C-O and C-O-Se containing ruthenium catalysts studied by Extended X-ray Absorption Spectroscopy (EXAFS)

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It was demonstrated by Alonso-Vante and Solorza [1-2] that catalysts based on Ru, Se and Mo can be used for oxygen reduction in Polymer Electrolyte Membrane (PEM) fuel cells. Recently, we have demonstrated that the low overvoltage in the 4-electron-reduction process of oxygen is independent of the Se and Mo content in the samples [3]. In desorption measurements it was found that the catalyst prepared from Ru$_3$(CO)$_{12}$ released considerable amounts of the gas species CO and CO$_2$ upon heating in vacuum, which belong to an amorphous layer protecting the metallic core of Ru nanoparticles detected by XRD. Also in Se containing catalysts, no crystalline Ru$_x$Se$_y$ phase could be detected by XRD at temperatures below 400°C. To elucidate Ru-Se, Ru-O and Ru-C distances of the amorphous part of the catalyst EXAFS measurements were performed at the RÖMO II X1.1 station at HASYLAB.

The spectra were monitored in transmission mode at the Ru and the Se edge using pellets of the catalysts diluted by BN powder.

Figure 1 shows spectra of the as grown and heat treated, carbon supported Ru-Se catalysts. As references simulated and measured EXAFS profiles of crystalline phases such as RuO$_2$, RuSe$_2$, RuC and Ru$_4$Se$_4$(CO)$_{12}$ are depicted.

Catalysts prepared by thermolysis of Ru$_3$(CO)$_{12}$ in a Se saturated xylene solution weakly showed the EXAFS pattern of Ru metal and additional features which can be addressed as Ru-Se, Ru-C and Ru-O bondings. The Ru EXAFS pattern becomes dominant heating the catalysts to 450 and 900°C, respectively (Fig. 1).

From XRD measurements it is known that with increasing temperature the Ru particles coalesce increasing from 4 nm to 20 nm in size. Ru oxides and selenides present in the catalyst remain amorphous even after heat treatment as long as the catalyst is carbon supported. Otherwise the crystalline phases RuO$_2$ and RuSe$_2$ appear.

Inferring the Ru-Se distance by adjusting EXAFS profiles it was found that the distance in the as grown material amounts to a value of $d_{\text{Ru-Se}} \approx 2.56$ Å which is typical for metal organic compounds such as Ru$_4$Se$_4$(CO)$_{12}$ [4]. The Ru-C and Ru-O distances are 1.95 Å and 1.6 Å, respectively. After annealing of the catalysts at 450°C and 900°C both distances become close to those met in Ru$_2$Se$_2$ and RuO$_2$. This behaviour can be explained by the presence of ruthenium oxides or hydroxides and metal organic complexes covering the surface of the Ru nanoparticles. However, the observation that the catalytic activity can be increased by heat treatment of the catalyst in vacuum, where the most of such complexes thermally decompose, might be an indication that the presence of the complexes is sufficient but not necessary to achieve high catalytic activity of this catalyst.
Figure 1. Fourier transform of EXAFS spectra of three Ru catalysts as grown and heat treated as well as the reference spectra RuSe₂, RuO₂, RuO₂ and Ru₄Se₄(CO)₁₂.

References