

FORMATION OF CLUSTER STRUCTURES ON THERMOEXFOLIATED GRAPHITE BY ELECTROCHEMICAL METHOD

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Abstract

Nickel-plating thermoexfoliated graphite particles were prepared by cathodic polarization of three-dimensional electrodes in diluted nickel sulphate aqueous solutions. X-ray photoelectron spectroscopy and X-ray diffraction techniques were employed for analysis of the particles surface. It has been found that oxidation process of the electrodeposited nickel clusters occurs due to their high reactivity. The presence of essential amounts of bound oxygen on surface of thermoexfoliated graphite particles was demonstrated by cyclic voltammetry and X-ray photoelectron spectroscopy methods. The role of oxygen-containing groups on the surface of thermoexfoliated graphite in the processes of adsorption and subsequent reduction of nickel ions at cathodic polarization as well as the behaviour in neutral aqueous solutions of natural graphite electrodes, intercalated with sulfuric acid and thermoexfoliated, are discussed.

Introduction

At transition from macrostructure to microstructures, which sizes lay in the nanometer range, properties of substance essentially vary. Metal nanoclusters in the condensed state have another parameters of crystal lattice, melting point and electrical conductivity as compared with the appropriate macrocrystals. Besides, they have new optical, magnetic and electronic characteristics [1]. Presence of dimensional effects in the electronic and structural properties of nanostructures means that their reactivity differs as against of the massive metal. Therefore the dispersed materials with particles, covered with the clusters of metals, represent a significant interest as highly-effective catalysts of various chemical reactions. The properties of the nanoclusters, prepared by the method of sedimentation on a matrix, differ from those of the clusters, prepared by other methods, due to isolation each from other by a matrix. Catalytic properties of the deposited particles essentially differ from those of the massive metals and change depending on size distribution of the particles [2]. At industrial synthesis of the supported metal catalysts (it includes stages of the carrier granules impregnation by a solution of active metal compound with following incandescence and reduction) the integration of particles is observed in consequence of sintering.

There are some routes of the given problem solution, for example modification of the carrier with the intention to create of enough amount of germ centres for metal particles formation, selection of the materials, which ensure epitaxial growth of the nanoparticles due to structural conformity of the crystal lattices parameters, use of the carriers with original pores geometry, etc. One of the methods ensuring uniformity of system is realization of synthesis in the controlled kinetic conditions, and in particular by electrodeposition. For application of this method the matrix must exhibit an electronic conductivity and advanced surface area. Carbon fibres and graphite are suited to these requirements. Last years the interest of the researchers to such materials tends to widen because of an opportunity of their use in the electrochemical

reactors with three-dimensional electrodes intended for non-ferrous metals extraction from industrial waste water [3, 4].

The process of non-ferrous metals electrodeposition onto the thermoexfoliated graphite particles surface is of obvious interest because its conductivity are comparable with that of a carbon fiber, however the former have more advanced surface area. In the present work, the process of nickel clusters electrodeposition onto plate and three-dimensional electrodes of thermoexfoliated graphite was investigated.

Experimental

Thermoexfoliated graphite with the filling density of $4\text{--}5\text{ g}\cdot\text{dm}^{-3}$ was prepared by fast heating in the previously warmed up to 900°C the electric furnace of natural graphite GAK-2 intercalated with sulfuric acid using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidizer.

The voltammograms were obtained using three electrode glass cells with the potentiostat PI-50-1.1 with rate of potential scanning of $5\text{ mV}\cdot\text{s}^{-1}$. The graphite plate with the sizes of $40\times 10\times 3\text{ mm}$ served as an auxiliary electrode. The potential value was referred to the silver chloride electrode saturated with KCl. Electrodeposition of nickel on the surface of thermoexfoliated graphite particles was carried out in a flowing type glass electrochemical reactor. The techniques of investigation have been described in more detail in [5]. The analytical grade reagents were used for the working solutions preparation. The specific surface area was determined by the standard technique of argon adsorption at liquid nitrogen boiling temperature.

The X-ray diffractometer DRON-3M with CuK_α radiation was used to measure the Bragg refraction from the powder patterns of thermoexfoliated graphite with nickel plating. The X-ray photoelectron spectra were obtained with the spectrometer XPS SERIES-800 (Kratos Analytical), using AlK_α X-ray source (1486.6 eV).

Results and discussion

As it is known, the first stage of electrochemical reaction is adsorption of the ions, discharged on an electrode when electrical current passes through an electrolyte. The process of adsorption does not proceed on entire surface of a solid but only on some active sites. On the carbon materials the oxygen-containing groups of such sites, which be able to absorb the non-ferrous metal ions, have acidic or basic character. The concentration of these groups may be determined by traditional methods of chemical analysis [6] or by more effective method of cyclic voltammetry that was applied for research of electrical oxidation process of the carbon fibers [7]. The mechanism of surface anodic oxidation of graphite carbon in aqueous electrolytes is complex and depends in a large extent on the kind of an electrolyte. A simple secondary oxidation of carbon with reactive oxygen species formed in the primary electrochemical step is common assumed but it is true only for alkaline solutions. Surface anodic oxidation in the diluted alkaline solutions (0.01 N) is at least 20 times more effective than that in the concentrated ones (0.5 N).

Mechanism of carbon materials oxidation in neutral and acidic aqueous solutions is considerably more complicated. Various kinds of oxides arise obviously here and in particular bulk oxides are formed as result of the “graphite salt” hydrolysis. Anodic intercalation of anions into graphite is observed even in the very diluted acids. Cyclic voltammetry indicates on the formation of short-lived intercalation compounds even in neutral aqueous electrolytes such as $1\text{ M Na}_2\text{SO}_4$ what may be related with the fact that the anode surface becomes acidic because of electrolysis of water. As may be inferred from the Fig. 1, at anodic polarization of natural graphite electrode (curve 1) at potential $+0.6\text{ V}$ referred to saturated silver chloride electrode the formation of surface oxides is observed.

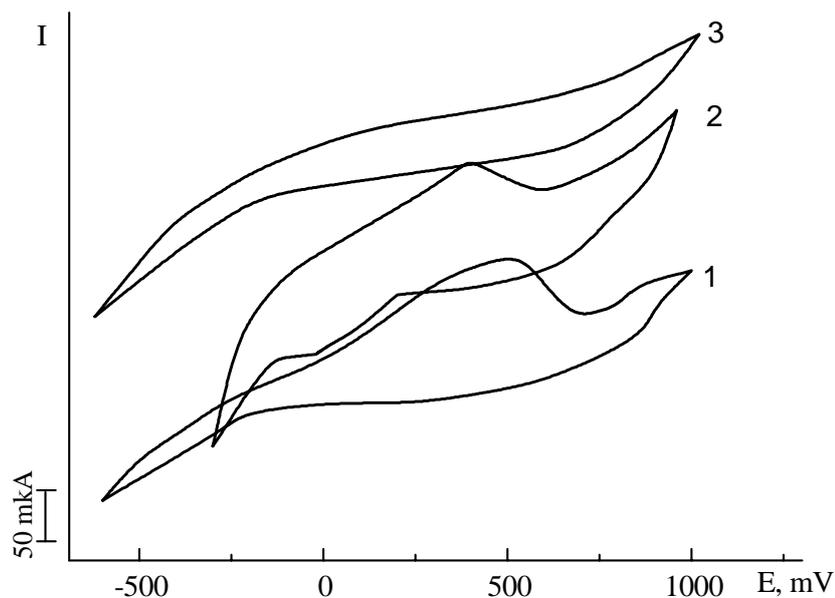


Fig. 1. Cyclic voltammograms of: (1) natural graphite; (2) graphite intercalated with sulfuric acid; (3) thermoexfoliated graphite electrodes in 0.01 N Na_2SO_4 solution.

The conclusion that the process of “surface oxides” formation proceeds on surface of natural graphite electrode rather than that of sulfuric acid intercalation in bulk of graphite occurs is confirmed by the fact of hydrosulfate-ions inculcation into the crystal lattice of graphite, as it was noted in previous investigations [8, 9]. This process begins at higher potentials, and on the curves of the opposite direction potential scanning the process of deintercalation is not noticed (Fig. 1, curve 2). Moreover, identical voltammograms were obtained in 0.01 N solution of potassium chloride without ions HSO_4^- , which be able to form the intercalation compounds with graphite.

As it is seen in Fig. 1, voltammogram of the thermoexfoliated graphite electrode essentially differs from the curves of another forms of graphite electrodes. It is caused substantially by oxidation of thermoexfoliated graphite surface. Presence of essential amounts of oxygen on the surface of thermoexfoliated graphite is confirmed by the results of X-ray photoelectron spectroscopy study (Fig. 2).

Although there are no peaks of the surface oxides reduction on voltammograms of thermoexfoliated graphite electrodes, when these electrodes were cathode-polarized in Na_2SO_4 solution under potentiostatic regime (-1 V), the current decrease was observed. This phenomenon is connected with slowing of surface oxides reduction process [10].

With cathodic polarization of thermoexfoliated graphite electrode in 1 N nickel sulphate solution on the surface of particles, instead of the metal clusters, the unbroken nickel film is formed. Therefore based on the results of our previous investigations, the process of nickel electrodeposition on particles of thermoexfoliated graphite was carried out in 0.01 N solution. Wide scan spectra within the binding energy range of 200-900 eV were used to identify the presence of the surface elements. A representative XPS wide scan spectrum for thermoexfoliated graphite with nickel plating is shown in Fig. 3. The spectrum shows three distinct peaks representing the major constituents: carbon, oxygen and nickel. No other elements were detected on the surface of the samples. It is follows from results of these researches that coating particles of island type are formed on the surface of thermoexfoliated graphite.

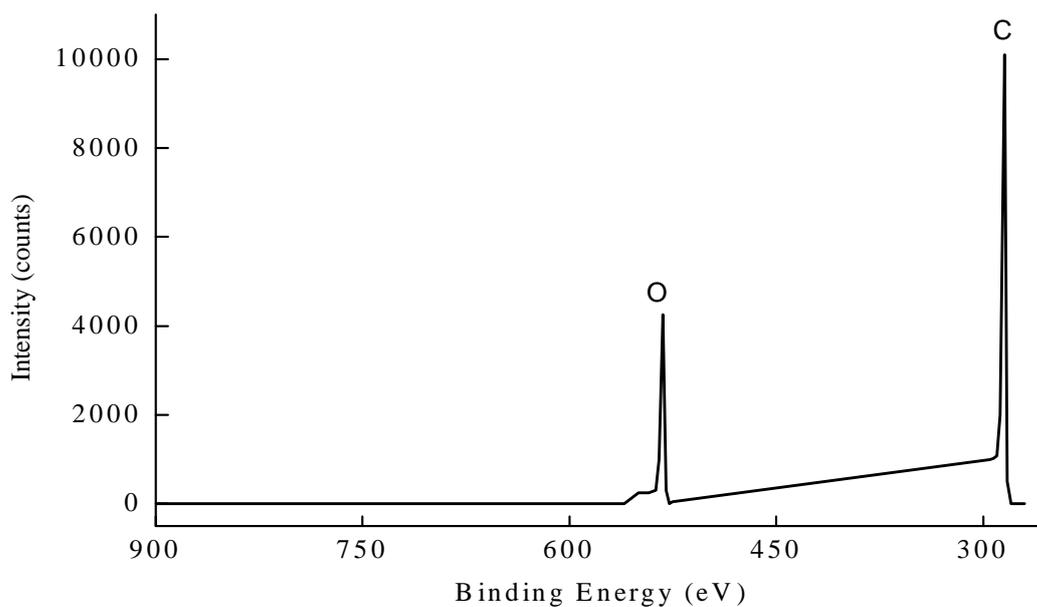


Fig. 2. X-ray photoelectron spectrum of thermoexfoliated graphite.

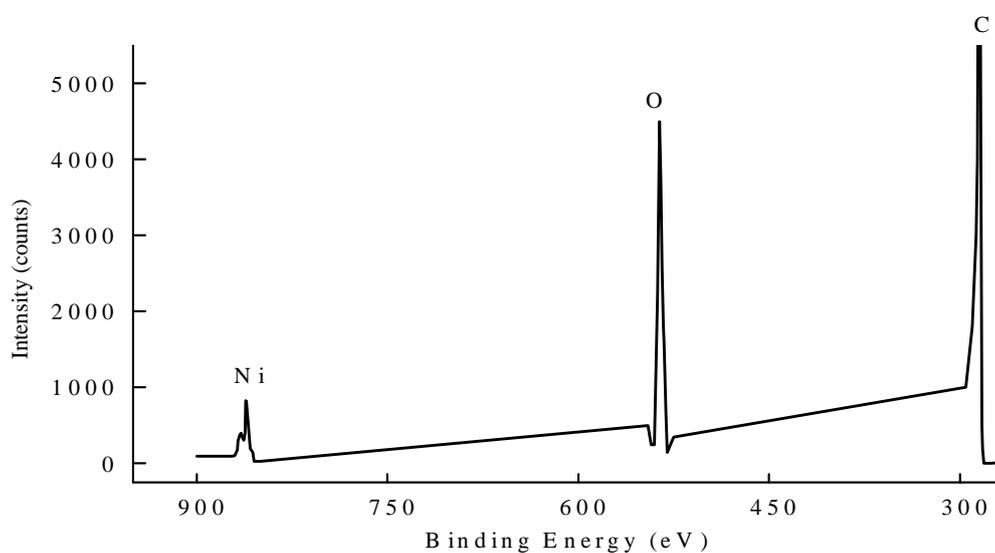


Fig. 3. Wide scan XPS spectrum of thermoexfoliated graphite with nickel plating.

Fig. 4 shows an XPS narrow scan spectrum of the Ni 2p region at 860 eV. The intensive peak at binding energy range 852.5 eV belongs to non-oxidized nickel. The peak of oxidized nickel is energetically heterogeneous that specifies in the presence of nickel at several oxidized forms: $\text{Ni}(\text{OH})_2$, Ni_2O_3 and NiO . These results correlate with the data of work [11].

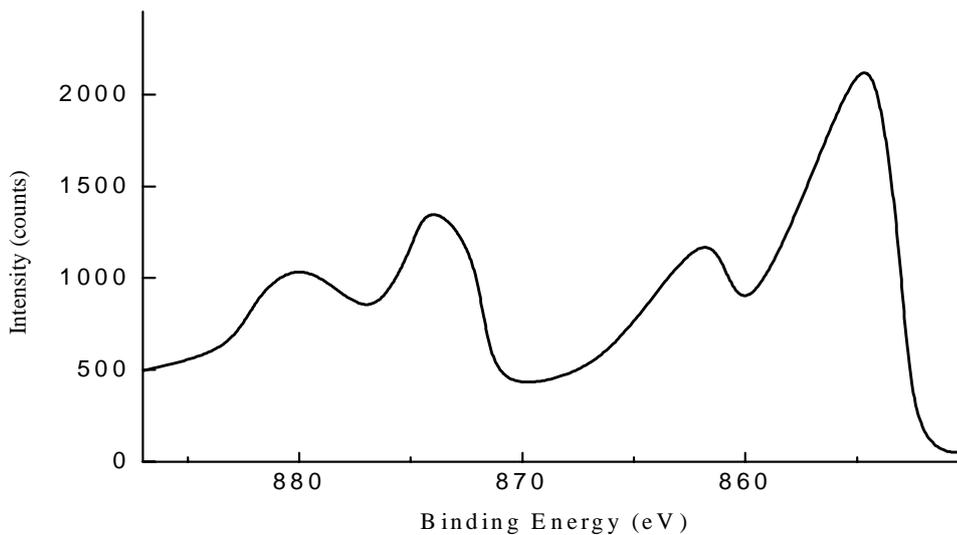


Fig. 4. Narrow XPS scan spectrum of thermoexfoliated graphite with nickel plating.

In Fig. 5 the X - ray diffraction powder patterns of thermoexfoliated graphite with nickel plating is shown.

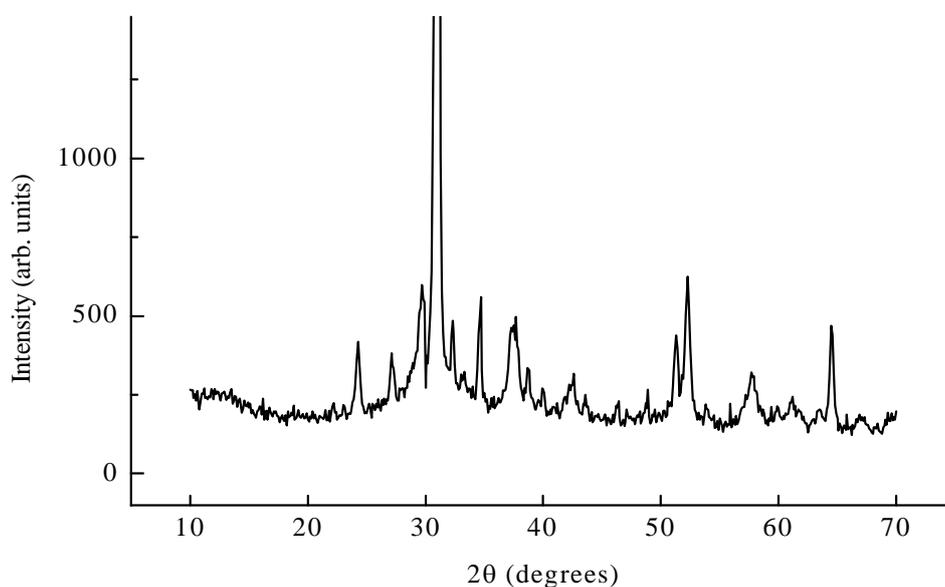


Fig. 5. X - ray diffraction powder patterns of thermoexfoliated graphite with nickel plating.

The spectrum is complex. More than 20 peaks are manifested in it. The most intensive peak belongs to graphite. Appearance of other peaks is connected with the presence of nickel and its above-mentioned compounds.

Conclusion

The presence on the surface of thermoexfoliated graphite particles essential amounts of oxygen-containing functional groups, which be able to absorb the non-ferrous metals ions, was shown by the cyclic voltammetry and X-ray photoelectron spectroscopy techniques. It was demonstrated that when the electrode of thermoexfoliated graphite is anode-polarized the process of the surface oxidizing does not proceed unlike that of the natural and intercalated with sulphuric acid graphite electrodes.

It was shown by the X-ray photoelectron spectroscopy and x-ray diffraction techniques that clusters electrodeposited on the surface of thermoexfoliated particles nickel undergo to particular oxidizing due to their high reactivity.

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