural effects in electrocatalysis

#### 3.1. Electrocatalysis on single-crystal surfaces

The idea that the activity of a heterogeneous catalyst depends on the structure of its surface dates back to Taylor's original concept of the "active site" [24]. The surface-science approach to identifying the active site on a surface is to study the reaction under consideration on a number of single-crystal surfaces. Ideally, these surfaces sample a relevant part of the stereographic triangle, as illustrated for *fcc* metals in Fig. 2. Such studies should give insight into which arrangement of surface atoms leads to the highest activity and should thereby identify the active site(s) for a reaction.

Many relevant electrocatalytic reactions have been studied using this surface science approach, having generated a wealth of information of the activity of a large variety of electrocatalytic reactions on single-crystal surfaces of different metals. A recent comparison of these single-crystal studies suggested that many electrocatalytic reactions fall within one of three categories of structure sensitivity [11]:

- (1) Electrocatalytic reactions that take place preferentially on step and defect sites within (111) terraces. Typically, the key step in these reactions involves the breaking or making of an O–H or C–H bond, such as the oxidation of methanol or the oxidation of carbon monoxide (which depends on the activation of water).
- (2) Electrocatalytic reactions that take place preferentially on (100) terrace sites. For these reactions, steps and defects in the (100) terraces lead to a decrease in catalytic activity. These reactions invariably involve the breaking or making of a C–O, C–C, N–O, N–N, or O–O bond.
- (3) Electrocatalytic reactions that do not appear to have a clear preference for a particular site or crystal surface. Typically, the structure sensitivity of these reactions is very sensitive to the presence of other ingredients of the electrochemical interface, such as anions, especially if the specific adsorption of these anions is structure sensitive. These reactions often involve intermediates that are only relatively weakly adsorbed on metal surfaces.

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