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Electrochemical Immobilization of Silver Nanoparticles in a Polymethylolacryalmide Matrix[1]

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Abstract—The possibility is studied of electrochemical synthesis of a nanocomposite of polymer/silver nanoparticles. The composite was formed in two stages including synthesis of a polymethylolacrylamide film by electropolymerization and the further immobilization of silver nanoparticles in a polymer matrix using the method of electrochemical reduction of metal ions to Ag^0 in a film impregnated by $AgNO_3$ solution. Physical, chemical, electrochemical, and catalytic characteristics of hybrid materials are studied. The presence of Ag^0 in the polymer is confirmed both visually and using the methods of X-ray phase analysis, plasmon resonance, scanning electron microscopy, energy—dispersive and atomic absorption analysis. The optimum modes of electrochemical immobilization of Ag^0 nanoparticles in the polymer are determined. The effect of the potential sweep rate, number of cycles and $AgNO_3$ concentration on the completeness of reduction of Ag^+ and amount of silver immobilized in the composite is studied. It is found that electroreduction of Ag^+ to Ag^0 occurs predominantly in the first cycle. The method of small—angle X-ray scattering is used to obtain the functions of silver particle distribution by radii. It is established that the average diameter of Ag nanoparticles is about 20 nm. It is found that polymer methylolacrylamide films containing silver nanoparticles manifest electrocatalytic activity towards hydrogen peroxide.

Keywords: electropolymerization, electroreduction, acrylamide, metal/polymer composite, silver nanoparticles

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INTRODUCTION

Hybrid metal—polymer materials are increasingly used worldwide. They are ever more in demand owing to the fact that these materials optimally combine the properties of polymers and inorganic particles [1—12]. Besides, combining polymers with other materials can provide new properties, untypical for individual composite components. The polymer matrix to be used can be both conducting polymers (polyaniline, polypyrrole, polythiophene, and their derivatives [3]) and nonconducting polymers (polymethylolacrylamide [4]). Inorganic fillers can be noble metal (Au, Ag, Pt, and Pd) nanoparticles and also Cu, Ni, Fe, Co, graphene [6], and metal oxides (SnO_2, Fe_3O_4) [8, 9]. Particular attention is attracted by composites based on polymers including noble metal nanoparticles. Such materials are promising for application as efficient catalysts of chemical, electrochemical, and photoelectrochemical reactions [10—20].

A special place among metal—polymer composites is occupied by materials including silver nanoparticles (AgNPs). The predominant fields of application of such materials include medicine [16—25] and production of optical, chemical, and biological sensors and catalysts [21—25]. Such materials are actively used as electrochemical sensors for quantification of hydrogen peroxide formed in the course of biological and enzyme—catalyzed reactions that have to be thoroughly monitored [13, 14, 22].

Silver nanoparticles are introduced into a polymer matrix for their mechanical fixation. Usually the process of formation of such materials is multistage and rather complicated. Therefore, it is necessary to search for simpler and readily available technological solutions. From this viewpoint, we believe the method of monomer electropolymerization with further electrochemical or chemical reduction of silver ions to AgNPs directly in a polymer matrix to be very promising. One can assume that such an approach can reduce the overall duration of synthesis of polymer—silver composites, allow uniformly distributing AgNPs in the polymer layer, preventing or reducing sticking

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Table 1. Composition of the monomer mixture for electropolymerization

Components of the monomer mixture	Concentration, M
Acrilamide	3.00
N,N'-methylene-bis-acrylamide	0.05
Formaldehyde	3.00
Zinc chloride	0.20

together (aggregation) of silver particles within the fixing polymer layer. We suggest using as a polymer matrix polymethylolacrylamide (PMAA) films that we have well studied with respect to their synthesis by electropolymerization (EP), their molecular and bulk structure [26–28]. In this case, immobilization of AgNPs in a chemically and electrochemically stable polymer matrix is most preferable, as such a matrix produces no destabilizing effect of silver nanoparticles and does not interact with them.

The principal methods of formation of polymer/metal nanoparticle composites are chemical metallization of polymers and precipitation polymerization in the presence of metal colloids. However, these both methods are technically imperfect, multistage, labor–consuming. An alternative can be electrochemical formation of a polymer matrix with the further chemical or electrochemical immobilization of silver nanoparticles. The method noticeably facilitates the technology and reduces the time of composite synthesis to several minutes. We showed in [29, 30] that a PMAA/AgNPs composite can be formed using a two-stage method involving EP of a polymethylolacrylamide film and further chemical reduction of silver in a matrix saturated by $AgNO_3$ solution. However, silver can also be reduced electrochemically. There are no data on such reduction in the literature. Therefore, the aim of this work is to study the alternative possibility of electrochemical immobilization of AgNPs in an electropolymerized PMAA matrix and investigate physico-chemical, electrochemical, and catalytic properties of the obtained hybrid materials**.**

EXPERIMENTAL

Acrylamide 2K (99%) and *N*,*N*'-methylene-bis-acrylamide (99%) (Acros, USA) were used without additional purification for formation of polymethylolacrylamide films. Formaldehyde FM (“v/s” (highest grade), Nevareaktiv, Russia) was used in the form of a 29–31% predistilled solution. The mass fraction of formaldehyde was determined according to *GOST 1625–89* [31]. Zinc chloride (Pharmpur, Spain) was used in the form of 2–4 M solution with pH 3–4. The exact concentration of zinc chloride was determined by complexometric titration using a versene primary standard (UralKhimInvest, Russia). Silver nitrate, 99.98% (pure for analysis, REAKhIM, Russia) was used for immobilization of silver ions. Ag^+ was electrochemically reduced to Ag^0 in 0.1 M potassium nitrate solution (especially pure grade, NevaReaktiv, Russia).

Solutions of monomer composites for synthesis of polymer films were manufactured directly before the beginning of the experiment. Deionized water was used as a solvent.

Electrochemical measurements and synthesis of polymers and composites were carried out using IPC-Pro 8.0 (“Cronas,” Russia) and Solartron (UK) potentiostats/galvanostats. The cell was connected with a potentiostat according to a three–electrode scheme. The working electrode (cathode) was a stainless steel (AISI 314) rod, $\varnothing = 2.5$ mm. The auxiliary electrode (anode) was a platinum plate with $S = 7.5$ cm^2. The reference electrode was a saturated silver–silver chloride EVL-1M3 electrode separated from the solution by a salt bridge. The working electrodes were prepolished, degreased by fine magnesium oxide paste, and thoroughly washed by distilled water. Electrolysis was carried out in 10–20 cm^3 glass cells without degassing and without separation of anodic and cathodic compartments. Polymer films were formed from the electrolyte described in Table 1. The zinc sublayer deposited on the cathode simultaneously with formation of a polymer layer was dissolved in 0.1 M HCl.

Silver ions were immobilized in the polymer by immersion of an electrode with a PMAA film into an $AgNO_3$ solution (with the concentration of 10^{-3} to 10^{-2} M). Ag^+ was reduced to Ag^0 in 0.1 M KNO_3 in 5–10 potential cycles in the range of (100–450) mV at different potential scan rates.

Studies of the structure, morphology, and microtopography of polymer films were carried out using TM300 and S5500 field–emission scanning electron microscopes (Hitachi, Japan). The local content of silver immobilized in the polymer film was determined using a Thermo Scientific energy–dispersive spectrometer (USA) equipped as an add-on to the Hitachi S5500 microscope (Japan).

The amount of silver electroreduced in a PMAA matrix and on the cathode surface was determined using the method of atomic absorption analysis on a SOLAAR M-series device (Thermo, USA). To separate a PMAA/AgNPs film from the working electrode, a stainless steel rod with a composite coating was placed into hot deionized water, as a result of which the polymer film containing silver particles swelled and was separated from the working electrode. Later, silver deposited on stainless steel and reduced in PMAA was separately dissolved in hot concentrated (65%) nitric acid. X-ray phase analysis was carried out using an Advance D-8 diffractometer (Bruker) on a polymer film applied onto a glass cuvette.

Spectra of plasmon resonance absorption of composite films were measured using a Shimadzu UV-2550

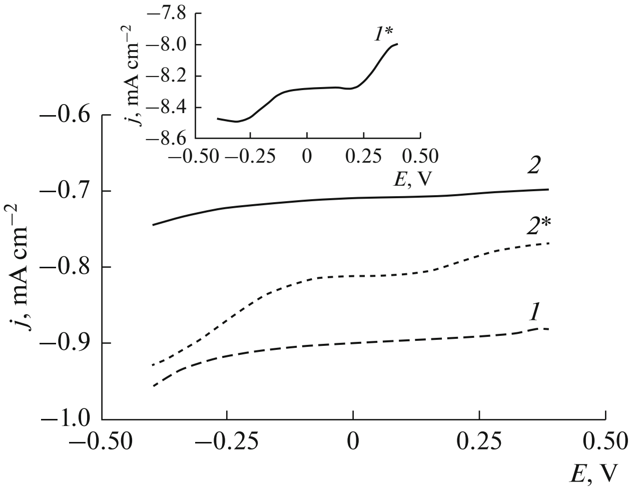

Fig. 1. Cathodic polarization curves for (*1*, *1**) stainless steel and (*2*, *2**) the composite elecytrode with silver in (*1*, *2*) 0.1 M potassium nitrate solution and in (*1**, *2**) 0.1 M potassium nitrate solution with the additive of 10^{-3} M $AgNO_3$. The potential sweep rate is 20 mV/s.

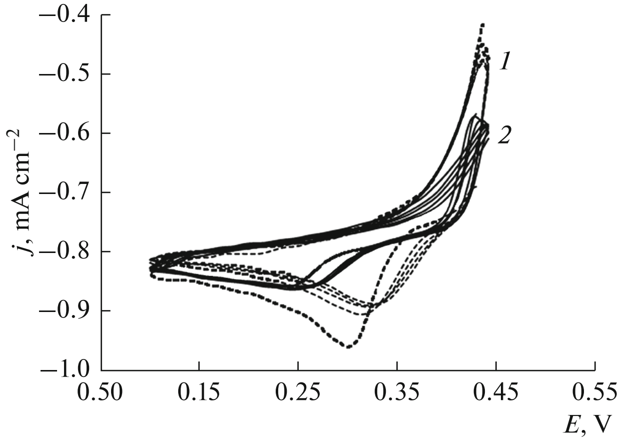

Fig. 2. Voltammetric dependences in 0.1 M sodium nitrate solution containing 10^{-3} M $AgNO_3$. (*1*) Stainless steel, (*2*) the polymer/silver composite. The potential sweep rate is 20 mV/s.

spectrophotometer (Japan). Silver particle distribution in a polymer was determined using small angle X-ray scattering (SAXS) on a Hecuss 3-Micro-Pix diffractometer (Austria).

RESULTS AND DISCUSSION

As follows from [26–28], the best studied compositions for formation of coatings and films on metals using the EP technique are compositions based on aqueous solutions of acrylamide (AA) and its derivatives. The PMAA films are insulating, which excludes direct electroreduction of metals on their surface. One of the methods of modification of such films is immobilization of particles of different metals in them to create composite materials with new properties. As shown in [4, 32], a single stage formation of such composites is possible by adding chloraurate or chloroplatinates directly into the monomer solutions. As a result, a polymer film is formed on the cathode in the course of electropolymerization with simultaneous electroreduction of metal particles captured by the growing polymer matrix. Such an approach is impossible in the case of silver immobilization in a PMAA matrix, as the initial monomer composite contains the $ZnCl_2$ additive as an indirect initiator (Table 1). Interacting chlorides and silver ions form the AgCl salt insoluble in water. But, as shown in [29, 30], the problem can be solved using a two–stage technology, according to which EP of a PMAA film, its saturation by the $AgNO_3$ solution and chemical reduction of silver are conducted consistently. In this work, we studied the possibilities of electrochemical embedding of silver nanoparticles into a PMAA matrix.

Electrochemical Reduction of Silver Ions in the Polymer

PMAA coatings formed on stainless steel were washed by deionized water, placed in 0.1 M HCl to remove a sublayer of zinc reduced in the course of electropolymerization. Then, the thoroughly washed films were immersed in 10^{-3} to 10^{-2} M $AgNO_3$ for 48–120 h.

Electrochemical reduction of silver ions Ag^+ to Ag^0 was carried out by the cycling of potentials in the range of 100–450 mV. The above range of potentials was chosen on the basis of the data of polarization dependences obtained in 0.1 M KNO_3 with an additive of 10^{-3} M $AgNO_3$. These data show that the maximum rate (current density) of silver electroreduction can be achieved both on a clean cathode at E_{max} = 215 mV (Fig. 1, curve *1**) and a cathode with a PMAA film at E_{max} = 116 mV (Fig. 1, curve *2**). Such an approach allows, firstly, to eliminate the occurrence of side processes of decomposition of the KNO_3 supporting electrolyte and water, because, as follows from Fig. 1, the cathode material (Fig. 1, curve *1*) and the PMAA film (Fig. 1, curve *2*) are inert towards the KNO_3 solution in the chosen range of potentials. Secondly, no dissolution of freshly deposited silver occurs under the above conditions in the anodic potential sweep.

The further studies show that peak potential E_{max} on a clean cathode reaches 300 mV in the first cycle of silver electroreduction, while an anodic shift in E_{max} is observed in the second and further cycles to 312–322 mV (Fig. 2, curves *1*). Such an effect is related to a change in the state of the cathode (stainless steel) surface owing to deposition of a silver layer. A similar dependence is observed on a cathode coated by a composite PMAA/AgNPs film. In this case, the peak potential

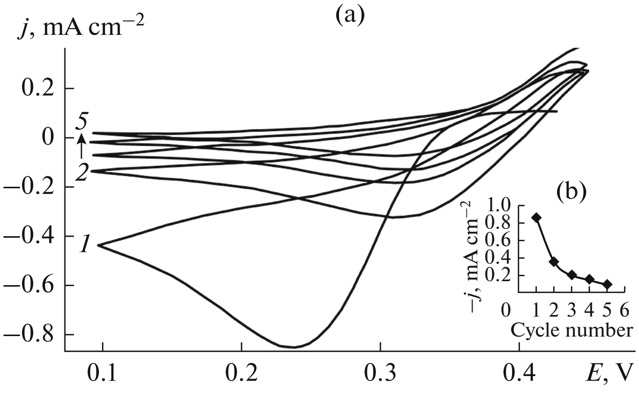

Fig. 3. (a) Cyclic voltammograms of Ag^+ reduction and (b) dependence of the current density of the current density maximum on the number of potential sweep cycles. The impregnating solution concentration is 10^{-2} M $AgNO_3$; the impregnation time is 96 h. The potential sweep rate is 20 mV/s.

shifts from 245 to 265 mV (Fig. 2, curves *2*). However, as seen in Fig. 2, the presence of a PMAA film on the cathode surface limits the process of silver electrodeposition by decreasing the current density on the first cycle peak as compared to a clean cathode from 0.96 (Fig. 2, curves *1*) to 0.86 mA/cm^2 (Fig. 2, curves *2*). Simultaneously, the potential of the peak of Ag^+ reduction to Ag^0 shifts into the cathodic region by 55 mV for stainless steel/PMAA as compared to stainless steel (E_{max} = 300 mV and 245 mV, respectively).

The effect of the number of potential scan cycles on the completeness of silver reduction in the film is studied (Fig. 3).

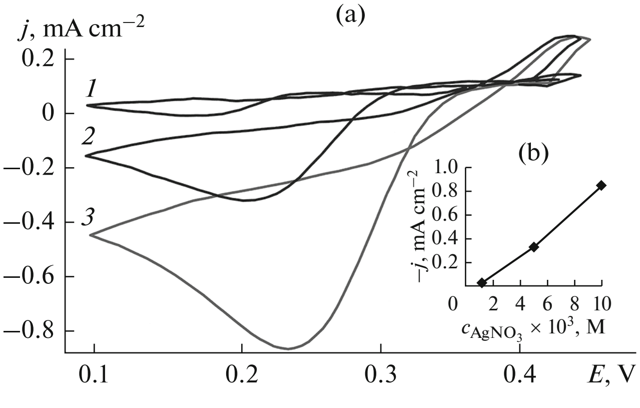

Fig. 4. (a) Cyclic voltammograms of Ag^+ reduction in the film in 0.1 M KNO_3 and (b) the dependence of the current density maximum on the concentration of the $AgNO_3$ impregnating solution (M): (*1*) 10^{-3}, (*2*) 5×10^{-3}, (*3*) 10^{-2}. The impregnation time is 96 h. The potential sweep rate is 20 mV/s.

It is found that electroreduction of Ag^+ to Ag^0 occurs predominantly in the first cycle (Fig. 3a) at the maximum current density (j_{max} = 0.85 mA/cm^2), which is 51.8%. In the second cycle, the current density decreases 2.4-fold and is 21.3% (j_{max} = 0.35 mA/cm^2) reaching its minimum value at the end of 5 cycles (j_{max} = 0.09 mA/cm^2). The dependence of the current density maximum on the number of cycles in the course of successive cycling is shown in Fig. 3b.

The effect on the kinetics of silver electroreduction of the $AgNO_3$ concentration in the solution for impregnation of the PMAA film on stainless steel is studied (Fig. 4a). It is found that the value of the current density maximum changes in proportion to the concentration of the impregnating solution (Fig. 4b).

The dependence is studied of the electrodeposited silver mass in a polymer matrix on the concentration of the $AgNO_3$ solution, polymer impregnation time by silver nitrate, and potential sweep rate (Table 2). It is found that the amount of Ag^0 in the composite increases at a low potential sweep rate (10 mV/s) at an increase in the initial $AgNO_3$ concentration and duration of the film immerseing in the silver nitrate solution (samples 1, 2). An increase in the potential sweep rate to 40 mV/s causes a decrease in the overall reduced metal mass in the composite (samples 3, 4), which can be related to a replacement of Ag^0 deposition directly to the cathode surface. Here, the process is much better pronounced at an increase in the duration of impregnation of a polymer film by silver nitrate.

Formation of a composite is accompanied by a change in the film color from colorless to silvery gray as dependent on the amount of silver added to the composite. The presence of Ag^0 in the polymer is confirmed using the methods of XRD, plasmon resonance, atomic absorption, and scanning electron microscopy.

Figure 5 shows the X-ray pattern of the film conditioned in the solution of 10^{-2} M silver nitrate for 96 h with the further electrochemical reduction of silver

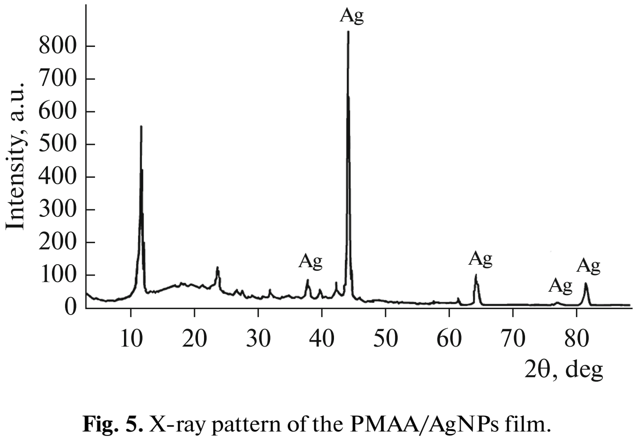

Fig. 5. X-ray pattern of the PMAA/AgNPs film.

Table 2. Effect of the conditions of electrochemical silver embedding into the polymer matrix on the reduced silver mass

Sample no.	Potential sweep rate, mV/s	$AgNO_3$ concentration, M	Duration of impregnation by $AgNO_3$ solution, h	Silver mass, mg cm^{-2}
1	10	0.001	96	0.0020
		0.005		0.0035
		0.010		0.0052
2	10	0.001	120	0.0024
		0.005		0.0063
		0.010		0.0087
3	40	0.001	48	0.0009
		0.005		0.0019
		0.010		0.0042
4	40	0.001	144	0.0017
		0.005		0.0017
		0.010		0.0038

ions. As follows from the figure, the polymethylolacrylamide film contains metallic silver Ag^0, which is confirmed by Bragg reflexes in the ranges of 38.1°; 44.1°; 64.4°; 77.3°; 81.7° [33–35].

For all composite PMAA/AgNPs systems obtained by electrochemical reduction of silver, spectra of plasmon resonance absorption were measured for wet films in the far UV and visible regions (Fig. 6). The spectra contain a weakly pronounced absorption band in the range of 410–420 nm (the main peak), where plasmon resonance of silver nanoparticles is registered. The shape of the absorption band points to a wide nanoparticle size distribution. According to [36–38], the location of the maximum of the plasmon resonance band at 410 nm and higher in the longwave spectral range implies that the diameter of the obtained nanoparticles is about 20 nm.

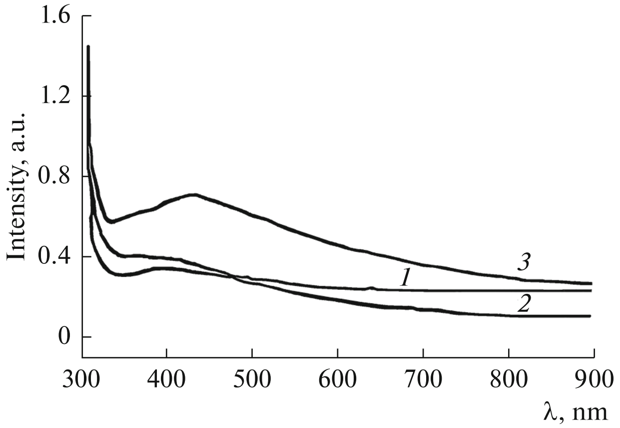

Fig. 6. Plasmon resonance absorption spectra in the far UV and visible regions in the range of 300–900 nm for PMAA/AgNPs. The concentration of the $AgNO_3$ impregnating solution (M): (*1*) 10^{-3}, (*2*) 5 10^{-3}; (*3*) 10^{-2}.

The SAXS method provides the functions of silver particle distribution by radii (Fig. 7). The shape of the spectrum indicates that the particle shape is close to spherical. It is found that the average radius of AgNPs is 11.8 nm (∅ = 23.6 nm), which corresponds to the data obtained using other methods.

Study of Morphology and Elemental Composition of PMAA/Silver Composites

The morphology and elemental composition of silver–containing polymer films were studied using the method of scanning field–emission electron microscopy with an add-on for energy–dispersive analysis. Figure 8 shows SEM images of the surface of polymer composites containing electrochemically reduced silver for the composite/solution interface (outer composite side or the side adjacent to the solution)

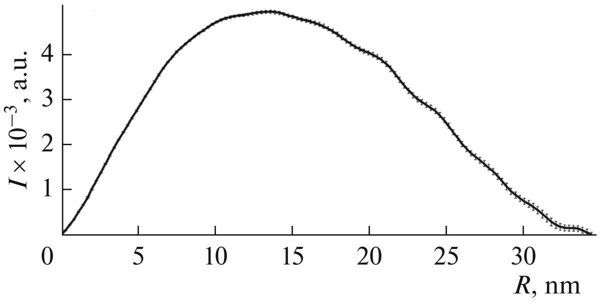

Fig. 7. Silver particle size distribution (the method of small angle X-ray scattering) in a PMAA/AgNPs film. The impregnating solution concentration is 10^{-2} M $AgNO_3$; the impregnation time is 96 h.

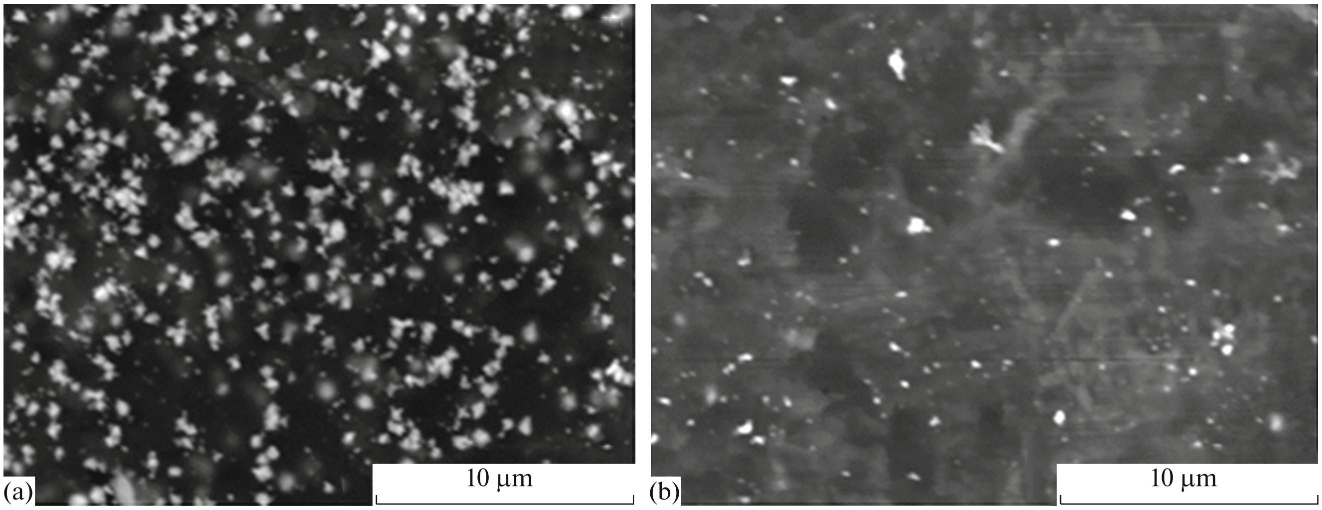

Fig. 8. SEM images of the polymer–silver composite surface: (a) the film side adjacent to the solution, (b) the film side adjacent to the electrode.

(Fig. 8a) and the composite/electrode interface (inner composite side or the side adjacent to the electrode) (Fig. 8b).

As seen from the microphotographs in Fig. 8, the amount of silver particles on the inner polymer side is lower than on its outer side. This agrees well with the data of energy–dispersive analysis, according to which the average amount of silver on the outer polymer surface is 6.51 ± 0.94 at %, while that on the inner side is 0.91 ± 0.23 at % (the detected elements are Cl, P, N, O, C, Zn, Ag). This effect is probably related to the fact that, firstly, the silver nitrate solution where polymer films were immersed does not sufficiently saturate the nearelectrode film layer that, as shown in [27], is very compact and finely porous. Secondly, silver redistribution is occurring on the cathode/polymer film interface to the cathode surface, as confirmed by the data of atomic absorption analysis (Fig. 9, *1*, *1**). Here, an increase in the duration of PMAA conditioning in the $AgNO_3$ solution results in an increase in the amount of Ag^0 in the film (Fig. 9, *2*, *2**) by 1.5 times (Fig. 9, *2**) owing to the saturation of the compact polymer layer by silver nitrate. Simultaneously, a 1.4-fold decrease is observed in the mass of silver reduced on a stainless steel cathode (Fig. 9, *1**). (The experiments were performed under identical conditions at the similar working electrode and polymer composite surface areas.) Here, it is necessary to point out that the data of XRD and atomic absorption analysis show that there is no metallic silver in the film conditioned in the $AgNO_3$ solution with no electrochemical Ag^+ reduction, which shows that the polymer matrix is inert.

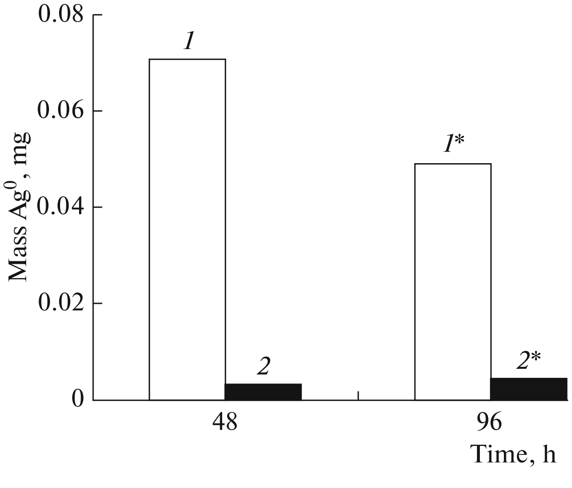

Fig. 9. Dependence of the reduced silver amount on the (*1*, *1**) stainless steel cathode and (*2*, *2**) in a PMAA/AgNPs film on the duration of impregnation in 10^{-2} M $AgNO_3$.

Study of Electrochemical Properties of PMAA/AgNPs Electrodes

Electrocatalytic properties of the stainless steel/PMAA/AgNPs electrodes were studied in the reaction of H_2O_2 electroreduction in a phosphate buffer solution (pH 6.68). The variation of the electrode potential under contact with H_2O_2 was first studied in the absence of polarization (Fig. 10). The immersion potential remained constant for 60 s, after which after which hydrogen peroxide was added into a phosphate buffer and the potential variation was registered for 180 s until a constant value was established. The potential drop on a cathode of pure stainless steel under contact with hydrogen peroxide is 143.7 mV (Fig. 10, curve *1*). In the case of a cathode modified by a silver–free PMAA film, the potential drop decreases

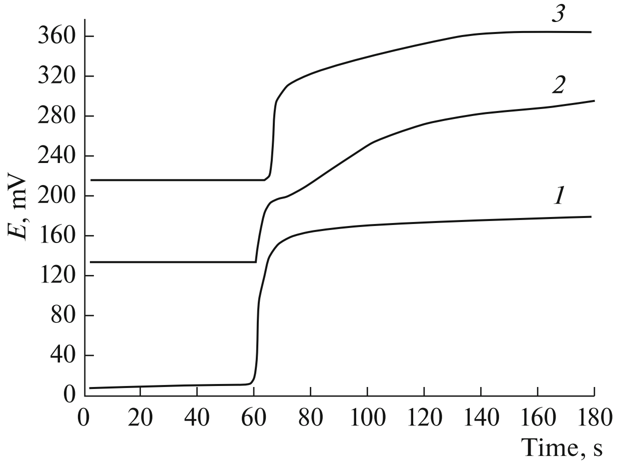

Fig. 10. Electrode potential variation in a phosphate buffer solution (pH 6.68) at its contact with H_2O_2 (0.24 M) in the absence of electrode polarization: (*1*) stainless steel, (*2*) stainless steel/PMAA, (*3*) stainless steel/PMAA/AgNPs.

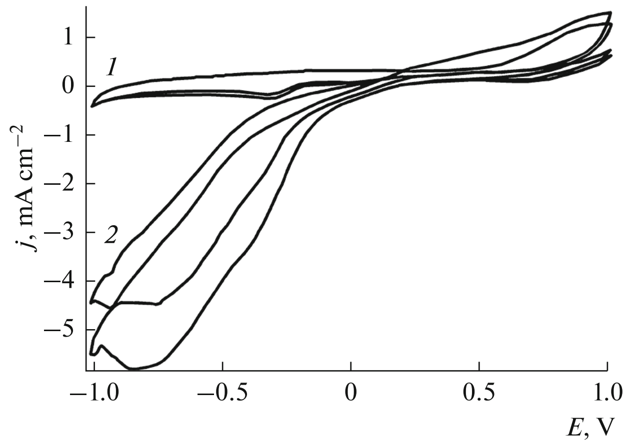

Fig. 11. Cyclic voltammograms for stainless steel/PMAA/AgNPs (*1*) in a phosphate buffer solution and (*2*) in the presence of 0.24 M H_2O_2. The potential sweep rate is 100 mV/s.

almost by half and is 80.8 mV, as the polymer layer limits the hydrogen peroxide diffusion to the electrode (Fig. 10, curve *2*). Meanwhile, for the stainless steel/PMAA/AgNPs composite in contact with hydrogen peroxide, the potential drop increases to 129.5 mV, which is closer to the value obtained on stainless steel. This points to participation of silver nanoparticle immobilized in the polymer matrix in the catalytic process.

The electrocatalytic activity of stainless steel/PMAA/AgNPs towards hydrogen peroxide was studied. As seen from the cyclic voltammograms obtained on a composite electrode in the phosphate buffer solution (Fig. 11, curve *1*) and in the presence of 0.24 M hydrogen peroxide (Fig. 11, curve *2*), the buffer solution is electrochemically stable in the region of electrochemical reduction of H_2O_2 (curve *1*), while addition of H_2O_2 results in an increase in the current density in the cathodic region at $E = -0.8$ V by almost 6 times in the first cycle and by 4.5 times in the second cycle.

When similar amounts of H_2O_2 are successively added in the cell (0.24 M each time) (Fig. 12a), a clear linear dependence of the electrochemical response (current density of the fist cycle of H_2O_2 electroreduction) on the hydrogen peroxide concentration ($R^2 = 0.9845$) is observed (Fig. 12b). One can conclude on the basis of the obtained results that the composite electrode manifests electrocatalytic properties in the reaction of H_2O_2 electroreduction, which allows using it as the corresponding electrochemical sensor. Comparison of the catalytic characteristics of this composite with the earlier obtained results for a similar composite with chemically immobilized silver [29] shows that the electrochemical response of the studied electrocatalyst to the presence of H_2O_2 is almost 1.5 times higher.

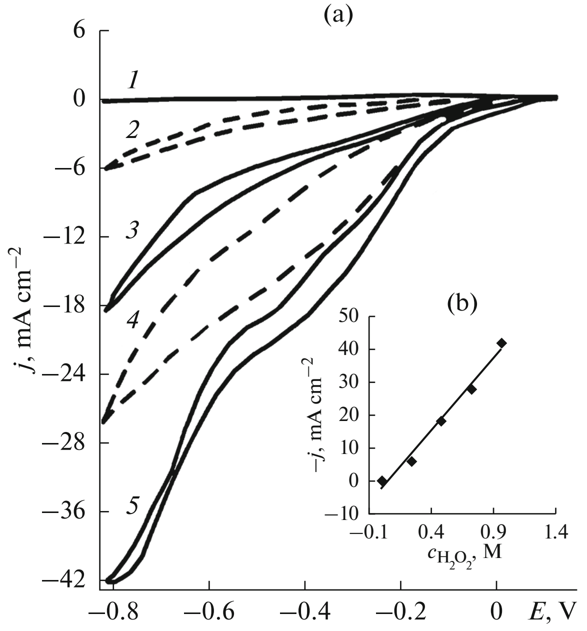

Fig. 12. (a) Cyclic voltammograms and (b) the dependence of the current density on the H_2O_2 concentration for stainless steel/PMAA/AgNPs in a phosphate buffer solution. The H_2O_2 concentration (M): (*1*) 0, (*2*) 0.24, (*3*) 0.48, (*4*) 0.72, (*5*) 0.96. The potential sweep rate is 100 mV/s.

CONCLUSIONS

The performed studies show the possibility of electrochemical immobilization of silver nanoparticles in a polymethylolacrylamide matrix formed by electropolymerization.

Inclusion of metallic silver nanoparticles into the composite is confirmed using the methods of X-ray phase analysis, microscopy, plasmon resonance, and small angle X-ray scattering. It is found that silver nanoparticles are spherical and their diameter is 20–23 nm.

The optimum conditions are determined for the embedding of Ag^0 nanoparticles into the polymer. The effect of the potential sweep rate and $AgNO_3$ concentration on the completeness of reduction of Ag^+ and amount of silver immobilized in the composite is studied. It is found that electroreduction of Ag^+ to Ag^0 occurs predominantly in the first cycle. It is found that the amount of Ag^0 in the composite increases at a low potential sweep rate (10 mV/s) at an increase in the concentration of the $AgNO_3$ impregnating solution and duration of the film conditioning in it. An increase in the cycling rate to 40 mV/s causes a decrease in the overall reduced metal mass in the PMAA/AgNPs composite, which can be related to a shift in the potential of Ag^0 deposition directly to the cathode surface.

The method of scanning electron microscopy is used to study the surface morphology and silver distribution in the composite. It is found that the silver content in the film at the composite/solution interface is 7–10 times higher than that at the nearcathode composite side, which may be due to the asymmetric polymer film structure (through–thickness matrix density variation).

It is found that polymer methylolacrylamide films containing silver nanoparticles manifest electrocatalytic activity towards hydrogen peroxide. Here, comparison of the catalytic characteristics of this composite with the earlier obtained results for a similar composite with chemically immobilized silver [29] showed that the electrochemical response of the studied electrocatalyst to the presence of H_2O_2 is almost 1.5 times higher.

Thus, one can conclude on the basis of the performed studies that formation of the PMAA/AgNPs composite by electrochemical silver reduction in a polymer matrix is not only possible, but also has certain advantages as compared to the chemical silver immobilization in a film. In addition to the higher catalytic activity, the applied electrochemical approach allows eliminating the use of chemical reagents as reducing agents and thus permits cheapening the process and avoiding secondary contamination of the composite material.

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CONFLICT OF INTEREST

The authors declare the absence of any conflict of interest.

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