

**Multifunctional Nanostructured Materials for
Electrocatalytic and Bioelectrocatalytic
Oxidation of Ethanol**

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Our research interests concern development of the direct alcohol fuel cells as alternative technology to hydrogen based electrochemical energy systems. For example, ethanol can be ideally oxidized to carbon dioxide thus delivering 12 electrons. But realistically the 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 (one or two), such as Ru, Sn, Mo, W or Rh, 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 monolayer-type films of polyoxometallates, particularly heteropolymolybdates. Also gold in combination with platinum has been demonstrated to produce novel high performance bimetallic catalysts.

We are going to describe a concept of utilization of functionalized titanium dioxide, tungsten oxide or zirconium oxide matrices (by admixing them with polyoxometallate-modified gold nanoparticles) for supporting and activating noble metal nanoparticles (Pt, Pt-Ru or Pt-Rh) during electrooxidation of ethanol. Remarkable increases of electrocatalytic currents measured under voltammetric and chronoamperometric conditions have been observed. The most likely explanation takes into account improvement of overall conductivity (due to the presence of nanostructured gold) at the electrocatalytic interface (formed by metal oxide support), as well as and possibility of specific Pt-metal oxide or Pt-Au electronic interactions and existence of active hydroxyl groups on transition metal oxo species in the vicinity of catalytic Pt sites. Further, the capping layers of Keggin-type phosphomolybdates, which are known to undergo fast stepwise multi-electron redox processes as well as to activate Pt-based electrocatalysts during ethanol oxidation,

may also contribute to the overall enhancement effect.

Having in mind a wide spectrum of powerful catalytic activities of zeolites, it is reasonable to expect that application of certain protonically/electronically conducting zeolite-type matrices shall lead to enhancement of the overall reactivity of anode electrocatalysts. Among potential candidate materials for rigid and active matrices in electrocatalysis, there are cesium salts of Keggin-type heteropolyacids of molybdenum and tungsten. These salts are insoluble in water and organic solvents, and they possess micro and mesopores of high surface area (often exceeding $100 \text{ m}^2 \text{ g}^{-1}$). Contrary to typical alkali-exchanged zeolites, the analogous heteropolyacid salts retain their strong acidity. In the present work, we describe preparation and physicochemical (including electrochemical) properties of cesium salts of selected Keggin-type heteropolyacids of molybdenum and tungsten, as well as address their influence on catalytic activity of Vulcan-supported Pt, PtRu and PtSn nanoparticles (Pt40%/Vulcan XC-72) during electrooxidation of methanol and ethanol.

Oxidation of ethanol can also be pursued under neutral conditions in so called biofuel cells. In our work, we have exploited unique characteristics of multi-walled carbon nanotubes (CNTs) to construct the efficient anodic bioelectrocatalytic system of potential utility for biofuel cells and biosensors. Some attention has been also paid to the choice of the modifying agent poly(diallyldimethylammonium chloride) (PDDA) used to stabilize CNTs. While PDDA seems to form stable ultra-thin layers on CNTs, it is not expected to serve as a good charge (electron) mediator but it is reasonable to expect that PDDA would interact or attract electrostatically with negatively charged sites of the enzyme (or combination of dehydrogenase enzymes). Our highly porous CNT-based films have presumably acted as three-dimensional network of nanowires around the enzyme molecules and have promoted the efficient electron transfer. On the whole, combination of PDDA-modified MWCNTs and two distinct dehydrogenase enzymes within the film has produced a catalytic system capable of oxidation of ethanol at fairly low potentials (ca. 0.15 V versus Ag/AgCl). Among important issues are good stability and reproducibility of responses both under voltammetric and amperometric conditions.