Electro-Conductive Composites Based on Metal Oxides and Carbon Nanostructures

A.A. Volodin\textsuperscript{1,}\textsuperscript{*}, A.A. Belmesov\textsuperscript{1}, E.V. Gerasimova\textsuperscript{1}, A.D. Zolotarenko\textsuperscript{2}, D.V. Shchur\textsuperscript{2}, B.P. Tarasov\textsuperscript{1,}\textsuperscript{†}

\textsuperscript{1} Institute of Problems of Chemical Physics of RAS, 1, Prosp. Akademika Semenova, 142432 Chernogolovka, Russia
\textsuperscript{2} Frantsevich Institute for Problems of Materials Science of NASU, 3, Krzhizhanovsky str., 03680 Kyiv-142, Ukraine

(Received 24 June 2012; published online 14 August 2012)

Optimal conditions were found for the formation of carbon-oxide composites by the treatment of mixtures of oxides of aluminum or titanium with carbon nanotubes and nanofibers in a planetary ball mill. The dependences of the electrical conductivity of composites on the content of carbon nanomaterials (1-5\% by mass) were determined. It is shown that the addition of 3\% (wt) to the oxides leads to a sharp increase in the electrical conductivity: from 5.0×10\(^{-4}\) to 2.8×10\(^{-4}\) S/cm for Al\(_2\)O\(_3\) and from 5.0×10\(^{-4}\) to 2.2×10\(^{-2}\) S/cm for TiO\(_2\). It was shown that the carbon-oxide composites are promising carriers of the catalysts of electrode processes in electrochemical devices. It was revealed that Pt/TiO\(_2\) - CNT catalyst containing 5\% (mass) of carbon nanotubes has the best catalytic activity in oxygen reduction, in an electrode-modelling cathode of a fuel cell.

Keywords: Carbon nanotubes, Carbon-ceramic nanocomposites, Electrical conductivity, Catalytic activity.

PACS numbers: 61.48.De, 81.05.Mh, 72.80.Tm

1. INTRODUCTION

Composites based on ceramics and carbon materials have wide prospects for the modern industry [1-5]. Of certain interest is to use carbon nanotubes as modifying components. Thus the high thermal conductivity of nanotubes suggests that their introduction to the ceramic material, even in small amounts, would improve thermal conductivity and resistance to thermal shock [2]. The electrical conductivity of such composites can be useful for creating various electrochemical devices [3]. Thus, to give conductive properties through the introduction of small additions of carbon nanomaterials is attractive compared to other composite systems.

In the production of electrically conductive composites with the dielectric matrix and conductive filler there are of particular importance the intrinsic conductivity of the filler particles, the amount of injected filler, as well as the shape of the filler particles. Currently, a huge number of composites based on Al\(_2\)O\(_3\) [4-8], Si\(_3\)N\(_4\) [8, 9], SiC [10], SiO\(_2\) [11], TiO\(_2\) [12-14], ZnO [14, 15], TiN [16], ZrO\(_2\) [17] etc. are investigated. At the same time one use carbon black, nanofibers, multiwall and single-wall nanotubes, and graphene structures as fillers [4-20].

To create high-performance composite materials is necessary to introduce additives, which will either improve the properties of the base material, or give it new ones, but it is important to maintain existing properties. Therefore, to achieve the best effect it is necessary to introduce a minimum amount of additives, which give new properties to composites. In the literature data studied by us the content of carbon materials in the composites ranged from one percent to several tens of percent. In this connection, one of the problems is the determination of the minimum content of carbon in the composite material that provides the desired properties.

The aim of this work is to obtain conductive carbon-oxide composites based on Al\(_2\)O\(_3\) and TiO\(_2\), and study the dependence of the specific conductivity of composites on the conditions of their formation and types of carbon nanostructures (CNS).

\textsuperscript{*} alexvol@icp.ac.ru
\textsuperscript{†} tarasov@icp.ac.ru
3. RESULTS AND DISCUSSION

To investigate the dependence of conductivity on the content of carbon nanomaterial mixtures containing from 1 to 5% (wt) of CNTs were prepared. After processing in a planetary ball mill the samples of oxide powders and nanotubes had a homogeneous appearance, however, at the study by electron microscopy in mixtures containing 1% and 2% (wt) CNTs, the tubes on their own are almost not observed. At the content of 3% (wt) as bundles of nanotubes, as well as individual tubes could be observed. At the content of 5% (wt) a large number of nanotube bundles, distributed between the oxide particles were observed. This pattern was observed in the case of aluminum oxide, as well as in the case of titanium oxide (Fig. 1).

![Fig. 1 – TEM image of the composite MCNT/Al₂O₃ with 5% (wt) of MCNT](image)

We selected optimal conditions for processing time, the degree of load, type and content of the carbon nanomaterial. Investigation of the electrical conductivity of composites based on Al₂O₃ with different content of carbon nanotubes have shown that the dependence is exponential. At the content of CNT 1–2% (wt) the electrical conductivity remains practically unchanged and amounts to about 5×10⁻⁸ S/cm. The increase of the nanotubes content up to 5% (wt) leads to a sharp increase in conductivity up to 3×10⁻⁶ S/cm. In this case one can observe a jump of conductivity at 3% (wt) to 4.5×10⁻⁵ S/cm. In the case of TiO₂ this effect also occurs at 3% (wt) of CNTs and the electrical conductivity of this composite is 2.2×10⁻² S/cm. In general, the conductivity varies from 5×10⁻⁶ S/cm for pure TiO₂ up to 2.2×10⁻² S/cm for the composite containing 5% (wt) of CNTs (Fig. 2).

For selection of the optimum degree of load and milling time in the future we used a composite with 3% (wt) of carbon nanostructures. The experiments revealed that the highest conductivity of milled composites reached at 100 rpm, for 30 min (Fig. 3, 4). A further increase in time or number of revolutions leads to a refinement of carbon nanostructures and, consequently, reduces the conductivity.

At the study of the electrical conductivity of composites according to the type of carbon nanostructures, it was found that the composites with multiwall carbon nanotubes have the best conductivity (Fig. 5), the conductivity of composites with single-walled carbon nanotubes (SWNT) is worse by two orders of magnitude; a composite with carbon nanofibers (CNF) has the worst conductivity.

![Fig. 2 – Dependence of the conductivity of the composites MCNT/Al₂O₃ and MCNT/TiO₂ on the mass content of carbon nanotubes](image)

![Fig. 3 – Dependence of the conductivity of the composites TiO₂/MCNT (3% wt) on the number of revolutions](image)

![Fig. 4 – Dependence of the conductivity of the composites TiO₂/MCNT (3% wt) on the milling time](image)
ing ball-milling was calculated [21]. This method uses a universal value that allows one to be independent on the type of mill and sufficiently facilitates the production and optimization of the processes of formation of composite materials in conditions of a variety of grinding and mixing machines.

To evaluate the effectiveness of the use of CNT/TiO$_2$ composite as a carrier of catalysts in electrochemical devices Pt/TiO$_2$-CNT samples with different contents of carbon nanotubes were prepared and their electrocatalytic activity was investigated using an electrode-modeling cathode of a fuel cell. According to scanning electron microscopy Pt particles are distributed over the surface of titanium oxide fairly evenly. The average particle size is in the range 5-10 nm (Fig. 7). According to the EDX Pt content is at a level of 10%(wt).

According to literature data, at the presence of CNT/TiO$_2$ with different content of carbon nanotubes are shown on Figure 8. The composite with 5%(wt) of MWNT is the most effective. The composite with 3%(wt) content of CNT has lower quantity of extended carbon structures providing electron transport, and in samples with 15 and 50%(wt) of CNT the low efficiency of Pt-catalyst may be related to difficulties of contact with the reaction medium because of the large amount of carbon material.

As can be seen from the figure, the samples obtained by mechanical action 76 J/g have the highest conductivity ($4.5\times10^{-8}$ S/cm). Further increase of the load and processing time leads to a decrease in electrical conductivity, which is obviously due to the oxide shredding and destruction of carbon nanotubes. This assumption is confirmed by the values of specific surface area of the composites, which vary from 55 m$^2$/g for the composites obtained at a dose of strain effect 38 J/g to 80 m$^2$/g for the composites obtained at 9.6 kJ/g. A similar pattern is observed in the case of composites based on aluminum oxide.

To determine the type of carbon nanostructures contained in it the samples were constructed (Fig. 6).

Fig. 6 – Dependence of the conductivity of the composite MWNT/TiO$_2$ on the dose of strain effect on the samples

Fig. 7 – SEM image of TiO$_2$ with Pt clusters deposited on it

Current-voltage characteristics of the system Pt/TiO$_2$–CNT with different mass content of carbon nanotubes are shown on Figure 8.

The composite with 5%(wt) of MWNT is the most effective. The composite with 3%(wt) content of CNT has lower quantity of extended carbon structures providing electron transport, and in samples with 15 and 50%(wt) of CNT the low efficiency of Pt-catalyst may be related to difficulties of contact with the reaction medium because of the large amount of carbon material.
than 10%. In the case of composites obtained by the synthesis of carbon nanostructures directly on the surface of oxide powders, apparently, there is a tight contact both between the carbon tubes and between tubes and particles of oxides.

CONCLUSIONS

Optimal conditions were determined for the formation of carbon-oxide composites by the treatment of mixtures of oxides of a metal with carbon nanomaterials in a planetary ball mill. The dependences of the electrical conductivity of composites on the content of carbon nanomaterials (1–5% wt) were determined. It is established that the addition of 3% (wt) of CNT to the oxides leads to a sharp increase in the electrical conductivity: from $5.0 \times 10^{-8}$ to $2.8 \times 10^{-4}$ S/cm for Al$_2$O$_3$ and from $5.0 \times 10^{-6}$ to $2.2 \times 10^{-2}$ S/cm for TiO$_2$. It was shown that the carbon-oxide composites are promising carriers of the catalysts of electrode processes in electrochemical devices. It was revealed that Pr/TiO$_2$–CNT catalyst containing 5% (wt) of carbon nanotubes has the best catalytic activity in oxygen reduction, in an electrode-modeling cathode of a fuel cell.

ACKNOWLEDGEMENTS

The work was supported by RFBR (Project № 11-03-90454 Ukr_f_a) and by the Program OChNM-02.

REFERENCES