Metallopolymer nanocomposites based on platinum nanoparticles for chemical fuel cells

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Platinum nanoparticles were synthesized by radiation chemical reduction in solutions of reverse micelles for the modification of Nafion films. The effect of the degree of solubilization and sizes of water pools of micelles on nanoparticle formation was shown. The platinum nanoparticle size in the polymer matrix does not exceed 10 nm.

Key words: platinum nanocomposites, polymer film Nafion, radiation reduction, reverse micelles, specific adsorption, UV spectrophotometry, scanning electron microscopy.

Solid polymer matrices (SPM) serve as a basis part of membrane electrode units for chemical fuel cells (CFC). Proton-exchange perfluorinated polymers with ionogenic sulfo groups ($-SO_3H$) of the Nafion type are widely used as SPM. Hydrated hydrogen ions migrating along the polymer channels are charge carriers

$$RSO_3H + nH_2O = RSO^-_3 + H^+ \cdot nH_2O,$$

where R is the perfluorinated fragment of the membrane. Chemical stability, a low permeability of the fuel, and a high unipolar conductivity are among the main requirements imposed on SPM. A substantial problem of the use of SPM is the crossover effect: the penetration of the fuel-reducing agent (especially H_2 and CH_3OH) through the membrane, which sharply decreases the output parameters of the CFC.

The direction related to the modification of SPM by inorganic additives is intensely developed in the recent time.[1—3] These systems are named hybrid or metallopolymer (when modified by metals) systems. The introduction of inorganic components makes it possible to enhance the exploitation characteristics of the SPM.[2] The modification by nanoparticles of metal-catalysts of not only the surface but also the volume of the SPM stimulates the additional catalytic oxidation of the fuel (H_2, CH_3OH, C_2H_5OH, HCOOH, *etc.*) and the reduction of the oxidant (molecular oxygen).

The results of studies of the morphology of the SPM, including those of the Nafion type, and the mechanisms of proton conductivity in membranes on the basis of theoretical models are reviewed in detail in several works.[1—5]

$$(CF_2CF_2)_{\overline{n}}-CF_2CFO-(CF_2CF_2(CF_3)O)_{\overline{m}}-CF_2CF_2SO_3H$$

Nafion

$n = 5—11$, $m = 1—3$

Structural features of membranes of the Nafion type were studied by a complex of physicochemical analytical methods.[1,3,4] Several models of proton transfer through the Nafion SPM were proposed: transfer through comb-like blocks,[1] the model of asymmetric transport,[3] the model of ion pairs,[3] and some other.[5] Based on the experimental data and theoretical concepts, we can conclude the following. A specific feature of the Nafion SPM is the nanometer pore size at the membrane thickness less than 0.2 mm. Hydrated protons are transported *via* membrane channels with a characteristic size of 1—2 nm, which connect the sulfo-containing nanosized cavities with an average diameter of 6 nm. The proton transfer along the narrow channel of the membrane is considered to be the rate-determining step (especially at a low moisture content) responsible for the conductivity of the membrane.[1,3]

There are data on the stabilization of Pt nanoparticles inside the Nafion films,[4] the effect of Pt particles on the crossover, and the oxidation of the fuel inside the membrane.[6] The developed composite electrodes polypyrrole—Nafion with Pt possess an enhanced electrocatalytic activity in the hydrogen—air CFC based on porous silicon.[7] Hybrid electrodes of polytungstates with carbon nanotubes and Pt make it possible to obtain the best electrochemical parameters compared to those of the commercial samples in the catalytic reaction of H_2 oxidation.[8]

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The ion conductivity of the membranes increases upon the modification of proton-exchange membranes of the MF-4SK type (analog of Nafion) by Ag and Cu nanoparticles.[9] The hybrid nanocomposite catalysts based on polypyrrole and polyaniline containing up to 5 wt.% Pt were obtained for the reduction of O_2.[10] It was found that the co-immobilization of peroxidase enzyme with Nafion increased the bioelectrocatalytic activity in the reduction of H_2O_2 compared to the adsorption-immobilized enzyme.[11] Inorganic additives to proton-conducting SPM can both generate an additional number of protons and improve their transport along channels of the membrane.[12]

The properties of electrocatalysts are determined by the nature of the metallic phase and also by the specifics of its interaction with the matrix (support). For this reason, the Pt nanoparticles incorporated into the Nafion polymer film can be considered as a single composite platinum—Nafion (Pt/Nf).

In our previous publications we presented the examples for the synthesis of the metallopolymer composites[13] and studied the influence of the structure of the polymer units on the nonequivalence of protons due to the electron density redistribution.[14,15] The difference in reactivities of protons in the fulvene copolymers with vinyl butyl ether and in the hybrid composites of a series of lanthanides with substituted silaoxocyclohexanes was shown by ^1H and ^{13}C NMR.[15]

Thus, the introduction of metals into the SPM seems to be a promising approach to the development of the new type of nanostructured membranes for CFC. The purpose of our work is the development of metallopolymer nanocomposites based on the Nafion membrane with Pt nanoparticles by the radiation chemical reduction of metal ions in solutions of reverse micelles. The results of studying the structure, composition, and distribution of metal nanoparticles in the polymer matrix are presented.

Experimental

The initial solutions of Pt nanoparticles were obtained by the radiation chemical synthesis in solutions of reverse micelles according to a procedure described earlier in detail.[13,16] Reverse micelles are microdrops of an aqueous solution of salt (pools) stabilized by a surfactant in an organic solvent. Metal nanoparticles are formed in the micelle pool upon the ^{60}Co γ-irradiation in the range of doses 5—30 kGy at a dose power of 5.2 Gy s^{-1}. A 0.15 *M* solution of the surfactant sodium bis(2-ethylhexyl)-sulfosuccinate (AOT) (99%, Sigma) in isooctane was used for the formation of reverse micelles. A 0.02 *M* solution of H_2PtCl_6 (OAO "Aurat") was introduced into the first solution according to the degree of solubilization $\omega_0 = [H_2O]/[AOT]$. The degree of solubilization ω_0 was varied in a range of 1.5—5. Bis(2-ethylhexyl)sulfosuccinate was preliminarily dried *in vacuo* (10^{-3} Torr) at 30 °C to a constant weight. Doubly distilled water and chromatographically pure hydrocarbons were used. The concentration of Pt for ω_0 = 1.5, 3, and 5 was $1.12 \cdot 10^{-4}$, $2.8 \cdot 10^{-4}$, and $3.26 \cdot 10^{-4}$ mol L^{-1}, respectively. A Nafion solution (5 wt.%, Aldrich) and the membrane Nafion 115 (Aldrich) with a thickness of 0.127 mm were used for the formation of solutions and films of metallopolymers.

Solutions of metallopolymers were obtained by the direct interaction of micellar solutions of metal nanoparticles with a solution of Nafion in the volume ratio 1 : 1.

Solutions were solubilized on an UZDN-2T ultrasonication setup (Russia) for 15 min at 25±1 °C. For the preparation of metallopolymer films, samples of the membranes Nafion 1×2 cm in size were placed in cells with a solution of nanoparticles. The films with the solution were stored in the dark at room temperature.

The optical absorption spectra of solutions and films were measured in a wavelength range of 190—1000 nm on a Shimadzu UV-VIS-3101 PC spectrophotometer (Japan) at room temperature. A 0.15 *M* solution of AOT in isooctane was used as a reference solution. The morphology of the surface of the polymer films was studied by scanning electron microscopy (SEM) on a JSM-7401F instrument (Jeol, Japan) with an INCA analyzer (Oxford Instruments, England). The sizes of water pools of reverse micellar solutions were determined by the method of dynamic laser light scattering on a Delsa Nano particle analyzer (Beckman Coulter, Ireland).

Results and Discussion

The optical absorption spectra of the initial solutions of Pt nanoparticles in reverse micelles are shown in Fig. 1. As can be seen from Fig. 1, in solutions of reverse micelles at ω_0 = 1.5, 3, and 5 the Pt nanoparticles have a pronounced plasmon absorption band in the range 200—400 nm with maxima at 230—270 nm, whose intensity increases with an increase in the Pt content. Note that at ω_0 = 1.5 the half-width of the band (curve *1*) is smaller than that at ω_0 = 3 (curve *2*) and at ω_0 = 5 (curve *3*), and the hypsochromic shift is observed for this band. The position, width, and intensity of the absorption band mainly depend on the sizes, shape, and number of nanoparticles.[17,18]

The fragments of the optical absorption spectra of Nafion solutions with Pt nanoparticles with various values

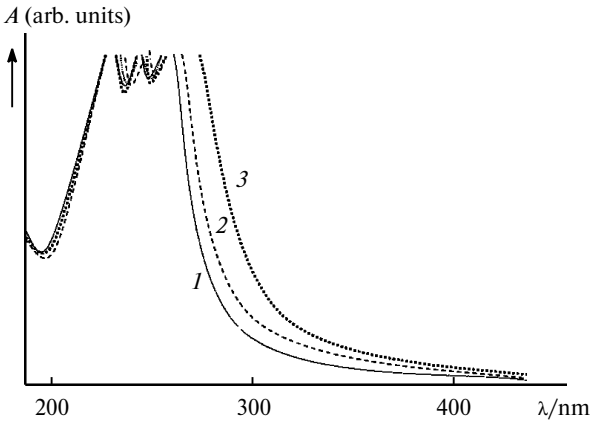

Fig. 1. Optical absorption spectra of the Pt nanoparticles: ω_0 = 1.5 (*1*), 3.3 (*2*), and 5 (*3*).

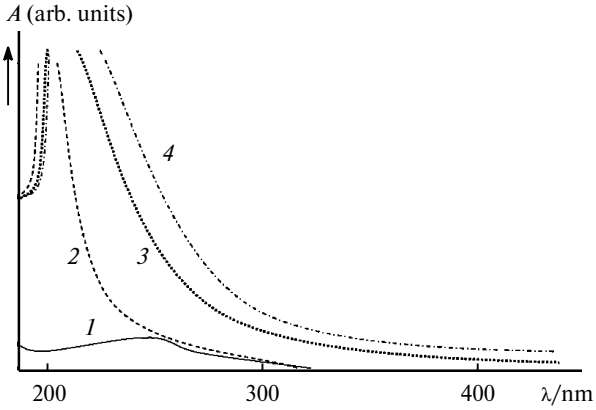

Fig. 2. Optical absorption spectra of solutions of the solid polymer membrane Nafion in the absence (*1*) and in the presence (*2—5*) of the Pt nanoparticles: ω_0 = 1.5 (*2*), *3* (*3*), and 5 (*4*).

of ω_0 are presented in Fig. 2. A Nafion solution without nanoparticles (curve *1*) is characterized by the absorption maximum at λ = 260 nm typical of the excitation of electrons of the σ-bonds of the ether group FCOCF. Solutions with Pt nanoparticles have the intense optical absorption spectra in a range of 200—400 nm with maxima in the range λ = 210—250 nm.

It seemed interesting to study the optical absorption spectra of the membrane containing Pt nanoparticles from micellar solutions with various values of ω_0. The optical absorption spectra of the metallopolymer films based on the Nafion membrane with Pt nanoparticles are presented in Fig. 3. The spectra of the films has an absorption band at λ = 210—240 nm. The band intensity increases with an increase in ω_0 (curves *2* and *3*).

A comparison of the optical absorption spectra shows that both the solutions and films of metallopolymers contain only the Pt nanoparticles to which the absorption band at λ = 210—240 nm corresponds to the initial solutions with ω_0 = 1.5, 3, and 5. One fraction of the Pt nanoparticles with sizes from 2 to 10 nm corresponds to this absorption band.[19] Both a slight bathochromic shift of the absorption band from 240 to 260 nm and its broadening are observed with an increase in ω_0 for solutions of Pt. These data indicate some increase in the fraction of large nanoparticles in the range from 2 to 10 nm and, possibly, the change in the shape of nanoparticles with an increase in ω_0 from 1.5 to 5 (see Refs 17, 18, and 20).

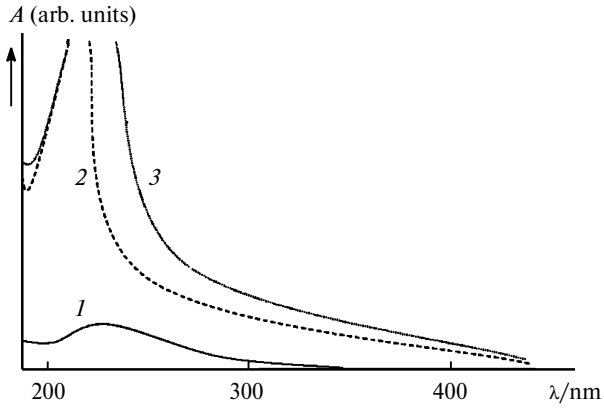

Fig. 3. Optical absorption spectra of the Nafion films in the absence (*1*) and in the presence (*2*, *3*) of the Pt nanoparticles: ω_0 = 1.5 (*2*), *3* (*3*).

Sizes of the water pool of micelles are significant for the formation of metallic nanoparticles in both the initial solutions of reverse micelles and metallocomponents with Nafion (Nf). The size distribution of water pools of micelles was studied by dynamic laser light scattering.

The data on laser light scattering of Pt solutions at ω_0 = 1.5 and 5 are presented in Fig. 4. Solutions of the Pt nanoparticles at both ω_0 = 1.5 and ω_0 = 5 are characterized by the unimodal size distribution of water pools of micelles. Note that only one absorption band is observed for the optical absorption spectra (see Fig. 1) of the Pt nanoparticles at ω_0 = 1.5 and 5. In solutions of Pt at ω_0 = 1.5, the diameters of micelles (*d*) range from 10 to 14 nm, whereas at ω_0 = 5 they range from 37 to 41 nm.

The size of nanoparticles formed inside the pool of a reverse micelle is determined by several factors. Among them are the characteristics of the aqueous phase: the nature of the surfactant, the nature of the metal, the degree of solubilization ω_0, the interaction with the interphase surface, the concentration of the components, diffusion of micelles in the organic phase, and others. The Pt nanoparticles can be stabilized due to the formation of strong bond of Pt with the polymer hydrophilic sulfo groups SO_3^- of AOT inside the water pools of the micelles.[4,18] The strong interaction of the Pt nanoparticles with the SO_3^- groups probably aligns the influence of other factors and prevents nanoparticle aggregation. The predominantly Lorentzian shape of the plasmon absorption band of nanoparticles is predominantly manifested in the absorption spectra at various values of ω_0 (see Fig. 1).[20,21]

The data obtained suggest that predominantly metal nanoparticles with sizes less than 8—10 nm are in the composition of the metallopolymer nanocomposites

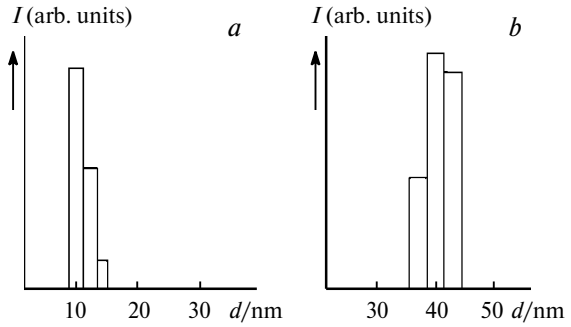

Fig. 4. Size distribution of micelles (*d*) in solutions of the Pt nanoparticles at ω_0 = 1.5 (*a*) and 5.0 (*b*).

Pt/Nf, and these nanoparticles are observed both in solutions (see Fig. 2) and films (see Fig. 3). The plasmon absorption bands of the Pt nanoparticles undergo hypsochromic shift (λ = 210—240 nm) relative to the initial solutions upon the formation of metallopolymers. It was established[1—3] by the complex of physicochemical methods that the wet Nafion membranes are characterized by the formation of hollow structures with an inner diameter of 6.2 nm. The metallopolymer Pt nanoparticles are characterized by higher frequencies of plasmon absorption than the optical absorption frequencies of the C—O—C bonds of the Nafion polymer chain (see Fig. 3). Therefore, the metallopolymer composition should predominantly include the Pt nanoparticles with sizes less than 6 nm corresponding to the sizes of cavities of the Nafion membranes.

Surface adsorption and incorporation of nanoparticles inside the polymer matrix are observed for the metallopolymer films.[4,6,10] The SEM image of the Pt particles obtained from solutions with ω_0 = 1.5 on the Nafion membrane surface is shown in Fig. 5. It is seen that the nanoparticles with sizes less than 10 nm predominate on the surface. Rare Pt aggregates with sizes up to 25 nm are observed. The size of the Pt nanoparticles is predominantly 8—12 nm in the SEM images of the film with the Pt/Nf nanocomposites obtained from solutions with ω_0 = 5. The agglomeration of nanoparticles with an increase in their content on the surface is absent with an increase in the contact time of the membrane with solution at ω_0 = 1.5 and 5. The SEM data agree with the data of the optical absorption spectra of the metallopolymer films (see Fig. 3). The Pt nanoparticles with the sizes less than 6 nm characterized by λ = 210—230 nm can be inserted into the film volume predominantly from solutions with ω_0 = 1.5 (see Fig. 3, curve *2*). The Pt nanoparticles with the sizes mainly less than 10 nm characterized by the band at λ = 240—260 nm from solutions with ω_0 = 1.5, 3, and 5 are localized on the film surface due to adsorption (see Figs 1 and 3).

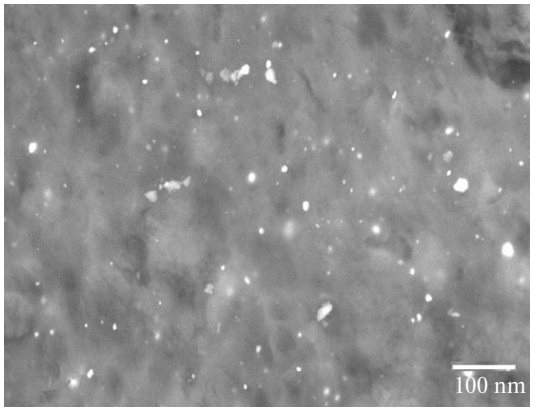

Fig. 5. SEM image of the Pt nanoparticles at ω_0 =1.5 on the surface of the Nafion membrane.

The presented results suggest that the Pt/Nf metallopolymer nanocomposites are metal nanoparticles surrounded by polymer molecules. Localization in the polymer matrix preserves nanoparticles from both desorption and agglomeration. Probably, the nanoparticle sizes in the membrane volume should not exceed 6 nm.

These results agree with the data on studying the sizes and morphology of the Pt nanoparticles in the composition of the Nafion films obtained by high-resolution transmission electron microscopy.[4] In solutions of Pt/Nf the average sizes of the Pt nanoparticles were less than 4 nm, in the Pt/Nf nanocomposites using commercial Nafion films (as in our work) they are 5—6 nm, whereas the average sizes are 5—13 nm when the films of the Pt/Nf nanocomposites are formed by casting from solutions. It was found that the Pt nanoparticles inside the film were cubic due to the controlling effect of the SO_3^- groups of the internal cavities.[4] On the membrane surface the fragments of the inner cavities of the polymer chain stimulate adsorption of low-size nanoparticles, restrict their agglomeration, and favor the uniform distribution of nanoparticles (catalysts) in the film. The choice of the value of ω_0 allows one to control the sizes and number of formed nanoparticles.

Conductivity in the Nafion membranes occurs due to the transport of hydrated protons through the nanopores, whose walls were formed by segmental mobile fragments of polymer chains. A specific feature of the proton transfer step is the molecular reorientation of the flexible perfluorinated chain with the hydrophilic sulfo groups, which determines the rate of the process.[3] Asymmetry of proton transport through the membrane is due to the energy nonequivalence of the active sites of the pore walls at segmental vibrations of the polymer chain.[1] The difference in energy states of protons in the copolymers of vinyl butyl ether and nonequivalence of protons of the CH_2OSi unit in the lanthanide complexes with silaoxocyclohexanes were proved by ^1H and ^{13}C NMR.[14,15] It is assumed that the proton transfer *via* inserted metal nanoparticles mainly contributes to the increase in the conductivity.

The optical absorption spectra show (see Figs 2 and 3) that inside the Nafion membranes the Pt nanoparticles have the higher values of absorption frequencies than those on the membrane surface or in the initial solutions. This high-frequency shift is due to the formation of complexes of the Pt nanoparticles with some SO_3^- sulfo groups in the membrane pores. Probably, the formation of these complexes increases asymmetry in segmental mobility of the polymer chain of the membrane and stimulates the formation of contact ion pairs with hydrated protons.[3]

Thus, we established the possibility of modification of the Nafion polymer film by the platinum nanoparticles obtained by the radiation chemical reduction of platinum ions in reverse micelle solutions. The effects of the con-

centration of the metal component, the degree of solubilization, and micelle sizes on the parameters of the nanocomposites were shown.

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