

## **Nanostructured-Metal-Oxide-Supported Noble Metal Nanoparticles for Electrocatalytic Processes of Importance to Fuel Cell Technology**

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Of particular interest to the preparation of advanced catalytic materials is efficient utilization of catalytic sites (metal and metal oxide nanostructures, their stabilization and intentional activation, as well as organization into two-dimensional arrays, ultra-thin films or three-dimensional networks. Graphene is, in principle, a promising material for consideration as component (support, active site) of catalytic materials, particularly with respect to reduction of oxygen, an electrode reaction of importance to low-temperature fuel cell technology. Different concepts of utilization, including nanostructuring, doping, admixing, preconditioning, modification of various graphene-based systems for catalytic electroreduction of oxygen are elucidated here.

There has been growing interest in utilizing small (simple) organic molecules, as alternative fuels to hydrogen, in electrochemical energy conversion systems. In addition to ethanol (biofuel), that can be ideally oxidized to carbon dioxide thus delivering twelve electrons, recent important systems include dimethyl ether as well. But realistically the respective reaction is rather slow at ambient conditions. Obviously, there is a need to develop novel electrocatalytic materials.

Platinum has been recognized as the most active catalytic metal towards oxidation of ethanol at low and moderate temperatures. But Pt anodes are readily poisoned by the strongly adsorbed intermediates, namely by CO-type species, requiring fairly high overpotentials for their removal. To enhance activity of Pt catalysts towards methanol and ethanol oxidation, additional metals including ruthenium, tin, molybdenum, tungsten or rhodium are usually introduced as the alloying component. More recently it has been demonstrated that catalytic activity of platinum-based nanoparticles towards electrooxidation of ethanol has been significantly enhanced through interfacial modification with ultra-thin films of metal (W, Ti or Zr) oxo species.

We pursue a concept of utilization of mixed metal (e.g. zirconium/tungsten or titanium/tungsten) oxide matrices for supporting and activating noble metal nanoparticles (e.g. PtRu) during electrooxidation of methanol, ethanol, formic acid and dimethyl ether. Among important issues is incorporation of Rh nanostructures capable of weakening, or even breaking, the C-C bond in the ethanol molecules. On the other hand, rhodium itself is not directly electrocatalytic toward oxidation of ethanol. The oxides and noble metal nanoparticles have been deposited in a controlled manner using the layer-by-layer method. Remarkable increases of electrocatalytic currents measured under voltammetric and chronoamperometric conditions have been observed. The most likely explanation takes into account possibility of specific interactions of noble metals with transition metal oxide species as well as existence of active hydroxyl groups in the vicinity of catalytic noble metal sites at low potentials that induce oxidation of passivating CO adsorbates (e.g. on Pt); they can potentially break C-H bonds (e.g. by hydrogen tungsten oxide bronzes). In addition, formation of “nanoreactors” where ethanol is partitioned (at Rh) to methanolic residues further oxidized at PtRu cannot be excluded.

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