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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Thermally Expanded Graphite as Functional Material in the Technology of Electrode Material with Mixed Conductivity

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Abstract—Methods of differential thermal analysis and cyclic voltammetry were used to examine the functional properties of thermally expanded graphite in an electrode material for electrochemical systems. This material contains platinum, carbon black, and proton-conducting polymer Nafion. It was shown that addition of thermally expanded graphite to the electrode material makes higher the thermal stability of Nafion. Under an electrochemical treatment, thermally expanded graphite compares well in stability against this treatment with the commonly used carbon black of the Vulcan XC-72 type. A mechanism is suggested for stabilizing the proton-conducting polymer Nafion in the presence of thermally expanded graphite. It was shown that thermally expanded graphite is promising for being used in the technology of electrode materials with mixed conductivity, which contain a proton-conducting polymer of the Nafion type, as a functional additive serving to improve the thermal stability.

Keywords: thermally expanded graphite, mixed conductivity, electrode material, thermal stability of Nafion, fuel cells

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Modern electrochemical electrodes of such devices as low-temperature fuel cells with a proton-conducting membrane of the Nafion type and water electrolyzers have a number of specific problems associated with the intensification of the mass transport, utilization efficiency of the catalyst surface, thermal and electrochemical stability, and long functioning duration without significant loss of technical characteristics, etc. One of well-reputed technological procedures for controlling the technical characteristics of a material consists in introduction of functional additives into this material (some technologies were described in [1–3]). A search for, and examination of new functional additives and the possibility and efficiency of their application are being permanently conducted at research centers of various countries.

The results of the study reported in the present communication are devoted to a detailed examination of the possibility and efficiency of using graphene materials in the previously described [4] technology of electrode materials for low-temperature fuel cells and water electrolyzers. These results are aimed to improve the service characteristics (thermal and electrochemical stability, longevity of operation) and raise the efficiency of electrode materials of the Pt(Me)|C–Nafion–functional additive system. These materials are widely used in fabrication of electrodes for low-temperature fuel cells and water electrolyzers. The results obtained make it possible to demonstrate the possibility of using graphene materials as a functional additive and the influence exerted by their introduction into the technological process on the improvement of technical characteristics of the electrode material.

The wide use of carbon materials in electrochemical electrodes with mixed conductivity for such devices as electrolyzers, supercapacitors, and fuel cells is due to a number of their physical and physicochemical properties

[3, 5–8]. It is well known that carbon nanostructured materials (CNMs) with graphite-like structure, such as carbon nanotubes and blacks, graphene-like materials, and graphites proper, have a relatively high electrical conductivity combined with a comparatively high chemical stability. Materials of this kind may have a developed surface (specific surface area may be as large as several thousand square meters per 1 g). They may have not only various porosities, but also various pore structures, which can be controlled by the technology of a material [8]. The application areas of these materials are wide. CNMs are mostly used as catalyst supports [9]. However, there also have been reports in the scientific literature that CNMs are used as structure modifiers [10] and activators of electrode processes [11–17].

In this context, a search for functional materials among CNMs is a topical development direction of the technology of electrochemical electrodes.

One of significant limitations to application of electrode materials in fuel cells (FCs) with a proton-conducting polymer of the Nafion type is the thermal stability. This is so because just Nafion is the most thermally unstable component of an electrode material. It is known that Nafion is contained in electrodes and simultaneously serves as the material of the proton-conducting membrane separating the cathode and anode and provides transfer of hydrated protons. The highest operation temperature of the presently existing devices is about 80°C. Studies concerned with the thermal stability of fuel cell materials are mostly devoted to the proton-conducting membrane proper, contained in the membrane-electrode assemply, and to raising its thermal stability via introduction of various additives into its composition [18–24]. For example, an addition of titanium dioxide into a Nafion membrane was used in to improve the thermal stability [18], and multiwall carbon nanotubes (CNTs) were used in [19, 20] for the same purpose. The authors of both the above studies attributed the effect of the increased thermal stability of the membrane to the formation of a bond between the sulfo group of the Nafion molecules and oxygen in TiO_2 in the first case and with the surface oxygen in a CNT in the second. In [24], the influence exerted by the cation of the sulfo group (alkali metals and ammonium) on the thermal stability of Nafion was examined. It was reported that the decomposition temperature of Nafion is inversely proportional to the size of the exchange cation, i.e., Nafion films exhibit an improved thermal stability upon a decrease in the cation size. In [22], the kinetics of thermal oxidation of the electrode material containing a platinized carbon black of the Vulcan XC-72 type and Nafion was examined. It was noted that the presence of surface protective groups make higher the activation energy of low-temperature/low-conversion (5%) oxidation of 46% Pt/Vulcan XC-72 (197 kJ mol^{-1}) as compared with the process with higher temperature/higher conversion (10–30%) (140 kJ mol^{-1}). In catalyst layers of a fuel cell with a proton-conducting membrane, the thermal decomposition temperature of Nafion decreases by approximately 100–300°C in the presence of Pt/C catalysts.

A laboratory technology for obtaining an electrode material for direct-energy-conversion systems (fuel cells, electrolyzers, electrochemical sensors) has been described previously [4]. This material contains platinum nanoparticles on carbon black, a proton-conducting polymer Nafion, and thermally expanded graphite. The structure of the material was examined, and dependences of the porosity of a material on composition were presented. A laboratory technology of electrodes containing platinized carbon black, thermally expanded graphite (TEG), and Nafion was developed, the fundamental aspects of structuring in the system under consideration were analyzed, and fundamental relationships between the composition and structure of a composite electrode were established.

The goal of the present study was to examine TEG in detail as a functional additive controlling the thermal and electrochemical stability of the electrode material.

Based on published data [19–21] and results of our studies [4], we can formulate several patterns manifested when the electrode material is formed in the presence of TEG. As shown in [4], Nafion is for the most part structurally bound in the Pt/C–TEG–Nafion system to TEG. In the course of an ultrasonic treatment, TEG is stratified, its structural elements are transformed to thin plates (stratification), with carbon black and Nafion distributed over their surface. Under an electrochemical treatment of TEG, the cyclic voltammograms are broadened. This indicates that the surface area of the material becomes larger as a result of the further expansion of TEG, which is accompanied by an electrochemical functionalization consisting in a partial oxidation with addition of oxygen-containing groups of atoms. It was shown in [18–20] that the interaction of the sulfo groups of Nafion with the oxygen-containing groups of the material contacting with Nafion makes

Component composition and the temperature T_{max} of the maximum rate of thermal destruction in air of the electrode material samples under study

Sample	Nafion, %	TEG, %	Pt/C	Vulcan, %	T_{max}, °C
1	20	80	0	0	–
2	10	45	45	27	347
3	20	0	0	80	379
4	20	20	0	60	421
5	20	0	80	48	305
6	40	30	30	18	331

higher its thermal stability, be it either titanium dioxide dispersed in Nafion, or multiwall carbon nanotubes with surface oxygen atoms [19, 20]. The increase in the thermal stability can be attributed to the decrease in the energy of the Nafion/support system because of the formation of surface compounds. It would be expected in terms of these concepts that, upon introduction of TEG containing surface oxygen groups into an electrode material, Nafion should be stabilized, with its thermal stability increasing. With consideration for the fact that Nafion is structurally related to TEG [4], it would be expected that the stabilization effect should be rather pronounced.

EXPERIMENTAL

To examine the functional properties of TEG as a stabilizing additive, we synthesized six samples of the electrode material with various component compositions. Three samples contained TEG. Of these, two also contained platinum in the form of platinized carbon black (Pt/C), and the third, carbon black without platinum. As a control, we synthesized samples containing no TEG, of which one also contained platinum in the form of a platinized carbon black (Pt/C), and another, a carbon black without platinum. For electrochemical measurements, we fabricated a sample containing only TEG. Nafion was present in all the samples. The compositions of the samples are listed in the table.

The samples we prepared were subjected to two kinds of treatment: electrochemical and thermal. The changes occurring in the course of these treatments were recorded by cyclic voltammetry and differential thermal analysis.

As starting components for preparing samples of the electrode material served the following.

– Commercial platinized carbon black with 40 wt % platinum, from E-TEK company, which is a nanostructured platinum on carbon black of the Vulcan XC-72 type.

– Carbon black of the Vulcan XC-72 type.

– TEG (carbon material from [26] was used).

– Commercial product Ion Power Inc. DUPONT DE2020, a water-propanol Nafion solution with concentration of 20%. Nafion was used in the H^+ form.

The technological procedures used to prepare a dispersion of the electrode material [4] included two stages: mechanical and ultrasonic dispersion of a mixture of precisely weighed portions of the components in an isopropanol–water mixture.

In the first stage, we performed a primary mechanical mixing of the starting components, platinized carbon black, TEG, and Nafion, in an isopropanol–water mixture in a Milaform MM-5M magnetic rabble at a stir bar rotation speed of ~400 rpm with a stir bar insulated into a plastic sheet. This was done until a visually homogeneous (without visible lumps) mass was formed in ~0.5 h. Prior to the introduction, Nafion was preliminarily coagulated from solution in the liquid phase [26]. A working Nafion solution containing 2% main substance in a 1 : 1 (v/v) isopropanol : water mixture was mixed with the equal amount of water and then poured onto the solid components. The ratio between the solid and liquid phases in the final dispersion (catalytic ink) was within the range from 1 : 40 to 1 : 80.

In the second stage, we performed an ultrasonic (US) dispersion in a Branson 3510 ultrasonic bath, until a stable homogeneous dispersion of the components was obtained. The treatment in a US bath with working ultrasound frequency of 40 kHz at a power of 130 W was performed during ~30–50 h until a visually homogeneous dispersion was obtained.

A part of the dispersion was dried in air for making a thermogravimetric analysis, another part of the dispersion was used to prepare a sample on a rotating disk electrode for electrochemical measurements.

A microscopic study was carried out as follows. Analytical measurements were optimized by using the previously described approach [27]. Prior to measurements, samples were placed on the surface of an aluminum table 25 mm in diameter and fixed there with a conducting adhesive graphite tape. The morphology of the samples was examined under native conditions to rule out surface effects caused by deposition of a conducting layer [28]. The microstructure of the samples was examined by the method of field-emission scanning electron microscopy (FE-SEM) on a Hitachi SU8000 electron microscope. The images were obtained in the secondary-electron mode at accelerating voltage of 30 kV and working distance of 6–10 mm. An EDX study of the samples was carried out with an Oxford Instruments X-max energy-dispersive spectrometer.

Electrochemical study. The electrochemical behavior of the materials was examined by the method of cyclic voltammetry (CVA) on a stationary disk electrode. The installation was of the VED-06 type with an IPC-Pro potentiostat. A sample dispersed in an isopropanol-water medium was applied to the polished surface of a glassy carbon disk electrode with area of 0.07 cm^2 and dried in air. Measurements were made in 0.5 M sulfuric acid in a solution that is in equilibrium with air. The electrode potential of a sample was multiply cycled within the range characteristic of the O_2/H_2 system, from –150 to +1000 mV, relative to a silver chloride reference electrode at a rate of 50 mV s^{-1}. Periodically, separate intermediate cyclic voltammograms were recorded to monitor the variation of such parameters as the capacitance of the electric double layer (EDL) and the electrochemical capacitance, which were calculated by the known relations [29–31].

The differential capacitance (DEC) was determined by measuring cyclic voltammograms at a working electrode potential of 600–650 mV (in the range in which there are no electrochemical reactions) by the relation

$$C = \frac{dQ}{dE} = \frac{i}{\nu}, \tag{1}$$

where C is the electrical capacitance: Q, charge; E, potential; i, current; and ν, polarization rate.

The electrochemical capacitance associated with the oxidation–reduction of the surface oxygen-containing groups of atoms on carbon materials, was calculated as the difference between the capacitance at the peak-discharge potential of surface groups, also calculated by relation (1), and the DEC capacitance.

The electrochemical stability of a platinum-containing sample was examined under similar conditions.

The area of the electrochemically active surface of platinum was found from the desorption of hydrogen [31, 32] (stationary electrode) by using the anodic branch of the cyclic voltammograms.

Thermogravimetric measurements were made on a Mettler Toledo TGA/DSC 1 derivatograph (Switzerland), with air blown through the chamber of the derivatograph at a rate of 30 cm^3 min^{-1} and temperature uniformly raised (10 deg min^{-1}) within the range 35–1000°C. A weighed portion of a material with a mass of several milligrams was placed in an Alundum crucible and the mass and heat curves were recorded in the course of heating.

RESULTS AND DISCUSSION

Figures 1 and 2 show characteristic TEM microscopic images of an electrode material containing platinized carbon black, thermally expanded graphite, and Nafion. The micrographs show TEG platelets, and spherical agglomerates of carbon black with platinum particles (dark spots). The average size of platinum nanoparticles corresponds to that specified by the manufacturer, but it is seen that there occurs a certain size scatter of platinum particles. The characteristic dimensions of carbon agglomerates (Vulcan XC-72) fall within the range 50–100 nm. The elemental composition on the whole corresponds to the charge composition. Certain discrepancies can be attributed to the microscopic heterogeneity of the material, as noted in [4].

Electrochemical measurements. Figures 3 and 4 show the results of an electrochemical study of samples in the TEG–Nafion and Pt/C–TEG–Nafion systems. In the case of pure TEG (Fig. 3a), the electrochemical treatment leads to a substantial rise in the differential capacitance, which probably occurs due to the continuing (after the US treatment) process of splitting of TEG layers, accompanied by an increase in the area of TEG

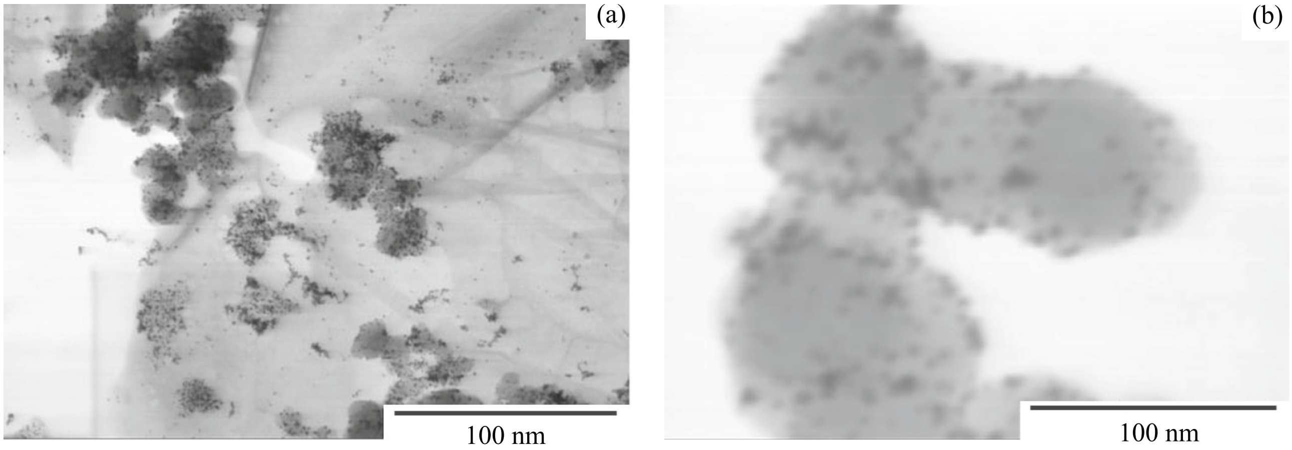

Fig. 1. Characteristic TEM images of an electrode material sample in the Pt/C-TEG–Nafion system (sample 6) at different magnifications.

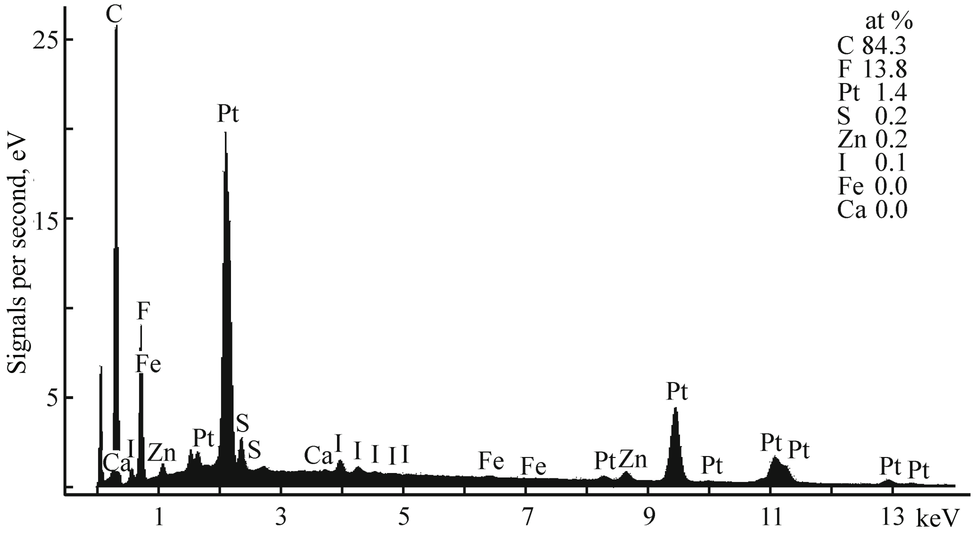

Fig. 2. EDX spectrum, results of an elemental analysis of the electrode material (sample 6).

contact with the electrolyte solution. In addition, there occurs a certain broadening of the peaks associated with the discharge of surface oxygen-containing groups of atoms. The dependence of the anodic peak potential on the number of cycles (Fig. 3b) exhibits an ascending run with leveling-off at ~300 cycles. The dependence of the DEC capacitance shows a similar behavior (Fig. 3c). At the same time, the electrochemical capacitance (associated with the charge transfer in redox processes involving surface groups of atoms) only slowly grows. This shows that the process of TEG splitting is nearly complete after 300 cycles (DEC capacitance ceases to grow), whereas the electrochemical oxidation of the TEG surface to give oxygen groups continues.

In the case of presence of platinum in a material, the cyclic voltammograms clearly show the range of hydrogen adsorption/desorption [31, 32] (potentials in the range from –150 to +120 mV). It can be seen that, in the process of an electrochemical treatment, the area under the curves decreases, i.e., the electrochemically active surface area of platinum becomes smaller. This behavior is commonly attributed to the dissolution and recrystallization of platinum nanoparticles [30, 33]. The area of the electrochemically accessible surface of platinum decreases with leveling-off at 1200 cycles (Fig. 4e), which is characteristic of E-TEK [30]. The discharge-peak potential of surface groups of atoms (Fig. 4b) grows, but, in contrast to pure TEG, no leveling-off of this potential

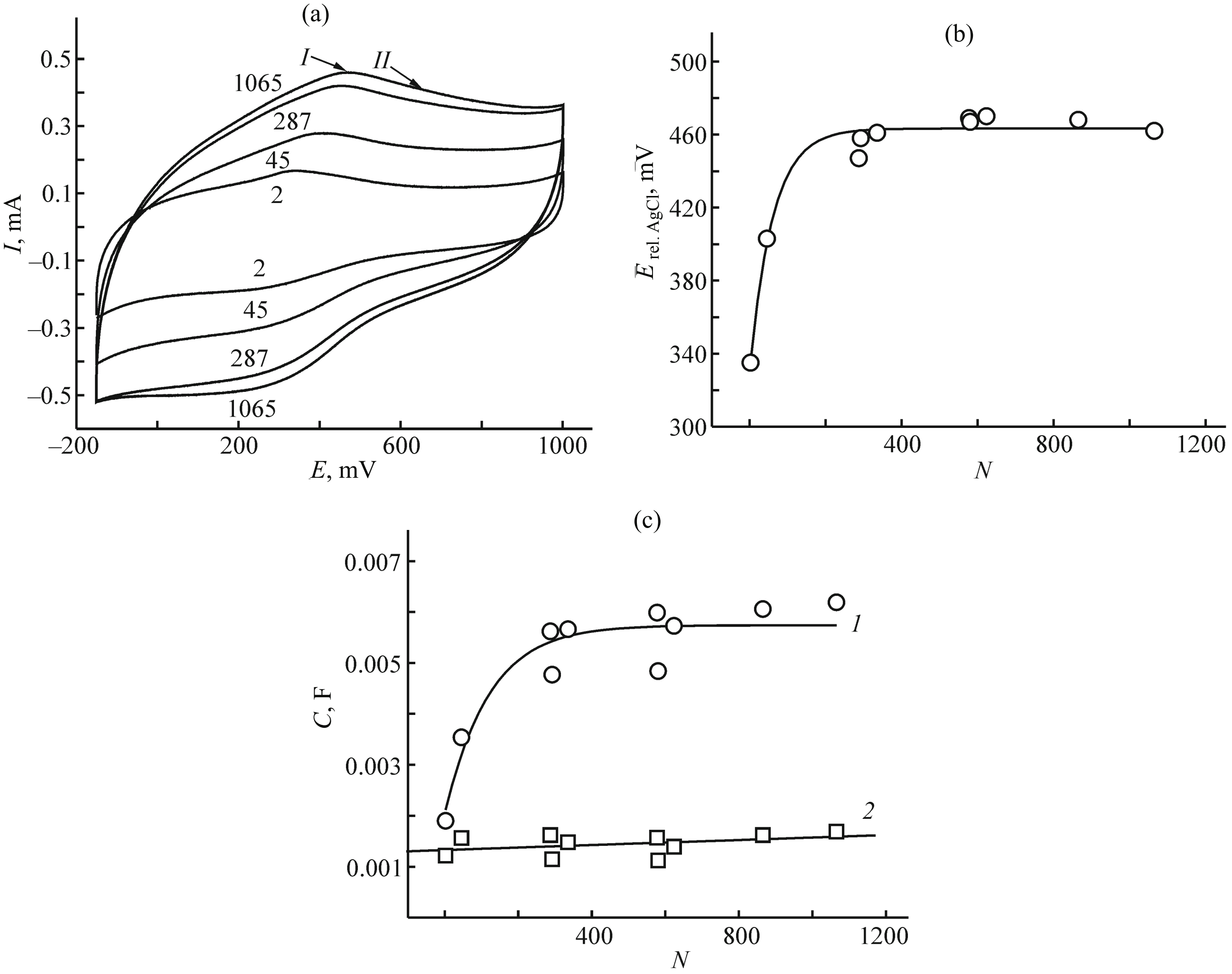

Fig. 3. Dynamics of the electrode characteristics in the TEG–Nafion system under prolonged electrochemical treatment. (a) Cyclic voltammograms, Arabic numerals denote the number of cycles; *I*, anodic peak of surface groups; *II*, DEC region; (b) dependence of the potential of the peak discharge of surface groups on the number of cycles; (c) dependence of (*1*) capacitance of the electric double layer and (*2*) electrochemical capacitance (slope ratio $B = 2.46 \times 10^{-7}$ F) on the number of cycles.

is observed. The DEC capacitance and the electrochemical capacitance linearly decrease in the course of cycling (Fig. 4c), but do so with different slope ratios. The electrochemical capacitance decreases more slowly. This indicates that there occurs a loss of the surface area of the carbon material (DEC capacitance decreases), which is due to the electrocatalytic properties of platinum. In the process, there occurs an electrochemical functionalization of the carbon surface due to the partial electro-oxidation and formation of surface oxygen-containing groups of atoms. The functionalization process is ahead of the process in which the surface area decreases, i.e., the surface concentration of oxygen groups of atoms grows.

In the cyclic voltammograms of the sample with platinum (Fig. 4a), subjected to an electrochemical treatment, the DEC capacitance does not increase, in contrast to what it does in the TEG sample containing no platinum (Fig. 3a), i.e., there is no splitting of TEG into platelets, accompanied by an increase in surface area of the sample. It can be concluded that the splitting of TEG in the presence of E-TEK was complete in the stage of US treatment, whereas pure TEG was also split in the stage of electrochemical treatment. Comparing the structural characteristics of the material, we obtained previously and reported in [4], we can conclude that, in the course of the US treatment, the platinized carbon black (E-TEK)

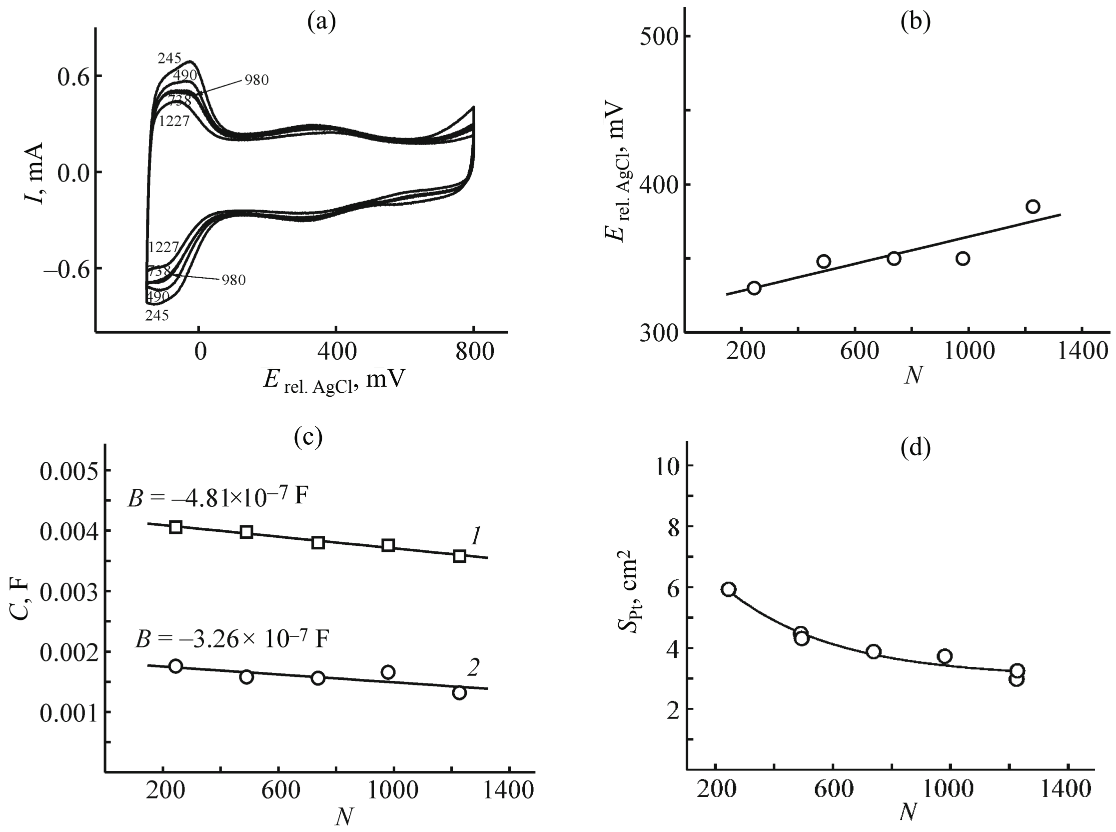

Fig. 4. Dynamics of the electrode characteristics in the TEG–Nafion system (sample 2) under prolonged electrochemical treatment. (a) Cyclic voltammograms, numerals denote the number of cycles; I, anodic peak of surface groups; II, DEC region; (b) potential of the peak discharge of surface groups; (c) (*1*) capacitance of the electric double layer and (*2*) electrochemical capacitance; (d)electrochemically accessible surface area of platinum.

is incorporated into the TEG structure and promotes its splitting.

Thermogravimetric study. Figures 5–7 shows thermograms of pure Nafion and pairs of samples containing and not containing TEG. According to the existing concepts [21], the thermal destruction of Nafion occurs in three stages: 50–180°C, loss of water (moisture); 310–380°C, loss of sulfo groups; 420–590°C, oxidative destruction of the perfluorinated matrix. The thermograms of pure Nafion, presented in Fig. 5, are on the whole consistent with this behavior, being somewhat shifted to lower temperatures. This shift can be accounted for by the use of various Nafion materials and various weighed portions when making DTA. Distinct peaks of decomposition of sulfo groups at 341°C and perfluorinated skeleton at 448°C can be seen in Fig. 5.

Samples that contain carbon components in addition to Nafion exhibit (Fig. 6) a tendency toward merging of these two peaks, with the sulfonic peak shifted to higher temperatures, and the skeletal, contrariwise. The temperature of the destruction peak was 379°C for the sample containing no TEG, whereas for the sample with TEG, it was substantially higher, 421°C.

In the presence of platinum the qualitative pattern is preserved, but the destruction peaks are shifted to lower temperatures, being, respectively, 305 and 331°C for samples with and without TEG. This is due to the catalytic effect of platinum, in agreement with the results obtained by other researchers [22].

Thus, it can be stated that the electrode material is thermally stabilized in the presence of TEG. Comparison of our experimental data and those reported in the scientific literature shows that this stabilization is based on two factors: (i) Nafion is for the most part structurally bound to the TEG surface and (ii) it is stabilized due to the formation of surface compounds with oxygen groups of atoms in TEG.

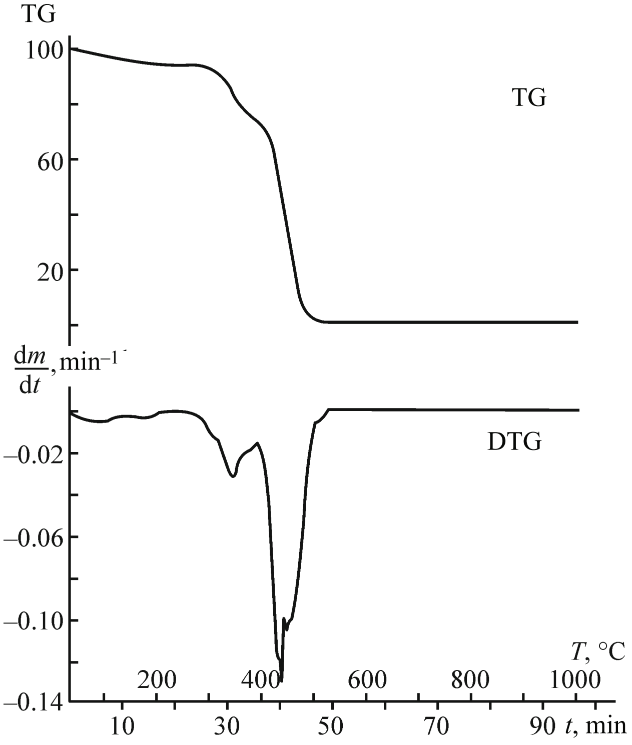

Fig. 5. Derivatograms of pure Nafion.

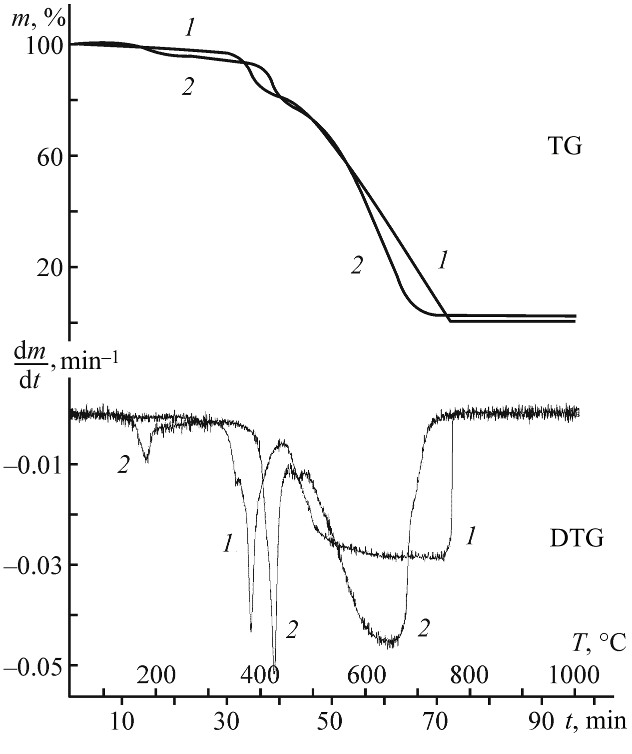

Fig. 6. Derivatograms of samples in the systems (*1*) Vulcan XC-72–Nafion and (*2*) Vulcan XC-72–TEG–Nafion.

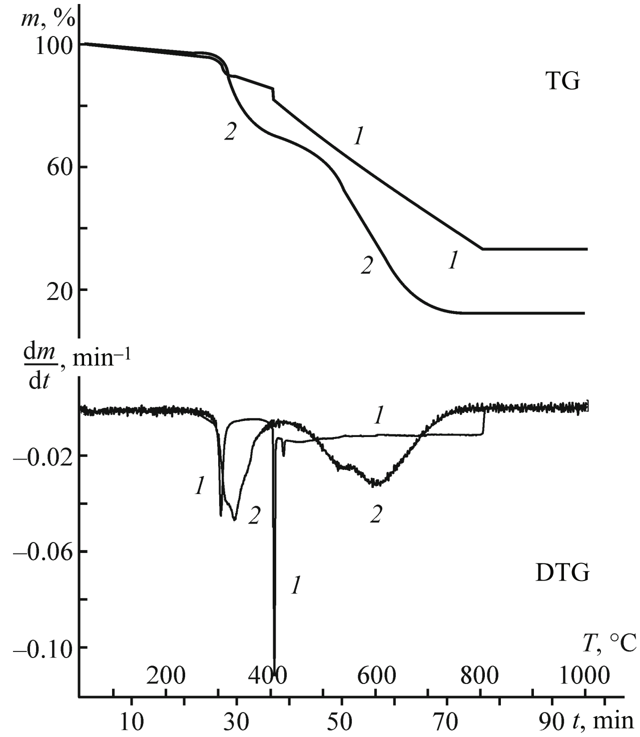

Fig. 7. Derivatograms of samples in the systems (*1*) Pt/C–Nafion and (*2*) Pt/C–TEG–Nafion.

CONCLUSIONS

(1) Thermally expanded graphite was studied as a functional additive controlling the thermal and electrochemical stability of the electrode material.

(2) When electrochemically treated, pure thermally expanded graphite (system thermally expanded graphite–Nafion) is split into platelets and a partial oxidation occurs to give surface oxygen-containing groups of atoms. The splitting is nearly complete after 300 cycles of variation of the electrode potential within the range –150…+1000 mV, whereas the electrochemical oxidation of the surface of thermally expanded graphite to give oxygen groups of atoms continues.

(3) The presence of platinized carbon black promotes completion of the splitting of thermally expanded graphite already in the stage of ultrasonic treatment, whereas pure thermally expanded graphite was also split in the stage of the electrochemical treatment, following the ultrasonic treatment. When subjected to an ultrasonic treatment, the platinized carbon black (E-TEK) is incorporated into the structure of thermally expanded graphite and promotes its splitting.

(4) When an electrochemical treatment is performed in the absence of platinum, no significant decrease in the surface area because of the oxidation of thermally expanded graphite is observed, whereas in the presence of platinum, this process occurs, which is due to its catalytic effect.

(5) The introduction of thermally expanded graphite into the electrode material strongly improves the thermal stability of the material because of the higher thermal stability of Nafion.

(6) In the system constituted by Vulcan XC-72, thermally expanded graphite, and Nafion without platinum, the temperature at which the thermal destruction rate is at a maximum increases by 42° upon introduction of 20% thermally expanded graphite. In the presence of platinum, addition of 45% thermally expanded graphite improves the thermal stability also by 42°. However, both temperatures are shifted to lower temperatures, which is due to the catalytic properties of platinum.

(7) The introduction of thermally expanded graphite into the electrode material leads to a higher characteristic temperature of the stage of destruction of sulfo groups (low-temperature stage) and to a lower destruction temperature of the fluorine-carbon skeleton (high-temperature stage) as compared with pure Nafion. This is manifested in that two peaks in the differential thermogravimetric curve are combined into a single peak.

(8) The thermal stabilization mechanism is based on two factors: (i) Nafion is for the most part structurally bound to the surface of thermally expanded graphite and (ii) it is stabilized due to the formation of surface compounds with oxygen groups of atoms in thermally expanded graphite.

(9) Using thermally expanded graphite in the technology of electrode materials as a thermally stabilizing functional additive is promising for raising the working temperature of electrodes based on a proton-conducting polymer Nafion in order to make higher the working current density, reduce the platinum charge, and prolong the service life.

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