The electrochemical behavior of ruthenium dioxide electrodes has been intensively investigated due to its electrocatalytic activity towards chlorine evolution reaction (CER)[1] and oxygen evolution reaction (OER)[1]. In this study, the effect of nanocrystal size/shape on the electrocatalytic behavior of RuO$_2$ was examined.

The samples were prepared using a sol-gel approach [2]. Synthesized amorphous precursor was annealed at 400, 500, 600, 700, 800 and 900°C in air in order to obtain nanocrystalline single-phase RuO$_2$ (rutile) samples of variable particle size. The samples were studied by XRD and TEM (JEM 3010 - LaB$_6$, 300kV). The RuO$_2$ powders were used for preparation of the electrodes for electrochemical experiments. Electrodes were made by sedimentation from a water based suspension on Ti mesh until obtaining the surface coverage of about 1-2 mg/cm$^2$. The deposited layer was stabilized by annealing for 30 minutes at 400°C in air. Electrochemical behavior was studied by cyclic voltammetry combined with differential electrochemical mass spectroscopy (DEMS).

The crystal shape of the nanoparticles was determined from HRTEM images by indexing the faces present on the surface of the nanocrystals using the Fast Fourier Transform (FFT). The relative abundance of individual faces on the nanocrystal surface was estimated from the models of the shape of crystallites and related to the electrochemical measurements.

Typical particle size of RuO$_2$ powders ranges between 15 and 40 nm. Regardless of particle size the nanocrystals are of isometric shape with polygonal prismatic part capped with two pyramids (fig. 1). The prismatic part of the nanocrystals features {110} and {100} faces in the case of small nanocrystals (d<20 nm) and {110}, {100} and {140} in the case of bigger nanocrystals (d>20 nm). The pyramidal parts are formed by {101} faces regardless of the nanocrystal size.

The ability of the RuO$_2$ nanocrystals to act as electrocatalyst for oxygen evolution decreases with increasing particle size, while the activity of the same electrode towards chlorine evolution remains unchanged (fig. 2). The observed tendency indicates that the oxygen evolution is significantly affected by the crystal edges while chlorine evolution reaction proceeds mainly on crystal faces. The resulting enhanced selectivity of the bigger RuO$_2$ nanocrystals for chlorine evolution, arising from suppression of oxygen evolution, may be connected with absence of edges separating {110}-{100} faces on the prismatic part of the bigger nanocrystals. The {110}-{100} edges can be therefore regarded as the preferential site for recombination/decomposition of surface oxide to gaseous oxygen.

Figure 1: Shape analysis of samples annealed at 400 and 900°C. Along [1-1-1] direction, there is no difference except in the size of the crystal. In contrast, projection along [001] changes significantly. In the low temperature sample, only \{110\} and \{100\} faces are observed, whereas in the high temperature sample, faces with higher indices also appear.

Figure 2: Cyclic voltammogram (top), ion current corresponding to oxygen evolution (middle) and ion current corresponding to chlorine evolution (bottom) recorded on nanocrystalline RuO$_2$ electrodes annealed at 400 and 900°C. Oxygen evolution is significantly lower in the high-temperature sample (900°C), while the chlorine evolution remains unaffected, the onset of the anodic current coincides with the onset of ion current for oxygen evolution in the sample annealed at 400°C, while in the sample prepared at 900°C the onset of the anodic current does not match the threshold potentials of either of the expected reaction products.