

**In situ Probing Active Centers of Ru Chalcogenide Electrocatalysts during Oxygen Reduction using EXAFS Spectroscopy**

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Investigation of the mechanism of the oxygen reduction reaction (ORR) is of key importance for both fundamental electrochemistry and development of fuel cells, in particular direct methanol fuel cells (DMFC). The disadvantage of Pt, the main cathode material for DMFC, is its depolarization due to the methanol crossover in the polymer (Nafion®) electrolyte. Therefore, a search for new materials catalytically active and selective in the ORR, is in progress.

In the present communication a family of novel catalysts for oxygen electroreduction is presented, based on nanostructured  $Ru_xX_y$  chalcogenide compounds ( $X = S, Se, Te$ ). These were prepared using a low temperature synthetic procedure, previously reported for  $Mo_xRu_ySe_z$  clusters ( $0.02 < x < 0.04, 1 < y < 3, z \approx 2y$ )<sup>1,2</sup>, and showed a high catalytic activity in oxygen electroreduction.  $Mo_xRu_ySe_z$ , which has been studied most thoroughly, provides four-electron mechanism for the ORR.<sup>2</sup> The activity of  $Ru_xX_y$  catalysts depends on chalcogene and increases in the range:  $Ru_xS_y < Ru_xTe_y < Ru_xSe_y \sim Mo_xRu_ySe_z$ .

EXAFS spectroscopy proves that the catalysts have a core of ruthenium atoms which has triangular co-ordination and a direct metal-metal bond. Depending on the chalcogene, the Ru-cluster consists of two or three metal layers of different size and mutual co-ordination. It is likely that chalcogene is coordinated outside the metal clusters and provides the binding of Ru triangle units to each other. Variation of the chalcogene affects the size of the Ru-cluster and the strength of its interaction with the chalcogene. This affects the interaction of Ru-clusters with oxygen and thus their activity in the ORR.

The transformations of the  $Ru_xX_y$  catalysts were followed in situ during the ORR using EXAFS spectroscopy in the transmission mode. Reversible changes of the spectra were revealed in the course of the electrochemical reaction (typical FT of the EXAFS spectra for  $Ru_xTe_y$  are represented in Figure 1). The observed changes were interpreted as a transformation of the structure of the active center. Thus, the shift of the potential in the anodic direction from 0.08 to 0.78 V/RHE in the presence of oxygen resulted in an increase of the Ru-O and simultaneous decrease of the Ru-Ru apparent co-ordination numbers in the first co-ordination shell of Ru (Figure 2). Along with the variation of the co-ordination numbers we observed reversible changes of the co-ordination distances: a decrease of the Ru-O and an increase of the Ru-Ru distance with the positive polarization. These changes witness the distortion of the catalytic center upon oxygen adsorption.

A tentative mechanism of oxygen activation on  $Ru_xX_y$  cluster materials will be discussed on the basis of the *in*

*situ* EXAFS data. The experimental results favor dissociative adsorption of molecular oxygen onto the  $Ru_xX_y$  active centers, which apparently accounts for the four-electron mechanism of the reaction.

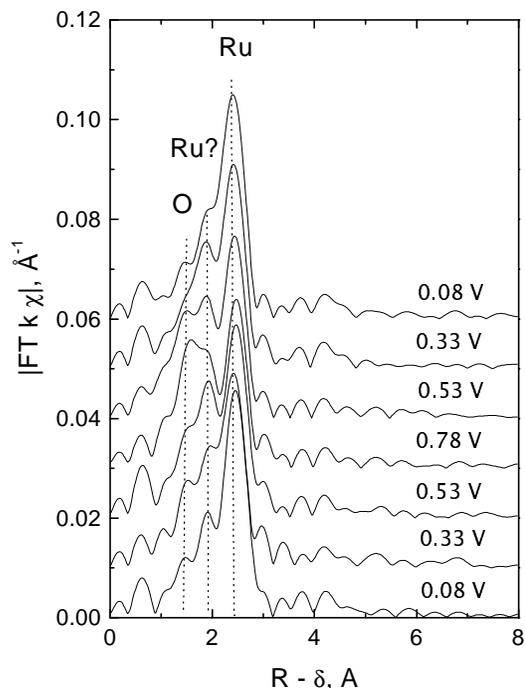


Figure 1. *In situ* EXAFS Fourier-transform moduli ( $k^1$ -weighted) for  $Ru_xTe_y$  catalyst as a function of the electrode potential during ORR.

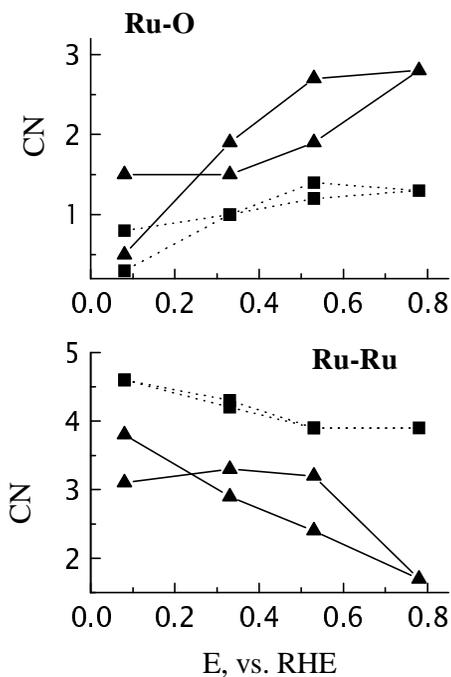


Figure 2. Plots of the Ru-O (top) and Ru-Ru (bottom) apparent co-ordination numbers in the first Ru shell vs. the electrode potential for  $Ru_xTe_y$  sample in Ar (solid line) and  $O_2$  (dotted line) atmosphere.

1. Solorza-Feria, O.; Ellmer, K.; Giersig, M.; Alonso-Vante, N. *Electrochim. Acta*, **1994**, *39*, 1647.
2. Alonso-Vante, N.; Tributsch, H.; Solorza-Feria, O. *Electrochim. Acta*, **1995**, *40*, 567.