Research Project #11

Oxygen Evolution and Dissolution Mechanisms on IrO_2 and RuO_2 Model Electrodes (IET-2, IET-3 & IET-4)

Context: Green hydrogen production via water electrolysis is essential for storing surplus renewable energy. Among available technologies, proton exchange membrane water electrolysis (PEMWE) is considered the most suitable. However, its reliance on Ir-based catalysts for the oxygen evolution reaction (OER) makes the technology prohibitively expensive. Current state-of-the-art catalysts suffer from dissolution, requiring high loadings of iridium and other PGMs (platinum-group metals) to slow down degradation. To reduce costs, catalyst loadings must be lowered without sacrificing performance, which demands materials that are both more active and more stable. Achieving this is challenging because activity and stability are often negatively correlated [1]. It has been proposed that OER and Ir dissolution share common intermediates: the OER pathway destabilizes the catalyst through formation and cleavage of metal–oxygen bonds, involving both adsorbates and lattice oxygen [2]. Stabilizing these bonds could enhance durability, but according to the Sabatier principle, overly strong binding may reduce OER activity, an argument that holds only if the reaction mechanism remains unchanged. Recent theoretical studies indicate that fundamental differences in OER mechanisms can explain the distinct activity and stability properties among PGM-oxide catalysts [3], and surface defects can introduce additional mechanistic pathways [4]. Moreover, distinct crystallographic orientations of IrO_2 and RuO_2 were found to exhibit different OER activities [5]. Despite these observations, the structure–performance relationships governing OER activity and stability on IrO_2 and other PGM-oxide catalysts remain poorly understood.

Aims: The overall goal of this project is to establish a mechanistic framework that explains both the OER and catalyst dissolution pathways on well-defined oxide model electrodes with controlled structure, morphology, and composition. This framework will guide the rational design of advanced electrocatalysts that simultaneously achieve high activity and high stability, ultimately enabling the replacement of Ir with more abundant and cost-effective elements such as Ru or even non-noble metals.

State of the art: Given its industrial relevance, the OER on Ir oxide electrodes has been intensively studied for decades. A major milestone was the experimental detection of IrO_3, proposed as a key intermediate in both OER and Ir dissolution [6]. This finding enabled refinement of existing mechanistic pathways and helped rationalize structural effects in the OER, such as differences between amorphous and crystalline Ir oxides. However, these insights were largely derived from ill-defined electrodes, which limit atomistic interpretation. A deeper mechanistic understanding can be achieved using single-crystalline electrodes, as demonstrated for Pt. There, the combination of experimental data on surface oxidation and dissolution with density functional theory (DFT) calculations of phase stability led to a comprehensive model explaining Pt dissolution during initial oxidation and during partial reduction of bulk-like oxides [7]. Extending this approach to Ir and Ru oxides is more challenging due to the scarcity of high-quality single-crystal IrO_2 and RuO_2. Recent advances in molecular beam epitaxy (MBE) and pulsed laser or arc plasma deposition have now enabled the fabrication of such model electrodes for electrochemical applications [5, 8]. Preliminary studies have already shown that OER activity depends strongly on the surface structure. However, dissolution was assessed only ex situ, revealing no clear trends in stability. While these initial findings reveal differences in activity and stability, they do not provide the mechanistic insight needed to explain them. Without this understanding, rational design of improved catalysts remains challenging.

Work plan: This collaborative project combines expertise available at different research units of the Research Center Jülich (FZJ), i.e., in experimental OER and catalyst stability (IET-2), vibrational spectroscopy at catalytic surfaces (IET-4), and theoretical electrocatalysis (IET-3) to develop a mechanistic framework for OER and catalyst dissolution. A PhD student will be hired to set up and validate the experimental work at IET-2, while spectroscopic and theoretical studies will be supported through collaboration with IET-4 and IET-3. Well-defined IrO_2 and RuO_2 facets, initially (001) and (110) and later other orientations, will be prepared by Prof. Holtz's group using the recently established MBE method [8].

The OER activity and dissolution kinetics will be measured using online ICP-MS. Only minor modifications to the setup will be required to increase the Ir detection limit, achieved by minimizing the electrolyte-to-electrode-area ratio. The small electrode area enables high-throughput screening, allowing rapid accumulation of a large dataset for further theoretical analysis. The project will systematically explore the effects of electrode potential, time, temperature, and pH on OER and Ir/Ru dissolution. Electrodes exhibiting extreme performance metrics will be selected for detailed mechanistic studies using *in situ* IR and Raman spectroscopy combined with X-ray photoelectron spectroscopy (XPS). In parallel, DFT calculations will be employed to model surface phases, reaction intermediates, and dissolution pathways, integrating experimental and theoretical insights into a unified framework. The framework will guide the design, preparation, and testing of model electrodes with enhanced functionality. The focus will be on replacing Ir with Ru and on improving surface stability through strategies such as surface modification and doping with Ti, Nb, or Ta.

Outcomes: The overall outcome of this project will be the establishment of a comprehensive experimental-theoretical framework for understanding the activity and stability of OER electrocatalysts for PEMWE. This framework will include improvements in the online ICP-MS setup aimed at lowering detection limits, the development of systematic experimental testing procedures considering variables such as potential, time, temperature, and pH, and the integration of spectroscopy with theoretical modeling to gain deeper insights into the coupled mechanisms and intermediates of OER and catalyst corrosion processes. Application of this framework to a variety of materials will enable a better understanding of structure–activity–stability relationships in OER electrocatalysis and support the development of active and stable catalysts with minimal or no Ir content, thereby reducing the cost of green hydrogen production. The PhD student will receive in-depth training and supervision in a network of dedicated experts in experimental and theoretical electrocatalysis, strengthening the collaboration between different FZJ units and the exchange in a vivid group of fellow PhD students. Results of this project will be disseminated through scholarly journals and conference presentations.

Location of the HITEC Fellow	Forschungszentrum Jülich, Institute of Energy Technologies - Helmholtz-Institute **Erlangen-Nürnberg** for Renewable Energy (IET-2 / HI ERN), Director: Prof. Dr. Karl Mayrhofer https://www.hi-ern.de/en
Partners of the HITEC Project	Forschungszentrum Jülich, Institute of Energy Technologies - Theory and Computation of Energy Materials (IET-3), Director: Prof. Dr. Michael Eikerling https://www.fz-juelich.de/en/iet/iet-3 Forschungszentrum Jülich, Institute of Energy Technologies - Electrochemical Process Engineering (IET-4), Director: Prof. Dr. Ralf Peters https://www.fz-juelich.de/en/iet/iet-4
Specific **requirements**	M.Sc. in Chemistry, Physics, Material Science, or equivalent. Good knowledge of physical chemistry and surface science.
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