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# Multi-walled carbon nanotube-supported tungsten oxide-containing multifunctional hybrid electrocatalytic system for oxygen reduction in acid medium

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ABSTRACT

Combination of multi-walled carbon nanotubes, cobalt porphyrin and tungsten oxide in the film (deposited onto glassy carbon electrode substrate) produces an electrocatalytic system capable of effective reduction of oxygen in such acid medium as 0.5 mol dm$^{-3}$ $H_2SO_4$.

Co-existence of cobalt porphyrin and tungsten oxide, together with dispersed carbon nanotubes, leads to the enhancement effect evident from some positive shift in the oxygen reduction voltammetric potential and the significant increase of voltammetric currents (relative to those characteristic of the system free of carbon nanotubes and $WO_3$). The multi-component electrocatalytic film has also exhibited relatively higher activity towards reduction of hydrogen peroxide. It is reasonable to expect that the reduction of oxygen is initiated at the cobalt porphyrin redox centers, and the undesirable hydrogen peroxide intermediate is further reduced at the tungsten oxide support. An important function of carbon nanotubes is to improve transport of electrons within the electrocatalytic multi-component film.

## 1. Introduction

In recent years there has been growing interest in fabrication of non-precious metal catalysts for applications as electrodes in sensors and fuel cells. As alternatives for platinum based catalysts, which are so far the most commonly used systems for the reduction of oxygen in acid media, nanoparticles of ruthenium modified by chalcogens (such as Se or S) [1–3] as well as macrocycle-based metal-containing porphyrins and phthalocyanines [4–9] are widely used. These compounds, in contrast to platinum catalysts, are largely methanol (or ethanol) tolerant what might to be very important when it comes to their use as cathodes in alcohol-utilizing low-temperature fuel cells. One of the fundamental problems related to the operation of such fuel cells is crossover of a fuel through the polymer membrane from the anode compartment to the cathode area where it can be oxidized at potentials comparable to those where oxygen reduction proceeds. The co-existence of two processes, the reduction of oxygen and the oxidation of a fuel, leads to the depolarization of the platinum based cathode and, consequently, to the decrease in the cell performance. Preparation of the alcohol-tolerant cathode catalysts is of primary importance to the development of so called compact mixed-reactant fuel cells in which highly selective anode and cathode catalysts are used together with perforated membranes through which a mixture of fuel and oxidant is passed [10].

The essential problem practically existing in all kinds of low-temperature fuel cells concerns optimization of oxygen reduction reaction. This process may occur in two pathways: through direct four-electron reduction to water or via two-electron step leading to the indirect product, hydrogen peroxide. Decomposition of the $H_2O_2$ intermediate is feasible via further two-electron electroreduction to water (typically at more negative potentials) or through its disproportionation (to oxygen and water). Furthermore, direct reduction of oxygen to water is energetically much more efficient when compared to the process proceeding through the hydrogen peroxide intermediate. What is even more important, the appearance of sizeable amounts of hydrogen peroxide may lead to degradation of membrane and electrode materials. Unfortunately, most of practical Pt-free catalytic systems are not capable of driving four-electron reduction of oxygen directly to water.

$N_4$-macrocyclic complexes of transition metals, especially of Fe or Co, exhibit remarkable catalytic activity towards oxygen reduction reaction. It has been established that most of the monomeric cobalt porphyrins (capable of adsorbing irreversibly on glassy carbon, graphite or gold electrodes) can catalyze the reduction of oxygen only through two-electrons pathway to produce $H_2O_2$ [11,12]. But there is also a group of cobalt porphyrins (without or only with small meso substituents in the ring) that can eas-

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ily dimerize or oligomerize. These systems are more efficient in driving oxygen reduction according to the four-electron pathway. The group is represented by cobalt porphine, protoporphyrin IX, or 5,10,15,20-tetramethylporphyrin [7,11]. To make oxygen reduction even more efficient, several concepts have been proposed that include utilization of face-to-face porphyrins [8,13], introducing porphyrin catalytic centers into conducting polymers [14,15] or onto different carbon nanoparticles, as well as heat treatments (partial pyrolysis) of porphyrins [5,16,17].

Porphyrins (as well as biomolecules) can interact non-covalently (via $\pi$ electrons from the ring or axial coordination to central metal) with graphene layers of carbon nanostructures. Under such conditions adsorption of porphyrins (with preservation of the $\pi$-networks of carbon) is feasible. Consequently, many properties of porphyrins are altered [18,19] including their activity towards oxygen reduction [20,21]. Among nanostructural materials, carbon nanotubes (CNTs) seem to constitute an attractive support for organometallic complexes because of their unique properties that include mechanical stability, high surface area and good electronic conductivity. However, even with the use of carbon nanoparticles or nanotubes, production of hydrogen peroxide during the oxygen reduction still remains the major problem.

It has been recognized that films of partially reduced $WO_3$, namely hydrogen tungsten oxide bronzes, provide highly reactive mixed-valence redox centers ($W^{VI,V}$) characterized by fast electron transfer capabilities, proton mobility and high reductive activity towards such inert molecules as bromate or hydrogen peroxide [22,23,24]. It has been reported [25,26] that introduction of carbon-supported $RuSe_x$ nanoparticles into tungsten oxide layers resulted in shifting the oxygen reduction potential to more positive values and in the decrease of the hydrogen peroxide formation. In this paper, we demonstrate the activating role of the tungsten oxide matrix during the electrocatalytic reduction of oxygen at Co protoporphyrin IX (CoPPIX) supported onto multi-walled carbon nanotubes. As $WO_3$ is known to exhibit electrocatalytic properties towards hydrogen peroxide reduction [23], it is reasonable to expect that $WO_3$-modified CNT-supported Co-porphyrin catalyst acts as multifunctional system, in which porphyrin centers induce oxygen reduction, $WO_3$ matrix drives reduction of undesirable hydrogen peroxide intermediate, and the CNT network makes the layer porous and facilitates distribution of electrons at the interface. In addition to the improved activity towards oxygen reduction, we demonstrate the system's ethanol tolerance, as well as we compare performance of the prepared electrocatalysts to the behavior of well-established highly active Vulcan-supported Pt-containing materials.

## 2. Experimental

All chemicals were commercial materials of the highest available purity (ACS reagent grade) and, except multi-walled carbon nanotubes (from Aldrich), they were used as received. CNTs were purified in HCl and $HNO_3$ in a similar manner as described in literature [27]. $H_2SO_4$ solutions were prepared from triply distilled subsequently deionized water. They were deaerated (using argon or nitrogen) or saturated with oxygen for at least 30 min prior to the electrochemical experiment. Experiments were conducted at room temperature (25 °C).

The electrochemical experiments were performed with CH Instruments (Austin, TX, USA) Models: 600B and 750A workstations. A mercury/mercury sulfate electrode ($Hg/Hg_2SO_4$), having the potential of 656 mV versus the reversible hydrogen electrode (RHE), was used as the reference electrode. All potentials are expressed against the RHE. Rotating ring-disk electrode (RRDE) voltammetric measurements were accomplished using a variable speed rotator (Pine Instruments, USA). The working electrode assembly utilized a glassy carbon disk and a Pt ring. The electrodes were polished with successively finer grade aqueous alumina slurries (grain size, 5–0.05 μm) on a Buehler polishing cloth. In the RRDE measurements, the radius of the disk electrode was 2.5 mm, and the inner and outer radii of the ring electrode were 3.25 and 3.75 mm, respectively. The collection efficiency of the RRDE assembly was determined from the ratio of ring and disk currents (at various rotation rates) using the argon-saturated 0.005 mol $dm^{-3}$ $K_3[Fe(CN)_6]$ + 0.01 mol $dm^{-3}$ $K_2SO_4$ solution [28]. Within the potential range considered here, and at rotation rates up to 2500 rpm, the experimental collection efficiency ($N$) remained unchanged and was equal to 0.23. During the RRDE measurements in oxygen-saturated solutions, the potential of the ring electrode was held at 1.2 V. At this potential, the generated $H_2O_2$ is readily oxidized under diffusional-convective control. All RRDE polarization curves were recorded at a scan rate of 10 mV $s^{-1}$.

To produce a suspension of carbon nanotubes, a known amount (20 mg) of the purified CNTs was dispersed in 1.6 $cm^3$ of ethanol, subjected to sonication for 10 min and than mixed at magnetic stirrer for 1 h. After that 0.13 $cm^3$ of 5% Nafion (from Aldrich) in water–alcoholic solution was added, and the mixture was left at magnetic stirrer for several hours. Later 9.3 μ$dm^3$ of the appropriate suspension was dropped onto the surface of a glassy carbon disk electrode (geometric area, 0.196 $cm^2$) and the suspension was air-dried at room temperature. In the next step, 9.3 μ$dm^3$ of 3 mmol $dm^{-3}$ solution of Co(III) protoporphyrin IX chloride (Frontier) in ethanol was dropped. $WO_3$ layers were electrodeposited (with use of a graphite slide as the counter electrode) on bare and CNT-modified glassy carbon electrodes by application 15 voltammetric cycles in the range −0.156 to 1.044 V in 2 mol $dm^{-3}$ $H_2SO_4$ containing 10 mmol $dm^{-3}$ $Na_2WO_4$ (Aldrich) [22,23]. The catalyst layers (bare or modified with $WO_3$) were subsequently over-coated with Nafion film by adding 2 μ$dm^3$ of diluted ethanolic Nafion solution (1:100). As a rule the catalytic films were activated by performing 50 full voltammetric potential cycles in the potential range from 0.1 to 0.094 V (at 100 mV $s^{-1}$) until steady-state currents were observed. The morphology of CNTs and $WO_3$ films were examined using LEO 435VP (Zeiss) scanning electron microscope (SEM) and JEM 1200 EX (JEOL) transmission electron microscope (TEM) operating at 80 kV.

## 3. Results and discussion

Typical scanning electron micrograph of the conventional tungsten oxide film (electrodeposited as described in Experimental section) is shown in Fig. 1A. The morphology of such film is granular and microporous. Fig. 1B and C illustrate scanning electron microscopic (SEM) and transmission electron microscopic (TEM) images of multi-walled carbon nanotubes suspended in the Nafion-containing ink. The diameters of CNTs are typically not exceeding 10 nm; their lengths are on the level of at least hundreds of nanometers or even micrometers. The results of Fig. 1B and C imply three-dimensional mezoporous structure of the CNTs networks.

Fig. 2A and B shows rotating disk electrode (RDE) and cyclic voltammetric responses of (a) bare and (b) $WO_3$-supported Co-porphyrin layers (deposited on glassy carbon electrode and investigated in the oxygen-saturated 0.5 mol $dm^{-3}$ $H_2SO_4$ solution). The peaks characteristic of oxygen reduction appear at potentials 0.3 V (Curve a) and 0.45 V (Curve b) in the case of the bare and $WO_3$-supported catalytic layers, respectively. The RDE catalytic current densities have increased following application of tungsten oxide film as a support. Thus, by shifting the oxygen reduction potential towards more positive values and by increasing current densities, tungsten oxide exhibited an activation effect on porphyrin catalytic