# Surface state of nanocrystalline RuO$_2$-based electrocatalysts probed by soft XAFS

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## Introduction

The perspectives of photo-electrochemical solar energy conversion and the development of sustainable chemical technologies attract considerable attention to the topic of electrochemical gas evolution reactions. Conducting oxides with rutile structure such as RuO$_2$, IrO$_2$ and PtO$_2$ present the benchmark electrode materials for electrochemical oxygen and chlorine evolution. In particular, ruthenium oxide is widely used for the anodes in electrolysis and as a co-catalyst in combination with photocatalysts for water splitting. Recent theoretical works [1, 2] on electrocatalytic O$_2$ and Cl$_2$ evolution on rutile-type oxides link the activity to the surface structure of these materials. At the same time it is little known about real structure of the surface layer of nanocrystalline RuO$_2$ materials. The objective of this project is to probe the atomic arrangement in the surface layer by use of soft XAFS and to explore the changes in the structure and electronic state of ions in the course of electrocatalytic oxygen evolution on RuO$_2$-based electrodes.

## Experimental

XAFS data were collected at BL-11A and BL-11B beam lines for pure RuO$_2$ and materials doped with Co and Ni. The series of the samples included as-prepared nanocrystalline powders of electrocatalysts and the materials after the electrochemical reaction. Two detection modes were used simultaneously by recording total electron yield (TEY) and by collecting Auger electrons emitted by the samples (AEY – Auger electron yield). Additionally the external bias of 100V was applied to the mesh placed in front of the electron detector, which should confine XAFS data collected as AEY to the surface of the material within less than 10 atomic layers. The experimental data were normalized and processed using IFEFFIT software package [3]. The full profile refinement of overlapping EXAFS spectra for the Ru-L1, 2, 3 edges (3224eV, 2967eV and 2838 eV) was carried out by GNXAS2 program [4].

## Results and Discussions

The first stage of the project aimed at the development of the methodology for data acquisition and local structure refinement of overlapping X-ray absorption spectra at L1, L2 and L3 edges. The small energy separation of ~130eV between L3 and L2 edges in the case of soft EXAFS does not allow to use conventional approach for analysis of EXAFS data. Therefore, a more complex method for modeling of $\chi(E)$ vs. E data had to be employed. First, we had to determine the correct atomic background functions, which would include the double-electron excitation events for Ru. To obtain precise values, we used theoretically predicted energies for Ru [5] and refined them using EXAFS data of Ru metal, which has relatively simple crystal structure. It turned out that the adequate refinement could be achieved if one takes into account three excitation energies with the refined values of 65.6, 305 and 520 eV, which correspond to $4p_{1/2}$, $3d_{5/2}$ and $3p_{1/2}$ excitations [5]. The contribution of the other excitation channels to atomic background was found to be insignificant. These refined energies were used to formulate the model for the refinement of local structure of RuO$_2$ using TEY and AEY data. Table 1 compares the results of the local structure refinement using conventional approach [6] for bulk samples, when the data were collected at the NW-10A beam line, with the refined values for TEY and AEY data at L- absorption edges. One may notice rather good agreement between

Table 1: Refined interatomic distances and DW parameters for pure RuO$_2$ using conventional Ru-K edge data and Ru-L EXAFS data at TEY and AEY

| Bond | Ru-K | | Ru-L (TEY) | | Ru-L (AEY) | |
|---|---|---|---|---|---|---|
| | d,Å | $\sigma^2 \times 10^3$ | d,Å | $\sigma^2 \times 10^3$ | d,Å | $\sigma^2 \times 10^3$ |
| Ru-O×2 | 1.983 | 2.2 | 1.991 | 2.6 | 1.99 | 2.5 |
| Ru-O×4 | 1.921 | 2.2 | 1.929 | 2.6 | 1.932* | 2.5 |
| Ru-Ru | 3.109 | 2.5 | 3.123 | 2.9 | 3.090 | 2.5 |

* Refined CN=3.5

refined parameters of local structure when conventional Ru-K data and Ru-L data collected in terms of TEY (sensitive to the bulk) were used. At the same time the AEY data (sensitive to the surface information) show that within the surface layer of the material the bonds tend to be shorter and the refinement had to anticipate possible oxygen deficiency.

## References

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