Ethanol electro-oxidation in an alkaline medium using the nanostructured platinum-nickel electrocatalysts L. Tamašauskaitė-Tamašiūnaitė, A. Balčiūnaitė, A. Zabielaitė, J. Vaičiūnienė, R. Juškėnas, A. Selskis, E. Norkus Center for Physical Sciences and Technology A.Goštauto 9, LT-01108 Vilnius, Lithuania

Direct alcohol fuel cells (DAFCs) are being developed especially for portable power supply. Ethanol is characterized by interesting options for electrochemical power generation as a source of anodic fuel for direct ethanol fuel cells (DEFC) due to its easy handling and production from the biomass. Although platinum is an effective electrocatalyst for the oxidation of ethanol, the use of a noble metal as an electrode material is limited by its high price. Alloying Pt with transition metals such as Ni, Co, Fe etc. allow reducing cost and provide catalytic characteristics better than the monometalllic ones [1].

In this study we use anodized titania nanotube arrays (TiO$_2$-NTs) as an alternative support for carbon (carbon black - Acetylene Black, Vulcan XC-72, Ketjen Black, etc.) for deposition of platinum crystallites. A simple galvanic displacement technique [2,3] was used for deposition of Pt-Ni catalyst on the titania (TiO$_2$) and TiO$_2$-NTs surfaces (denoted as Pt(Ni)/TiO$_2$ and Pt(Ni)/TiO$_2$-NTs). A series of Pt-Ni thin layers with different Pt loadings were deposited on the titania nanotubes arrayed and flat surfaces by electroless deposition of Ni onto the latter surfaces and their subsequent partial displacement by Pt upon immersion into the H$_2$PtCl$_6$ solution.

The morphology and composition of the prepared catalysts were characterized by means of Field emission scanning electron microscopy, Energy dispersive X-ray spectroscopy and X-ray diffraction. The electrochemical behavior of the prepared nickel and platinum-nickel catalysts deposited on the TiO$_2$ and TiO$_2$-NTs surfaces was examined by means of cyclic voltammetry and chronoamperometry. The electrocatalytic activity of the investigated catalysts towards the oxidation of ethanol was compared with that of pure Pt electrode. Well-adherent platinum-coated nickel films with nm-sized particles were formed on the titania nanotube arrayed and flat surfaces. The self-ordered TiO$_2$ nanotube arrays with the average tube diameter of about 100 nm and the thickness of titania layers of ~350 nm were used. The electroless Ni-P sublayer with the thickness of about 300 nm was deposited on the titania nanotubes and flat surfaces, which produces a layer of granular nickel particles about 200 nm in size. Immersion of the Ni/TiO$_2$-NTs and Ni/TiO$_2$-flat into the platinum-containing solution for 5 min results in the formation on the Ni surface of nonspherical and well separated platinum crystallites 50-100 nm in size. After immersion of the Ni/TiO$_2$-NTs and Ni/TiO$_2$-flat electrodes into the platinum-containing solution for 15 and 30 min, respectively, increase of the Pt crystallites and flowerlike character of the structures were evident. The Pt nanoflowers were not spherical and consist of a large number of spearlike nanorods of size ca. 200 nm which were bonded to each other to form bigger secondary 3D flowerlike architectures [4].

A higher electrocatalytic efficiency as compared to that of the bulk Pt. As evident from Fig. 1, the stabilized cyclic voltammograms after a long-term potential cycling (after 10 cycles) for the oxidation of ethanol on the Pt(Ni)/TiO$_2$-NTs and Pt(Ni)/TiO$_2$-flat catalysts are similar in shape to those obtained on the pure Pt, except for enhanced currents. The ethanol oxidation current densities are also ca. 2-4 and 2-7 times higher at Pt(Ni)/TiO$_2$-NTs and Pt(Ni)/TiO$_2$-flat catalysts, respectively, in comparison to bulk Pt.

![Figure 1. CVs (10$^6$ cycles) of pure Pt (dotted lines), Pt(Ni)/TiO$_2$-NTs (a) and Pt(Ni)/TiO$_2$-flat (b) catalysts in 2 M C$_2$H$_5$OH + 0.5 M NaOH at 50 mV s$^{-1}$](image)

A higher electroactivity of the platinum-nickel catalysts with the different Pt loadings deposited on the TiO$_2$-NTs and TiO$_2$-flat surfaces was also confirmed by the chronoamperometry measurements in an alkaline solution of ethanol as compared to Pt. The fabricated nanostructured Pt(Ni)/TiO$_2$-NTs and Pt(Ni)/TiO$_2$-flat catalysts seem to be a promising support for fuel cell catalysts.

References