Electro-Conductive Composites Based on Titania and Carbon Nanotubes[1]

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Abstract—Carbon-ceramic composites have been prepared by mechanical ball-milling and ultrasonic treatment of mixtures of titania with carbon nanomaterials, and the optimal preparation conditions have been determined. The dependence of electrical conductivity of the composites on the mass fraction of carbon nanomaterials (1–5 mass. %) has been ascertained, and it has been found that a carbon nanotubes mass fraction of 3% gives rise to a sharp increase in the electrical conductivity up to 2.2×10^{-3} S/cm. It has been shown that the carbon-ceramic composites are promising electrocatalyst supports for electrochemical applications.

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INTRODUCTION

Ceramic matrix composites with carbon materials are finding increasing use in modern industry [1–5], and the use of carbon nanotubes and nanofibers as components that modify the matrix has also received wide attention. For example, one immediate effect of remarkable electronic conductivity and extremely elongated shape of carbon nanotubes would be that their introduction into ceramic material, even at low amounts, would enhance the electrical conductivity of the latter. The composites being conductive may be useful for fabricating electrodes for use in various electrochemical devices. Thus, that electro-conductive composites can be obtained using small additions of carbon nanomaterials has certain advantages in comparison with other approaches to enhance the electrical conductivity of ceramics.

When fabricating electro-conductive composites with a dielectric matrix it is essential to take into account the amount and electrical conductivity of the filler, as well as the morphology of its particles. A large number of composites based on a wide variety of ceramics, such as Al_2O_3 [4–8], Si_3N_4 [8, 9], SiC [10], SiO_2 [11], TiO_2 [12–14], ZnO [14, 15], TiN [16], ZrO_2 [17] and others are currently investigated, including such carbon fillers as soot, nanofibers, multi- and single-walled nanotubes, and grapheme-like carbon nanostructures [4–20].

It makes it clear that the fillers introduced to obtain high-performance composite materials either improve the properties of the matrix or give the new ones to it, being also important to retain the original properties. Therefore, in order to obtain the best results one need to add the filler in amounts that are as small as sufficient to impart new properties to the composites. According to the available literature data the fraction of carbon fillers in composites varies from fractions of one percent up to several tens of percents. In this connection, a key problem is to determine the minimal fraction of the carbon filler in the composites, which provides the desired properties. But there often is a confusion, whether volumetric or mass percentage is reported, when specifying the content of composites in the papers. When carrying out the experiments, hundreds or even tens of milligrams are loaded for the measurements, whereby the effects are reported to be noticeable already at one volumetric percent of the carbon fraction; that is, the precision of the measurements should be taken into account. Also, it is often remains unclear, what kind of density (true, crystallographic, specific or packed) do the researchers actually mean when determining the volumetric fractions of the components.

In order to fabricate composite materials from the components either simple mixing, not giving uniform composition, or ultrasonic treatment, are commonly employed. Unfortunately, very often the treatment conditions are not specified, whereas they are of great importance, as carbon nanomaterials of different types (single- or multi-walled nanotubes, stacked graphene or herringbone nanofibers) exhibit different sensitivity toward this treatment, especially when it is

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[1] The article was translated by the authors.

conducted in aggressive environments such as a mixture of nitric and sulfuric acids. Besides, to determine the sensitivity of a carbon nanomaterial to ultrasonic treatment the synthesis method of these particular carbon nanostructure (electric arc or laser sputtering of graphite, catalytic pyrolysis etc.) is not less important. For example, nanotubes synthesized in a carbon arc reactor are more resistant to aggressive environment and ultrasonic treatment then "pyrolytic" ones, all other factors remaining equal.

Thus, the present work was aimed at the synthesis of electro-conductive TiO_2-based carbon-ceramic composites, as well as studying the dependence of electrical conductivity of the composites on their synthesis conditions and type of carbon nanostructures (CNS). From a practical point of view, one application where relatively high electrical conductivity of these composites could prove useful would be for instance electrodes for low-temperature hydrogen-air fuel cells and the similar electrochemical devices. Therefore, we also paid a particular attention to the study of electro-catalytic activity of noble metal particles (Pt) supported on the obtained composites in the oxygen reduction reaction.

EXPERIMENTAL

Earlier we have carried out extensive studies to optimize the conditions of catalytic synthesis of carbon nanostructures of different types [21–23]. In the present work, by using the developed methods, we prepared carbon nanofibers (CNF) and multi-walled carbon nanotubes (MWNT) by catalytic pyrolysis of ethylene on Ni/MgO, as well as thin, probably single–walled, carbon nanotubes (SWNT) by catalytic pyrolysis of methane on Fe–Mo/MgO. After the synthesis the carbon materials were purified by sonication in concentrated HCl at 70°C for 3 h in order to remove the substrate and the metal. The characteristics of the prepared nanostructures are given in Table 1. A starting powder of titanium dioxide was prepared by the hydrolysis of titanium tetrachloride followed by calcination at 440°C for 1 h.

Carbon-ceramic composites were prepared using two different procedures. The first one involved mechanical mixing of the carbon nanostructures with the titania in a planetary ball-mill Pulverisette 6 (Fritsch). Varied parameters were the rotational velocity, the ball-milling duration, the type of CNS and their weight fraction in the composites. In the second method, the components were sonicated together at a frequency of 35 kHz and power of 100 W, while varied parameters were the treatment duration, the type of CNS and their weight fraction as well.

The bulk microstructure and phase composition of the composites were studied by transmission electron

Table 1. Characteristics of the as-prepared carbon nanostructures

CNS type	C, mass. %	Diameter, nm	Surface area, m^2/g
CNF	99	100–200	90
MWNT	98	10–50	120
SWNT	98	5–10	280

microscopy (TEM) with JEOL JEM-100 CX microscopes, and powder X-ray diffraction (XRD) with a DRON-UM2 diffractometer. The surface morphology and elemental composition of the samples were investigated with the use of a scanning electron microscope (SEM) Zeiss LEO SUPRA 25, equipped with an energy dispersive X-ray spectrometer (EDX). Thermogravimetric analysis (TGA) was carried out using an STA 409C LUXX analyzer. The specific surface area was measured by the BET method with an analyzer QUADRASORB SI. The electrical conductivity of the samples was measured at a temperature of 20°C, with a potentiostat P-8S (Elins) using two-electrode and four-electrode cells that have electrodes of 0.5 and 0.3 cm in diameter. According to this procedure, equal amounts of the composites (0.15 g) were used in all measurements. The samples were pressed into the cells by applying a pressure of 3 MPa for 3 min.

Furthermore, we studied the electrocatalytic activity of platinum particles supported on the obtained composites in the oxygen reduction reaction. The metal particles were deposited on the surface of the titanium dioxide by reducing $H_2PtCl_6 \cdot 6H_2O$ with ethylenglycole for 1 h at 140°C followed by filtration, washing, and drying in vacuum for 5 h. A weighed sample of the carbon nanotubes was then added to the product and the carbon-ceramic mixture was sonicated in a 10% wt. aqueous dispersion Nafion® for 2 h. The resulted suspension was deposited on a gas-diffusion layer at 80°C to form a catalyst layer with a platinum loading of 0.4 mg/cm^2 (the calculated mass fraction of Pt was 10%). The prepared samples were tested in half-cell mode, where a sample serves as the cathode of fuel cell. Cyclic voltammograms were recorded at various voltage sweep rates, with air fed through gas channels. After recording the cyclic voltammograms current/potential curves for the oxygen cathodes were recorded using steady-state voltammetry. For the