

Oxidation of Methanol at the Nanostructured Film of Polyoxometallate-linked Ruthenium-stabilized Platinum Nanoparticles - P.J. Kulesza, M. Chojak (University of Warsaw), R. Włodarczyk (Czestochowa University of Technology), R. Marassi (Universita di Camerino), K. Karnicka, and K. Miecznikowski (University of Warsaw)

The electrooxidation of methanol involves ideally six electrons per molecule to produce carbon dioxide, and it has been extensively studied as a potential reactant for fuel cell technology during the last several years. During methanol oxidation, platinum shows appreciable catalytic reactivity towards C-H bond breaking, and this process is followed by several fast steps resulting in the formation of either surface CO or dissolved CO₂. The Pt-Ru binary metallic systems have been demonstrated to act as the best electrocatalysts for methanol oxidation. It is commonly accepted that the ruthenium addition to platinum results in the activation of water molecules on the ruthenium surface to yield the metal oxo species of the type Ru-OH. Thus the passivating CO intermediate can react with the Ru-OH species to yield CO₂. An important issue is that pure ruthenium forms surface hydroxides at potentials starting from 0.3 V vs. SHE, i.e. lower in comparison to platinum (0.6 V vs. SHE). Consequently, the removal of CO is much faster on the Pt-Ru surface than on pure Pt.

Binary Pt-Ru catalysts proposed for the oxidation of methanol have the following forms: Pt-Ru alloys, Ru electrodeposits on Pt, Pt-Ru codeposits, and Ru adsorbed on Pt. An interesting alternative originates from the possibility of the preparation of binary Pt-Ru electrocatalysts as a result of spontaneous adsorption of ruthenium [1].

There are numerous examples of electrocatalytic modified electrodes in which reactive centers are three-dimensionally distributed within thin films attached to electrode substrate [2,3]. Immobilization of metal nanoparticles embedded in a porous matrix results in the increase of the catalytic metal specific area. An important practical issue is the stabilization of nanoparticles that prevents their agglomeration leading to the gradual loss of activity. In the case of gold nanoparticles, recent attention has focused on the formation of alkanethiolate monolayer-protected clusters. Self-assembled alkanethiolates on gold tend to separate Au nanoparticles and reduce their agglomeration [4]. Very recently, we have demonstrated that platinum nanoparticles can be stabilized with polyoxometallates by exploring their ability to form stable anionic monolayers on solid surfaces [5]. The resulting polyoxometallate-protected (stabilized) Pt-nanoparticles can be subsequently linked with ultrathin conducting polymer layers to form network films [6].

In the present work, we demonstrate the usefulness of the layer-by-layer method to the fabrication of the hybrid films composed of the heteropolyanion (PW₁₂) linked oxoruthenium coated platinum nanoparticles. The approach seems to provide a novel concept of assembling bimetallic Pt-Ru nanoparticles (using polyoxometallate linkers) to form the network electrocatalytic structures. We explore here the fact that ruthenium oxo-species adsorbed on platinum nanoparticles are positively charged and they are expected to interact with anionic phosphododecatungstate (PW₁₂). The results are consistent with the view that PW₁₂ is not only stabilizing the ruthenium decorated platinum nanoparticles but also is enhancing the methanol oxidation currents under chronoamperometric conditions.

We have also found that that the derivatization of oxoruthenium coated Pt nanoparticles with phosphotungstate enhances (certainly not decreases) the activity of dispersed electrocatalyst towards electrooxidation of methanol in acid solution. Although no direct comparison of our system to the activity of commercial Vulcan-supported binary Pt-Ru catalyst has been made here (due to the distinct morphologies and metal loadings in both catalysts), our preliminary results show that the network film of polyoxometallate-linked ruthenium-stabilized platinum nanoparticles seems to be promising for the formation of anode catalyst. This catalytic enhancement may be due to the synergistic effect between Pt-Ru and PW₁₂. Having in mind the activity of tungsten oxides [3,7], tungstate units may provide

additional -OH groups or radicals capable of facilitating oxidation of passivating intermediates (CO_{ads}) on platinum. Alternatively, introduction of PW₁₂ may induce morphological differences and lead to the better platinum catalyst utilization. Further research is necessary to optimize distribution and size of PW₁₂-derivatized and linked oxoruthenium coated Pt nanoparticles.

References

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