Unveiling the OER Mechanism on IrO_2(110) - A Comprehensive DFT Analysis Beyond Traditional Pathways

MUHAMMAD USAMA[1], SAMAD RAZZAQ[1], CHRISTOF HÄTTIG[2] and KAI S. EXNER[1]

[1] *Universität Duisburg-Essen, Universitätstr. 5, 45141 Essen, Germany*
[2]*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum*
muhammad.usama@uni-due.de

ABSTRACT

The oxygen evolution reaction (OER) serves as a cornerstone for sustainable energy technologies, particularly in proton exchange membrane (PEM) electrolyzers for renewable hydrogen production. While IrO_2-based materials reign supreme due to their exceptional activity and stability, a thorough understanding of the OER mechanism on even the well-defined (110) facet of single-crystalline IrO_2 remains elusive as there are different reports on the elementary steps governing the kinetics of the oxygen-evolution reaction (OER) mechanism in the literature [1, 2].

In this contribution, we present a comprehensive density functional theory (DFT) investigation that disentangles the discrepancies surrounding the OER mechanism on a single-crystalline IrO_2(110) model electrode [3]. Crucially, we incorporate Walden-type mechanisms [4], where O_2 formation and H_2O adsorption occur concurrently, into our analysis of the elementary OER steps on IrO_2(110). This inclusion clearly goes beyond traditional approaches where it is tacitly assumed that the vacant metal site is part of the catalytic cycle. Employing the concept of free-energy diagrams along the reaction coordinate, coupled with Bader charge analysis of the active site under constant potential, we provide insights into why mononuclear- or bifunctional-Walden pathways outperform the traditional OER mechanisms for IrO_2(110). Our detailed analysis sheds light on the underlying factors that influence the reaction kinetics and paves the way for the development of superior OER electrocatalysts.

References

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