Combined *in situ* EXAFS and electrochemical investigation of the oxygen reduction reaction on unmodified and Se-modified Ru/C

Konstantin N. Loponov [a,1], Vladimir V. Kriventsov [a], Kyatanahalli S. Nagabhushana [b,2], Helmut Boennemann [b], Dimitrii I. Kochubey [a], Elena R. Savinova [c,*]

[a] *Boreskov Institute of Catalysis, Russian Academy of Sciences, Pr. Akademika Lavrentieva 5, 630090 Novosibirsk, Russia*
[b] *Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz-1, D 45470, Mülheim an der Ruhr, Germany*
[c] *l'Ecole Européenne Chimie Polymères Matériaux, Université de Strasbourg, UMR 7515 du CNRS-UdS-ECPM, 25, rue Becquerel, F-67087 Strasbourg, France*

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ABSTRACT

In this work we study the kinetics of the oxygen reduction reaction on carbon-supported Ru nanoparticles modified with various amounts of Se. Rotating disk electrode is used to determine kinetic currents for the ORR in 0.1 M H_2SO_4 at 298 K and O_2 partial pressures from 1 to 0.01 atm. The dependence of the ORR activity on Se/Ru ratio shows volcano-type behavior with ca. 10 fold increase of the mass activity at $0.1 <$ Se/Ru < 0.3. The reaction order in O_2 is close to 1 in the interval of overpotentials from 0.4 to 0.7 V, and is independent of the presence of Se. Regardless the amount of Se, the Tafel slope demonstrates continuous increase from ca. 70 mV/dec at 0.4 V to ca. 140 mV/dec at 0.6 V overpotential. *In situ* EXAFS spectra are measured at Ru K-edge (in the transmission mode) and Se K-edge (in the fluorescence mode) in argon and oxygen saturated 0.1 M H_2SO_4 solutions in the interval of electrode potentials from 0.050 to 0.750 V RHE. The data are used to explore the surface state changes of Ru and Ru_xSe_y particles and clarify the promoting role of Se during the ORR.

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1. Introduction

The Oxygen Reduction reaction (ORR) is one of the most complex and technologically important electrochemical reactions. High ORR overpotential is the source of major voltage losses in polymer electrolyte fuel cells [1]. Despite numerous efforts, the ORR mechanism has not been fully understood yet even for Pt electrodes, although these have been studied most extensively (see, e.g. review articles [2–6]). Hence, investigation of the ORR on various electrode materials continues attracting attention of experimentalists as well as of theoreticians.

In direct methanol fuel cells (DMFCs), methanol crossover through the polymer membrane from the anode to the cathode compartment with concomitant depolarization of the Pt cathode adds to the voltage losses decreasing efficiencies of DMFCs. Ruthenium-based cluster compounds containing selenium (Ru_xSe_y) have been introduced by Alonso Vante et al. [7–9] as methanol tolerant ORR catalysts. A method to prepare mixed non-stoichio-

metric Ru_xSe_y cluster materials has been suggested [9]. Later it has been found that the catalysts contained "Se-decorated" Ru particles rather than stoichiometric Ru_xSe_y compound [10–12]. Since then various procedures have been explored to prepare unsupported as well as carbon-supported Ru_xSe_y catalysts, which were investigated using electrochemical and structural methods [13–22]. However, despite numerous investigations, no consensus concerning the mechanism of the ORR on Ru_xSe_y catalysts and the role of Se in the enhancement of the catalytic activity has been reached yet.

In order to better understand the structure of Ru_xSe_y catalysts we have recently undertaken a systematic study of the structure evolution upon modification of carbon-supported Ru nanoparticles with the increasing amounts of Se [23]. Using a combination of TEM, XRD, XPS and EXAFS we have shown that deposition of Se on the surface of Ru nanoparticles results in formation of core-shell structures with hcp Ru core containing Ru selenide in their outer shell. Recently [24], the ORR kinetics on these catalyst samples was investigated using differential electrochemical mass spectrometry and double-disk electrode thin-layer flow-cell measurements. The authors have confirmed that modification of Ru/C catalyst with Se improves the ORR activity and reduces the tendency for H_2O_2 formation in the technically relevant potential region of 0.6–0.8 V vs. RHE.

The objective of this work is to better understand the role of Se in the ORR. We thus explore the kinetics of the ORR on Ru catalysts

modified with different amounts of Se with RDE at different O_2 partial pressures, and complement this data with *in situ* EXAFS investigation of the catalysts at Ru K and Se K-edge under the reaction conditions.

2. Experimental

2.1. Catalysts preparation and characterization

Preparation of Vulcan XC-72 supported Ru nanoparticles modified with various amounts of Se and their structural characterization with high resolution transmission electron microscopy (HRTEM), EDX, XRD, XPS and EXAFS has been described in detail in Ref. [23] and will be mentioned in this paper in as much as necessary for further discussion. Se-modified Ru/C samples with Se:Ru ratio from 0 to 1 (Table 1), were prepared by reacting carbon-supported 20 wt.% Ru/Vulcan XC-72 nanoparticles with SeO_2 in THF–water (1:1, v/v) mixture followed by reduction in a H_2 flow at 200 °C. The particle size for pristine Ru nanoparticles as determined in Ref. [23] from the particle size distributions reconstructed from TEM images was $d_N = \sum_i N_i d_i / \sum_i N_i = 3.9$ nm (number-average) and $d_S = \sum_i N_i d_i^3 / \sum_i N_i d_i^2 = 5.0$ nm (surface-average). Structural studies have confirmed that when Se is allowed to react with Ru nanoparticles, the size of *hcp* Ru core decreases, and a shell comprising Ru selenide is formed on the surface. The mass-average size of Ru core determined with XRD is given in Table 1.

2.2. Electrochemical measurements

Electrolyte solutions were prepared from Milli-Q water (18 MΩ cm) and H_2SO_4 (Suprapure, Merck or suprapure, Russia). The oxygen reduction kinetics on carbon-supported Ru_xSe_y catalysts of different composition was studied using rotating disc electrode (RDE). Thin catalyst layers were prepared by pipetting from 10 to 20 μl of aqueous suspension containing 1.5 mg ml^{-1} of Ru_xSe_y/Vulcan and 0.15 mg ml^{-1} Nafion® on the face (0.20 cm^2 geometric area) of a glassy carbon (GC) rod (polished to a mirror finish and cleaned in the ultrasonic bath in ethanol, acetone and water) and drying under the Ar flow. Nafion® was added in order to better spread the catalyst on the GC support and improve the adhesion. The resulting films were mechanically stable, and showed reproducible cyclic voltammograms (CVs). After each experiment Ru_xSe_y/Vulcan was removed from the substrate by wiping the surface under a water flow. Electrochemical measurements were carried out in a three-electrode cell at 298 K in 0.1 M H_2SO_4 solution saturated with Ar/O_2 mixtures containing 1, 3, 10, 50 and 100% O_2. The counter electrode was Pt foil and the reference electrode—mercury sulfate electrode (MSE) Hg/Hg$_2$SO$_4$/0.1 M H$_2$SO$_4$ connected to the working electrode compartment via Luggin capillary. Potentials were controlled using Autolab PGSTAT30 potentiostat and are quoted vs. reversible hydrogen electrode RHE (E_{MSE} = 0.73 V vs. RHE).

2.3. EXAFS measurements and data processing

In situ EXAFS spectra at Se K and Ru K-edges were obtained at the EXAFS Station of the Siberian Synchrotron Radiation Center. The storage ring VEPP-3 with the electron beam energy of 2 GeV and the average stored current of 90 mA was used as the radiation source, and a channel cut Si(1 1 1) crystal as monochromator. EXAFS measurements were performed in two different three-electrode spectroelectrochemical cells filled with 0.1 M H_2SO_4 solution, the first adapted for transmission (Ru K-edge) using ionization chambers as detectors, the second for fluorescence (Se K-edge) mode. The working electrodes were prepared by spreading the suspension containing the catalyst powder and Nafion® in water:isopropanol (2:3) mixture on 190 μm thick Toray Paper. Isopropanol was added in order to improve spreading of the catalyst on the hydrophobic surface of the Toray Paper. The resulting catalytic layers contained ca. 2 mg/cm^2 of the catalyst with 10 wt.% of Nafion®. Pt was used as a counter and mercury sulfate as a reference electrode. Measurements were performed at room temperature first in Ar and then in oxygen atmosphere under potentiostatic conditions. In order to explore the influence of the electrode polarization on the catalyst structure the electrode potential was increased from 0.05 to 0.750 V RHE in a stepwise manner.

The EXAFS spectra were treated using the standard procedure [25,26] by "Viper" code [27,28]. The background was removed by extrapolating the pre-edge region onto the EXAFS region by Victoreen's polynomials. Three cubic splines were used to simulate the smooth part of the absorption coefficient. The inflection point of the edge of the X-ray absorption spectrum was used as the initial point ($k = 0$) of the EXAFS spectrum. The radial distribution function (RDF) was calculated from the EXAFS spectra in $k\chi(k)$ as the modulus of the Fourier transform in the wave number intervals 3.3–11.5 and 3.3–12.5 Å^{-1} for Se K and Ru K-edges, respectively. Curve fitting procedure with EXCURV92 [29] code was employed to determine the co-ordination distances R and the *apparent co-ordination numbers* CN in similar wave number intervals after preliminary Fourier filtering using known XRD data for the bulk compounds. In order to diminish the number of independent variables, the Debye-Waller factors for all samples under study were fixed at 0.005 Å^2. The choice of the Debye-Waller factor has proven to be a reasonable compromise and allowed minimizing distortion of the fitted spectra. The quality of fit indicator (R-factor) in all cases was much below 20%, which proved good quality of the fits and reliability of selected structural models [29]. In order to judge the quality of the fits, the model fits and the experimental data were compared both in R- and k-space. Fig. 1 allows the reader to judge the quality of the fits. The relative errors may be estimated as 10–20% in the co-ordination numbers and 1–2% in the distances [26,30].

3. Results and discussion

3.1. Polarization in inert atmosphere

3.1.1. Cyclic voltammetry

Fig. 2a shows CVs for 20%Ru/Vulcan XC-72 in 0.1 M H_2SO_4 acquired at two different upper electrode potentials. The anodic and the corresponding cathodic peaks can be observed in the potential interval from 0.03 to 0.15 V vs. RHE. At more positive potentials a shallow anodic peak emerges in the potential interval from 0.2 to 0.7 V with a cathodic counterpart around 0.3 V. Comparison of Fig. 2a–c reveals that modification of the surface of Ru nanoparticles with Se results in drastic changes in CVs (note different scales in Fig. 2a–c): (i) the double layer splitting shrinks indicating the decrease in the interfacial capacitance, (ii) the peaks

Table 1
Sample description.

No.	Description	Se:Ru (atomic ratio)	Abbreviation	Average size of Ru core[a], nm
1	20 wt.%Ru	0	Ru/C	5.5
2	17.3 wt.% Ru + 13.5 wt.%Se	1.0	Ru$_1$Se$_1$/C	~3
3	18.3 wt.% Ru + 8.5 wt.% Se	0.59	Ru$_1$Se$_{0.59}$/C	3.5
4	19.7 wt.% Ru + 4.5 wt.% Se	0.30	Ru$_1$Se$_{0.3}$/C	4
5	19.6 wt.% Ru + 2.2 wt.% Se	0.146	Ru$_1$Se$_{0.15}$/C	4

[a] From Ref. [23] as measured by XRD.