

**Preparation and physicochemical characterisation of novel Ru-based catalyst for oxygen reduction reaction**

Anna Dobrzyniecka<sup>a,\*</sup>, Magdalena Blicharska<sup>a</sup>,  
Jadwiga Stroka<sup>a</sup>, Paweł J. Kulesza<sup>a</sup>

*Department of Chemistry, University of Warsaw,  
Pasteura 1, PL-02-093*

*\*adobrzyniecka@chem.uw.edu.pl*

The essential element of the civilisation evolution is associated with development of new technologies and hence increasing energy demands. The small, portable energy sources are of particular interest. Therefore in recent years the fuel cells are intensively investigated. Despite of great development achieved in recent years in this field there are still some technological limitations demanding solutions. The attractiveness of fuel cells is hidden in the mechanism of their operations where direct conversion of chemical to electric energy provides high efficiency of this energy source. At the moment the most promising and best known type is hydrogen-oxygen fuel cell. The oxidation of fuel at anode is a fast process while the oxygen reduction reaction (ORR) is a process limiting the cell efficiency. Among oxygen reduction catalysts used in acidic environment the most often examined is platinum and its alloys due to their unquestionable high electroactivity towards ORR. Platinum as catalyst is exploited in wide range of industrial application. Moreover, it is very rare in the earth's crust. That caused violent rise of Pt prices on world's market what in turn contributed to the limited widespread development of "green" (ecofriendly) fuel cell technology. Additionally, the potential for oxygen reduction on platinum catalyst in direct alcohol fuel cells steeply decreases reaching the stationary lower value due to crossover of alcohol molecules from anodic compartment through fuel cell membrane. It has been widely described in the literature that Ru modified with selenium exhibits both high oxygen activity and methanol tolerance [1,2]. Recently, there was also developed a group of RuN<sub>x</sub> – chelates where the ruthenium clusters are coordinated to pyridinic nitrogen atom. These catalysts shows high catalytic activity for oxygen reduction with low generation of hydrogen peroxide intermediate.

In our previous work we described a novel catalyst which was the combination of N-chelates and Ru-based chalcogenides[3]. As a selenium and nitrogen source selenourea was utilized which can coordinatively bind to ruthenium ion[4] and be chemically linked with partially oxidized carbon supports. The Ru and selenourea content within precursor blend, the annealing temperature and atmosphere were optimized to get high ORR

activity of the catalyst. The catalyst of the highest activity was prepared with the molar ratio of Ru to selenourea (*SeU*) of about 1:1.9 where Ru ion is expected to be completely chelated by selenourea ligand. The RuSeN active sites were generated during reductive annealing at 400° C where generated particles are composed by RuSe<sub>2</sub> phase with crystallites size of approximately 3-5 nm, as discussed above from XRD studies. The studies were focused on investigation of influence of Se content on catalytic activity.

In the present work we studied the effect of carbon support used on properties of new Ru-based nanoparticles. Altered catalyst-carbon support interactions affect catalyst particle size, which in turn, affect catalyst activity and subsequent catalyst life. In comparison to previously [3] used Vulcan XC-72® we suspect that MWCNTs supported catalyst will show improved stability while high active area of Norit support enables fabrication of RuSeN/Norit (with kept constant metal loading) of higher Ru concentration in material. Hence, for the second system deposition of thinner layers at fuel cell membrane is possible and may improve mass transport and the efficiency of the fabricated cathode.

A second aim of our work will be studies of influence of nitrogen doping on catalytic activity of Ru-based catalyst. The problem will be investigated by modification of RuSeN- type catalyst with urea, as a source of additional nitrogen, or by its deposition at N-doped carbon support. The improved oxygen adsorption at these catalyst films is expected.

The synthesized catalysts will be subjected to physical characterization studies such as X-ray diffraction, X-ray photoelectron spectroscopy, energy dispersive X-ray spectroscopy and scanning and transmission electron microscopy. The resulting catalytic layers will be characterized using diagnostic electrochemical experiments including rotating ring-disk voltammetry. The Electrochemical Impedance Spectroscopy studies will be performed to determine the charge transfer resistance during O<sub>2</sub> reduction.

- [1] M. Bron, P. Bogdanoff, S. Fiechter, I. Dorbandt, M. Hilgendorff, H. Schulenburg, H. Tributsch, J. Electroanal. Chem., 500 (2001) 510
- [2] N. Alonso-Vante, Pure Appl. Chem., 80 (2008) 2103
- [3] B. Dembinska, A. Dobrzyniecka, M. Głowienka, J. Stroka, Paweł J. Kulesza, ECS Transactions, 45 (2013) 77
- [4] A. Molter, J. Rust, C. W. Lehmann, F. Mohr, Issue in Honor of Prof. Heinz Heimgartner, ARKIVOC, 2011 (vi) 10