

Zn-Doped RuO₂ electrocatalysts for Selective Oxygen Evolution: Relationship between Local Structure and Electrocatalytic Behavior in Chloride Containing Media

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Nanocrystalline electrocatalytically active materials of chemical composition Ru_{1-x}Zn_xO₂ (0 < x < 0.3) were synthesized by freeze-drying technique. The diffraction patterns of the prepared samples corresponded to single-phase rutile type oxides. Local structure of the Ru_{1-x}Zn_xO₂ based on refinement of Ru K and Zn K edge EXAFS functions shows clustering of the Zn ions in the blocks with ilmenite structure intergrowing with Ru-rich rutile blocks. Ru_{1-x}Zn_xO₂ oxides are selective catalysts for anodic oxygen evolution. The selectivity toward oxygen evolution in the presence of chlorides is affected by the actual Zn content and can be ascribed to structural hindrance of the formation of the surface peroxo group based active sites for chlorine evolution. The selectivity toward oxygen evolution in presence of chlorides is accompanied by the drop of the total activity, which gets more pronounced with increasing Zn content.

Introduction

The electrochemistry of anodic oxygen evolution reaction (OER) as well as the cathodic process of oxygen reduction represent the major challenges of modern electrocatalysis. The interest in both types of processes is fuelled by the importance of the practical applications, which include fuel cells,¹ (photo-) electrochemical water splitting,² or technical electrolysis in chlor-alkali industry.³ Although the oxygen reduction seems to be so far best controlled on metal electrocatalysts, the oxygen evolution proceeds only on oxide type surfaces. Rutile type conducting oxides such as RuO₂ or IrO₂ are industrial benchmark anode materials because of their outstanding chemical stability and remarkable electrocatalytic activity. One of the remaining issues of this type of catalysts is relatively poor selectivity toward oxygen evolution if the electrolyzed solution contains chlorides. The systematic theoretical approach to qualify the electrocatalytic processes on the rutile type oxides in oxygen and chlorine evolution reactions

(CER) was presented by Rossmesl and co-workers.^{4,5} The density functional theory (DFT)-based thermodynamic analysis predicts that both electrode processes are strongly correlated on rutile type oxide surfaces. In the case of oxygen evolution, it is stated that the process proceeds preferentially via surface peroxide-route⁴ when the formation of the surface oxo- or peroxo- species represents the rate-limiting step. Extending the same DFT approach to chlorine evolution process one finds that the surface peroxo-groups simultaneously act as the active sites in chlorine evolution. Therefore, the presence of chlorides alters the selectivity of the rutile type surface from oxygen evolution process toward chlorine evolution as a result of the competition between both processes for the same surface active site. In addition to the effects of pH and chloride concentration, the selectivity of the oxide surface is also influenced by the electronic properties of the electrocatalysts, which are in the given theoretical model represented by oxygen adsorption energy.^{4,5} In the case of RuO₂-based systems when oxygen adsorption energy nears 2 eV, it is predicted that the selectivity of the surface toward chlorine evolution results from the oxidative attack of the Cl⁻ on the surface peroxo groups connecting two Ru atoms along [001] direction. It has to be noted, however, that the results of the theoretical calculations are restricted to the processes proceeding on crystal faces and do not account for reactivity of the sites with lower dimensionality (e.g., crystal edges, vertices, or defects), which may play a significant role in real nanocrystalline catalysts.⁶

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