Bericht zur Max-Buchner-Forschungsarbeit
*„Computer-aided design of nanoparticle catalysts
for proton-exchange membrane electrolysis"*
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Abstract

Iridium dioxide nanoparticles are important catalysts for proton-exchange membrane (PEM) electrolysers. PEM electrolysis is a promising technology to convert electrical into chemical energy for storage and as chemical feedstock. The efficiency and commercial viability of PEM electrolysers depends on the activity and stability of the catalyst. In the present work a computational model was developed to better understand the structure-property relationships of nanoparticle catalysts towards a rationale computer-aided design of catalyst materials.

1. Objectives

Central goal of the project was the development of first computational models with atomic resolution for the rational design of efficient and stable IrO_2 nanoparticle catalysts used in proton-exchange membrane (PEM) electrolysis [1]. A typical approach to predict the shape of a (nano-)crystal is the Wulff construction [2] which requires only information on the relative energies of all relevant crystal surfaces. The development of realistic nanoparticle models beyond the Wulff construction, which predicts only the geometry of a crystal, represents a great challenge. There exists already a very large number of surface terminations for traditional slab models of rutile crystals. The number of possible atomistic structures of nanoparticle is much larger, while the computational complexity of the computational tasks to perform simulations tremendously increases. The present study addressed these challenges with a methodology to identify important surface structures using computationally inexpensive slab models ("screening") and first-principles thermodynamics. In order to predict the catalyst morphology at operating conditions, the applied potential to an electrode during PEM electrolysis has been included in the screening study. Using the most important surface structures identified in the screening study, the predicted geometry from a Wulff construction was used to construct a first approximation of an atomistic model. The optimization and further analysis of such atomistic models have been performed using state of the art electronic structure theory.

2. Implemented work plan

The long-term stability of a surface structure is governed by thermodynamic principles and the identification of a sustainable operating regime is critical for the implementation of PEM-based electrolyzers on an industrial scale. The central property that determines the stability of a catalyst is the surface free energy. In an electrochemical cell, the surface free energy depends on the applied potential and represents a critical parameter for the atomistic structure of the surface of an electrode. Depending on the applied potential, different surface morphologies are thermodynamically stable and frequent changes in the potential, as envisaged for flexible load systems, may induce deactivation or dissolution of the catalyst.

In order to predict the thermodynamic stability of a crystal facet with a specific termination in an aqueous environment and under an applied potential U, the surface free energies of a large number of IrO_2 structures implemented as slab models have been computed [3-5]. The present screening study included more than 70 different model structures which have been analyzed with respect to their surface free energy, relative and absolute stability at different applied potentials. All energy contributions for this analysis have been computed using first-principles density-functional theory (DFT) with the generalized-gradient approximation. For relevant surface terminations determining the particle shape, solvation effects have been approximately taken into account through an implicit solvation model.

In a subsequent step and on the basis of results obtained from slab models, the computational models have been further developed towards real nanoparticles. A common approach to pre-dict the shape of nanoparticles applies the Wulff theorem, which links surface (free) energies to the crystal geometry. The model determines the shape but neither accounts for size effects nor considers the contributions of edges and vertices ("corners") to the stability of a nanoparti-cle. These effects have been investigated with fully atomistic models.

Using computational resources on the largest supercomputers in Europe and massively paral-lel computing, models for particle sizes similar to experimentally observed catalyst nanostruc-tures have been implemented. The complexity of the model development and computational constraints limited the study to nanoparticles which have been identified in the screening study of slab models as the presumably most relevant structures in an operating electrolysis cell. In particular, the presence of hydrogen could not be considered. For the implementation of the models, substantial software developments have been carried out. Additionally, the surface free energy models mentioned above were transferred to a different simulation software which is capable of the computational complexity of nanoparticle simulations.

3. Results

Mechanistic studies of the oxygen evolution reac-

$U = 0$ $U = 1.3$ V
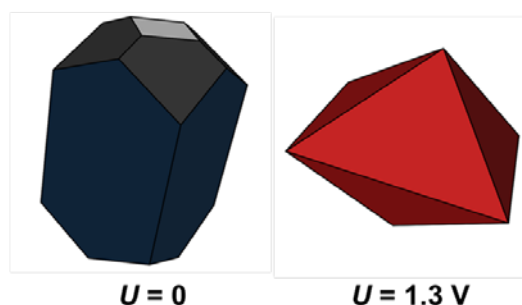
tion on IrO_2 surfaces primarily focused on slab models exposing $IrO_2(110)$ surfaces to the electrolyte. The consideration of an applied potential in our model, which takes into account the thermodynamic conditions in an electrolysis cell under operating conditions, shows that the assumption of a stable $IrO_2(110)$ surface morphology may require reconsideration. Based on our thermodynamic model, a transition to $IrO_2(111)$ terminated catalyst morphologies appears to be feasible and could explain experimentally observed changes of the electrode surface. The figure above shows the predicted thermodynamically stable shape of IrO_2 nanoparticles in the absence of a potential and at 1.3 V.
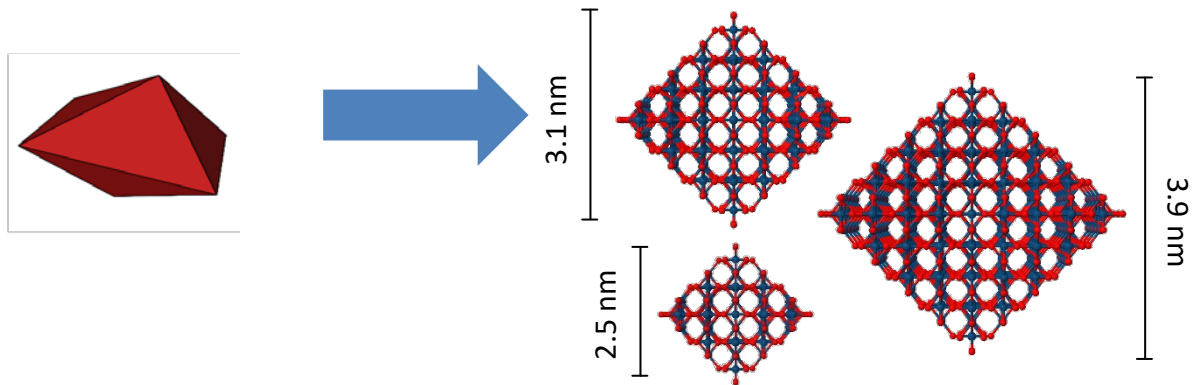

Starting from a Wulff geometry, atomistic models have been systematically constructed. Due to the complexity of the electronic structure calculations, the number of nanoparticle models has been reduced compared to the large number of possible structures. As a result, 17 mono-faceted structures have been selected which include the $IrO_2(111)$ models relevant at operating conditions. Additionally, nanoparticles exposing $IrO_2(101)$ surfaces have been included which allow the construction of mono-facetted crystals. Four different surface terminations for (111) facets and three crystal terminations of (101) surfaces have been analyzed for different particle sizes of each type in the range of 170-1200 atoms and with diameters of 1.6-4.75 nm.

The total surface energy of a nanocrystal can then be separated into different contributions, describing 2-, 1- and 0-dimensional features on the surface, corresponding to slab-, edge- and vertex contributions, respectively.

$$\gamma_{NP} = \sum_i \frac{a_i}{A} \cdot \gamma_{slab,i} + \sum_j \frac{l_j}{A} \cdot \gamma_{edge,j} + \sum_k \frac{n_k}{A} \cdot \gamma_{vertex,k}$$
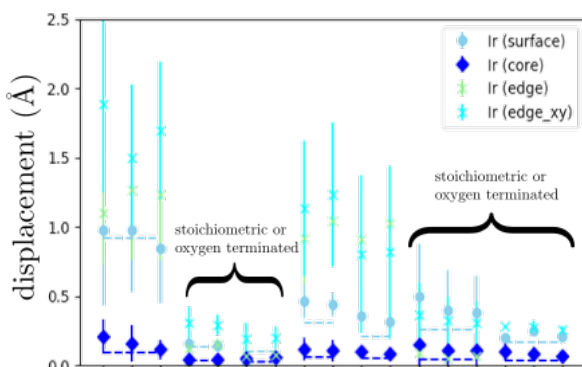
The analysis of structure relaxations (left) using electronic structure calculations

showed that the displacements of Ir atoms, measured w.r.t. an initial Wulff shape, during the geometry relaxation was small for stoichiometric/oxygen-terminated surfaces. The observed displacements for oxygen deficient terminations, on the other hand, were significant and indicate structural instability under reductive conditions.

In sum, the Wulff model proved to be an appropriate approximation for oxygen terminated surfaces which are likely to dominate the catalyst surface at operating conditions. Moreover, the geometry optimizations indicate that effects due to different surface terminations dominate over size effects in nanoparticle structures. The break-down of the overall surface energy of the nanoparticles into contributions from surfaces, edges and vertices show that the edges and vertices stabilize or de-stabilize a nanoparticle.

4. Conclusions and outlook

The computer-aided design of nanoparticle structures represents a modern and increasingly useful tool to develop a better understanding of the properties of real IrO_2 catalysts at atomic resolution. Computational screening approaches in combination with first-principles thermodynamics provide important insights in the structure and stability of IrO_2 catalysts. A further development of the techniques used in the present work to a more automated methodology that can be easily applied to a wide range of materials is a next step in the computer-aided design and discovery of improved catalysts. With the developments achieved in this work the first analysis of representative IrO_2 nanoparticles was performed. The effects of surface termination, which is determined by the pH of the electrolyte of an applied potential, edge and vertex contributions on the dimensional stability of nanoparticles demonstrate the importance of computational approaches beyond established slab models. Computational modelling therefore provides a valuable approach to explore potential catalyst morphologies for targeted experimental work.

5. References

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