

## Abstract

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### **Electrochemical and light-driven water splitting tracked by *operando* X-ray spectroscopy**

**Co-supervisor 1: Prof. Dr. Holger Dau, FU Berlin**

**Co-supervisor 2: Prof. Dr. Peter Strasser, TU Berlin**

In the worldwide strive for reduction of CO<sub>2</sub> emissions, the sustainable production of synthetic fuels plays a key role. Their production requires the efficient oxidation of water, also called oxygen evolution reaction (OER), powered by renewable electricity or in artificial photosynthesis devices, directly by sunlight. Inspired by biology, but aiming at knowledge-guided optimization of inorganic catalyst materials, we employ *operando* spectroscopy for following the reactions directly during operation of the catalyst material. The thesis project aims at investigation of structural changes of OER catalyst materials in the time domain from below one millisecond to tens of seconds. They are tracked with optical spectroscopy and X-ray absorption spectroscopy, the latter at the Berlin synchrotron radiation source (BESSY). For selected model catalysts, electrochemical and photochemically induced processes are investigated in novel time-resolved experiments, targeting changes in atomic and electronic structure. The prospective PhD student should be interested in (electro)chemical energy conversion and advanced physical experiments.

## Extended description version of the project

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#### 1. Overall goal of the project

It is the overarching goal to contribute to development of systems for sustainable production of alternative, synthetic fuels. These fuels are important because they can (i) store volatile renewable energies like wind or solar energy and (ii) can replace directly fossil fuels, e.g., in the transportation sector. In their production, it is mostly essential to split water into electrons, protons and molecular oxygen (denoted as water oxidation or oxygen evolution reaction, OER). Efficient OER requires excellent catalyst materials. This thesis project is on a new route of physical-chemical investigation of OER catalyst materials.

For selected (especially promising) materials, the project aims at improved understanding of electrochemical and photo(electro)chemical OER reaction kinetics (How fast?) and reaction mechanism (Why is it so fast?) by *operando* spectroscopy—as a basis for optimization of the catalyst materials. *Operando* spectroscopy has been applied successfully before for investigation of electrocatalytic materials equilibrated at various electrode potentials. The project targets advancement beyond the state-of-the art, by adding time-resolved *operando* experiments to the tool box of catalysis researchers.

#### 2. State of the art

[For an introduction to electrochemical, molecular, and biological OER, see ref.<sup>1</sup>. In the following, our own studies are cited, which contain many further references. For simplicity, 'oxide' is used to denote also oxyhydroxides and layered double-hydroxides abbreviated as LDH.]

Water oxidation is catalyzed by the protein-bound  $\text{Mn}_4\text{CaO}_5$  cluster of photosynthetic organisms, by molecular transition-metal complexes, catalyst films on electrodes (electrochemical water oxidation) or surfaces of photoactive semiconductors. Essentially all OER catalysts contain transition metal ions<sup>1</sup>. For electrochemical OER, electrodes have been coated with numerous materials. Co and Mn oxides are of high interest for water oxidation at near-neutral pH<sup>2</sup>; various NiFe oxides are among the best catalytic materials for alkaline water oxidation<sup>3</sup>, but also other materials, e.g., helical borophosphates were highly efficient. Catalytic OER oxides can be obtained by simple electrodeposition methods or by synthesis of complex materials, often involving nanoparticles.

A fascinating feature of OER catalyst materials is that they are dynamic: oxidation-state changes take place which are coupled to structural changes involving proton movements. These relate to proton-coupled electron transfer (PCET) as well as catalyst activation or deactivation (corrosion) and self-repair. These can be followed by X-ray absorption spectroscopy (XAS, XANES and EXAFS)<sup>2 4 3 5</sup>. Recently experiments have been developed to track investigate the structural catalyst dynamics during operation of the catalyst material in an aqueous solvent, which are denoted as "*operando*" or "*in situ*" experiments<sup>2 4 3</sup>. Oxidation state changes taking place in the sub-second time domain of have been followed in preliminary experiments<sup>4 3</sup>. Recently we improved the time-resolved

operando-XAS experiment by energy-resolved single-photon detection (unpublished). Time-resolved experiments with visible light can complement the X-ray experiments<sup>4 6</sup>.

### 3. Specific aims and how they may be reached

#### ➤ Objectives, work packages

WP1: Detecting sub-second changes in oxidation state and atomic structure for a previously investigated, electrodeposited OER electrocatalyst with operando spectroscopy. (1<sup>st</sup> year)

WP2: Investigating sub-second changes in oxidation state and atomic structure for a new type of OER electrocatalyst by operando spectroscopy, for variation of one synthesis parameter. (2<sup>nd</sup> year)

WP3: Investigating light-induced changes in oxidation state and atomic structure for one selected photochemical system. (3<sup>rd</sup> year)

For WP1, WP2, and WP3: Interpretation and publication of results with focus on reaction mechanisms and optimization of catalyst performance.

#### ➤ Training and experimental strategies

Training in basic and advanced electrochemistry, catalyst electrodeposition, elementary analysis by X-ray fluorescence methods, UV/visible absorption spectroscopy, and optional FTIR or operando Raman spectroscopy, X-ray absorption spectroscopy (XAS)<sup>1-5</sup>.

At the Berlin electron synchrotron (BESSY), we will have the opportunity to pursue X-ray experiments for ca. 8 weeks per year. This is intense work pursued in a team and also involving night shifts. A combination of electrochemistry with UV/visible spectroscopy<sup>4 6</sup> will complement the time-resolved operando-XAS experiments pursued at the BESSY synchrotron.

#### ➤ Planned collaboration partners include the synthetic groups of Prof. Matthias Dries and Prof. Kallol Ray and regarding light-induced processes, Prof. Roel van de Krol (photoelectrocatalysis with semiconductor materials) and possibly Prof. Holger Dobbek (light-induced reactions in semi-artificial metalloproteins).

### References

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