

Electrochemical method for the preparation nanocomposites based on carbon nanotubes and chromium oxides for oxygen electrodes

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Abstract An electrochemical method for the preparation of nanostructured composites based on multiwalled carbon nanotubes and chromium oxide is proposed. The method involves electrodeposition of chromium oxides from a solution of hexavalent chromium oxide in sulfuric acid on carbon nanotubes. By varying the electrolysis conditions one can obtain deposited—catalyst particles of different size and vary the amount of catalyst. Oxygen electrodes have been made from the materials obtained for fuel cells with alkaline electrolyte, which showed good electrocatalytic properties.

Keywords Oxygen electrode · Alkaline · Fuel cell · Carbon nanotubes · Chromium oxide

Introduction

The use of air or oxygen electrode in devices generating electrical energy has very good prospects since it does not give rise to environmental problems and makes it possible to save natural resources, such as oil and gas. Air or oxygen electrode in current sources is a three-phase electrode–electrolyte–gas system, where the current generation processes are localized at the interface between these phases. The current magnitude generated on such a gas-diffusion electrode depends on the size of the zone of the triple contact of these phases. The

electrode itself consists of catalyst and support; it is interaction between them that determines mainly the generated current magnitude, which depends on the catalyst used. The most efficient oxygen reduction catalyst is at present platinum, but it has a considerable disadvantage, a high price. There are a great number of works dealing with the investigation of other efficient catalysts. Another main problem is catalytically active and stable support. References [1–4] showed the advantage of carbon nanotubes as catalyst supports. Platinum deposition on carbon nanotubes (CNT) made it possible to improve the characteristics of oxygen electrodes as compared with the same electrodes with platinum deposited on activated carbon [3, 4].

Carbon nanotubes have a high electrical conductivity and a large specific surface area and can form mesoporous spatial structures, which makes them promising as catalyst supports. Moreover, thanks to the presence of tubular carbon structure, enlargement of the electrode–electrolyte–oxygen contact zone, in which the contact generation process takes place, is possible. This leads to an increase in working current density in comparison with activated carbons. This quantity is also affected by the low bulk density of carbon nanotubes as compared with activated carbons. The literature mentions the fact that chromium made a part of $Ru_xCr_ySe_z$ chalcogenide together with ruthenium possesses synergism in oxygen reduction reaction [5]. It also mentions electrocatalytic activity of Pt/C, obtained by chemical vapor deposition and modified by chromium, for the oxygen electrode of fuel cell in phosphoric acid [6]. Therefore, it was of special interest to study the catalytic activity of chromium oxide electrodeposited on carbon nanotubes. The electrochemical method for chromium oxide deposition on CNT allows one, in our view, to control the particle size and the mass of deposited compounds, which can be controlled by varying the electrolysis time.

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The aim of our work was to investigate the electrocatalytic properties of carbon nanotubes with chromium oxide electrodeposited on them as electrode material for the oxygen electrode of fuel cell with alkaline electrolyte.

Experimental

Multiwalled carbon nanotubes were used as catalyst support and electrode material for investigations [7]. The product was a black powder with a bulk density of 25–30 g/dm³. The outside diameter of nanotubes was about 10–30 nm, the specific surface area was 230 m²/g, the percentage of mineral impurities in unpurified product was 15–20%. Catalyst impurities were removed from multi-walled nanotubes (MWNTs) by treatment with a hydrofluoric acid solution.

Two-layer oxygen electrodes were prepared by pressing. The hydrophobic layer contained 0.07 g/cm² of acetylene black with 25% polytetrafluoroethylene (PTFE), and the active layer contained 0.02 g/cm² of MWNTs, modified by different amount of chromium oxides with 5% PTFE. Nanostructured composite based on carbon nanotubes and chromium oxides were prepared by electrodeposition. The electrolyte was a solution of CrO₃ (Merck company) with a concentration of 200 g/dm³ in sulfuric acid (Merck company) with a concentrations of 2 g/dm³. The electrolyte temperature was 40–60 °C, the current density was varied between 10 and 25 A/dm². Lead was used as the anode. The investigations were carried out in a fuel cell mockup, zinc being used as the anode. A mockup for the testing of gas

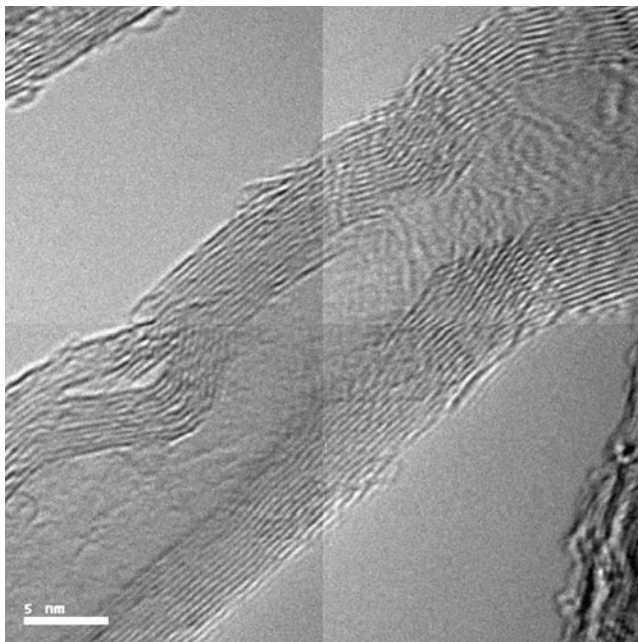


Fig. 1 Micrograph of a starting multiwalled carbon nanotube

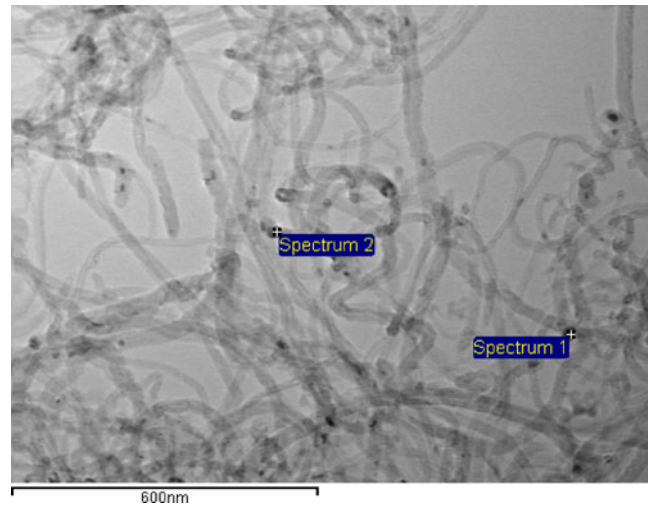


Fig. 2 Micrograph of nanotubes with deposited chromium oxide with an elemental chromium content of 4 mass %. Average particle size is nearly 25 nm

diffusion electrodes is described in [8]. The electrolyte was a 5 M KOH solution with 1 M LiOH. The reference electrode was a silver–silver chloride electrode connected through a salt bridge. All potentials are given with respect to the silver–silver chloride electrode. The electrochemical characteristics were measured under galvanostatic conditions. The oxygen source was a U-shaped electrolyzer with alkaline electrolyte. Oxygen was supplied to the gas electrode under an excess pressure of 0.01 MPa. Before carrying out investigations, the

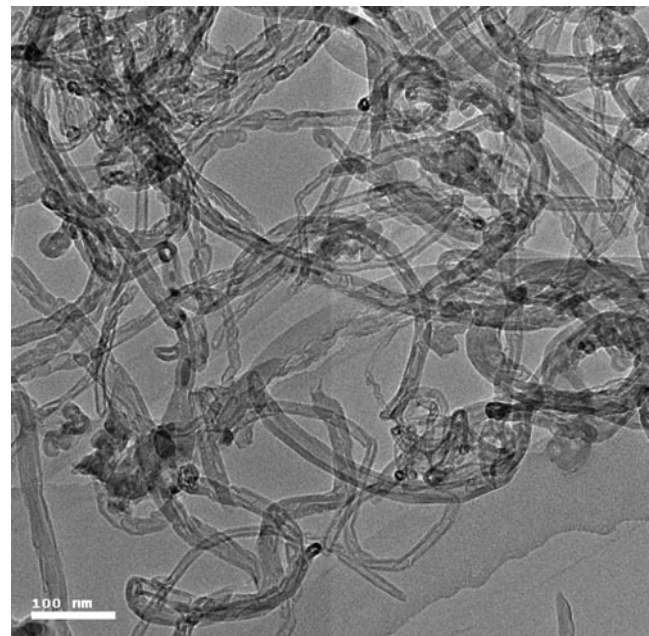


Fig. 3 Micrograph of nanotubes with deposited chromium oxide with an elemental chromium content of 10 mass %. Average particle size is nearly 30 nm

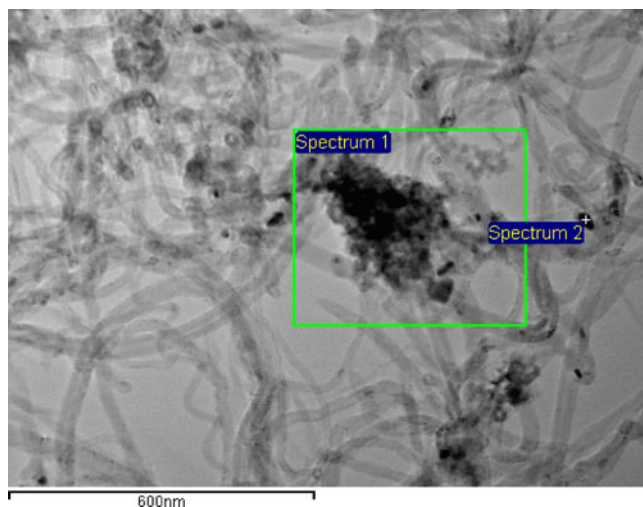


Fig. 4 Micrograph of nanotubes with deposited chromium oxide with an elemental chromium content of 21 mass %. Average particle size is nearly 300 nm

oxygen electrode was blown through with oxygen for an hour. The electron micrographs have been obtained by means of a JEM-100 CXII electron microscope. The X-ray photoelectron spectroscopic (XPS) studies were carried out with the aid of a Kratos analytical series 800 XPS device. The X-ray phase analysis was carried out on a “DRON-4” X-ray diffractometer (XRD; Russia), radiation $\text{CuK}\alpha$.

Results and discussion

Figure 1 shows an electron micrograph of the original MWNT, where carbon layers, which are formed during nanotube growth, are well discernible. Nanostructured composites based on carbon nanotubes with chromium oxides have been obtained by electrodeposition from a

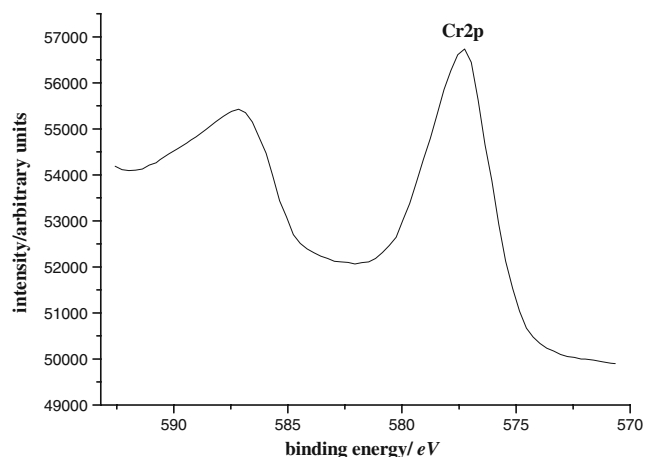


Fig. 5 Results of X-ray photoelectron spectroscopy of a sample of composite based on chromium oxide and carbon nanotubes with an elemental chromium content of 4 mass %

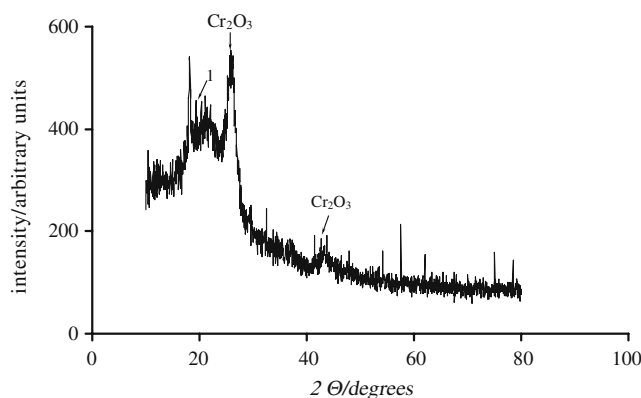


Fig. 6 X-ray phase analysis of a sample of composite based on chromium oxide and carbon nanotubes with an elemental chromium content of 4 mass % $1 - \text{Cr}(\text{OH})_3$

chrome solution consisting of CrO_3 dissolved in H_2SO_4 at different current densities and electrolysis time. The sample with a chromium content of 4 mass % of elemental Cr, was prepared within 6 min at a current density of 10 A/dm^2 . The composite with a chromium content of 8 mass % was prepared within 12 min at a current density of 10 A/dm^2 . The composite with a chromium content of 10 wt.% elemental Cr, was prepared within 9 min at a current density of 15 A/dm^2 . To prepare a composite with a chromium content of 21 mass %, electrolysis was carried out for 12 min at a current density of 25 A/dm^2 . Composites of chromium oxide and carbon nanotubes containing 4, 8, 10, and 21 mass % elemental Cr have been investigated. Figures 2, 3, and 4 show micrographs of composites of nanotubes with chromium oxide with different size of deposited catalyst particles with different amount of elemental chromium, obtained by varying the current density and electrolysis time. The samples obtained have been investigated by XPS method. Figure 5 shows

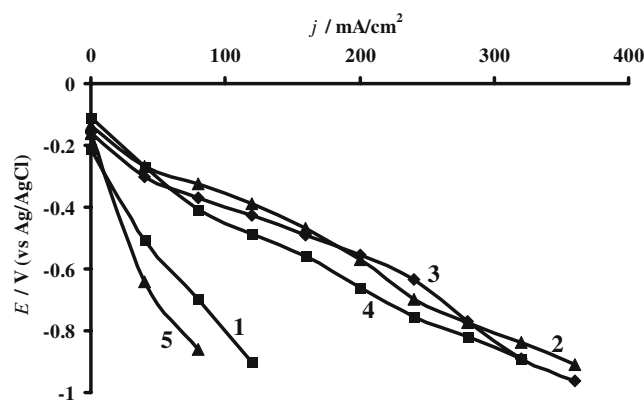


Fig. 7 Current–potential curves for an oxygen electrode based on nanocomposites (0.02 g/cm^2), which consist of carbon nanotubes with deposited chromium oxide, with different elemental chromium content (mass %), 1–21, 2–4, 3–8, 4–10, and 5–starting carbon nanotubes

results of XPS for a composite of chromium oxide and nanotubes. It has been found that Cr^{3+} with a binding energy of 577.3 eV corresponds to the sharp peak in Fig. 5. The binding energy for the peak for $\text{Cr}2p_{3/2}$ electrons for chromium deposited on carbon nanotubes is 577.3 eV, and according to the data presented in literature for CrOOH compositions deposited on various substrates by different methods, it is 577.4 eV [9–12]. In these papers, the binding energy of $\text{Cr}2p_{3/2}$ in the CrOOH close to that determined by us for chromium on carbon nanotubes. This proves the fact that the chromium obtained by us by the electrochemical method is most likely on the compound CrOOH in composites with carbon nanotubes. At the points shown as Spectrum 1 and Spectrum 2 on the photographs, an electron probe micro-analyzer of deposited catalyst particles has been carried out. Carbon, chromium, and oxygen have been found. An X-ray phase analysis of the nanocomposites obtained by us has been carried out. Figure 6 shows an X-ray spectrum of this composite. Because of carbon nanotubes being amorphous, we were able to identify only peaks at $2\Theta = 19.28^\circ$ as $\text{Cr}(\text{OH})_3$ and at $2\Theta = 22, 25.92, 32.48, \text{ and } 42.68^\circ$ as $\gamma\text{-Cr}_2\text{O}_3$. Thus, we have found from an analysis of XPS and XRD data that in the case of electrochemical preparation of nanocomposites based on carbon nanotubes and chromium, oxide compounds of chromium in the +3 oxidation state are obtained. Oxygen electrodes have been made from the nanostructured materials obtained, and their electrocatalytic properties have been investigated. Figure 7 shows plots of potential against current density for oxygen electrodes based on nanostructured composites of nanotubes with deposited 0.02 g/cm² chromium oxide with different content of elemental Cr (mass %), 1–21, 2–4, 3–8, and 4–10. As can be seen from this figure, oxygen electrodes containing 4 mass % Cr (curve 2) have the best electrocatalytic characteristics, next come composites with 8 mass % Cr (curve 3), with 10 wt.% Cr (curve 4), and finally with 21 mass % Cr (curve 1). This is due to the fact that as is seen from Figs. 2, 3, and 4, the particle agglomerate is formed at 21% chromium (Fig. 4; current density 25 A/dm², electrolysis time 12 min), the smallest particles are formed at 4 mass % chromium (Fig. 2; current density 10 A/dm², electrolysis time 6 min), slightly particles are formed at 10 mass % chromium (Fig. 3; current density 15 A/dm², electrolysis time 9 min). It follows from these results that under our conditions of preparation, the composites obtained at lower current densities (10 A/dm²) and a deposition time of 6 min have the best characteristics (Fig. 2). As is seen from the photographs shown in Figs. 2 and 3, the deposited catalyst particles are relatively uniformly distributed over the surface of nanotubes. Composite with high chromium content (21 mass % of elemental Cr) is an exception (Fig. 4). In our opinion, because of high current

density and relatively long electrolysis time in composition with other samples, the particles deposit nonuniformly on the surface of carbon nanotubes. In this case, agglomerates of these particles are formed on some surface portions. The electrical load characteristics of an oxygen electrode at 200 mV polarization, which corresponds to the voltage of 0.9 V for hydrogen–oxygen fuel cell, have been calculated, to be 145 mW/cm² for nanocomposite based on chromium oxide obtained by the electrochemical method. This allows one to conclude that composites of carbon nanotubes and oxide compounds of chromium in the +3 oxidation state obtained by the electrochemical method are promising catalysts for the oxygen electrode of fuel cell. Basing on the electrochemical method for the preparation of nanostructured composite of carbon nanotubes and chromium oxides as an example, the galvanic method for the deposition of catalysts can be recommended as a controllable method for the synthesis of catalytically active composites with adjustable size of particles and amount of deposited catalyst.

Conclusions

Composites of oxide compounds of chromium in the +3 oxidation state and multiwalled carbon nanotubes have been obtained by electrodeposition. It has been shown that an advantage of the electrochemical method for the deposition of catalyst is the possibility to control the size of particles and amount of deposited catalyst by varying the electrolysis time and current density, which makes it possible to obtain catalytically active composites for electrochemical power sources.

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