

The objective of the project is to use a combination of the targeted synthesis of nanocrystalline oxide synthesis with X-ray absorption spectroscopy to a) link the reactivity of oxide electrocatalysts in oxygen and chlorine evolution with local structure of electrocatalysts, b) identify the active sites for oxygen and chlorine evolution processes and c) develop the strategies for design of electrocatalysts with tailored properties.

To achieve the project's objectives a sequence of nanocrystalline ruthenium based oxides doped with Ni, Co, Fe and Zn. Prepared materials were characterized in terms of electrocatalytic activity and selectivity. The local structure of the prepared oxides was assessed by means of X-ray absorption spectroscopy both ex-situ and in-situ, i.e. at conditions of the electrocatalytic oxygen and chlorine evolution.

It was found that the heterostatic doping of the catalyst's structure leads to clustering of the dopant in the host oxide matrix. The formed clusters of the dopants can be viewed as extended defects in the catalysts structure. The nature of these defects depends on chemical nature of the dopant and on the dopant content as well. The structure of the dopant clusters conforms to rock salt (in the case of the Ni doping), pseudobrookite (in the case of Co and Fe doping) or ilmenite (in the case of Zn doping) structural types. These extended defects grow in the host oxide matrix first along the (111) direction, changing later into zig-zag arrangements eventually developing shear planes of the (121) or (232) orientations. Heterostatic doping of the original oxide catalyst as a rule improves the catalytic activity; all prepared materials with exclusion of the materials doped with zinc, however retain high selectivity towards chlorine evolution. In the case of the material doped with zinc the selectivity of the materials sharply changes in the favor of the oxygen evolution process (see Fig. 1). The change in the selectivity of the electrocatalysts can be linked to disruption of the cation stacking along (001) direction of the rutile structure which represents the active site for both processes.

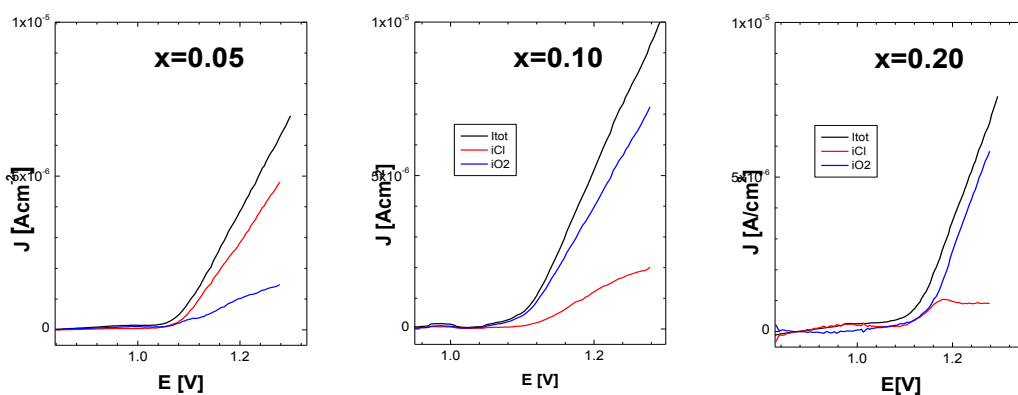


Figure 1. Current density (black) corresponding to parallel oxygen (blue) and chlorine (red) evolution during polarization of Zn doped ruthenium dioxide in 300 mM NaCl, 0.1M  $\text{HClO}_4$  at 5 mV/s. The actual Zn content is shown in Figure legend.

The behavior of the Zn doped oxides can be attributed a large social impact. It has to be recognized that currently introduced renewable sources of electrical energy (based on solar and wind) assume the storage of the excess electricity via controlled water electrolysis and connected hydrogen economy. It is often overlooked that the availability of the fresh water represents a bottleneck whole concept. In this respect the ability to control the selectivity of the anodic gas evolution catalysts in favor of oxygen evolution represents a significant progress allowing the electrolysis of seawater into the whole concept.