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## PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

# Properties of Proton-Conducting Materials Formed by the Sol-Gel Method

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**Abstract**—Proton-conducting materials produced by the sol-gel method were studied by spectroscopic methods. Films and xerogels were formed from silica sols modified with orthophosphoric and sulfuric acids, as well as with a mixture of these acids, with subsequent drying at room temperature and 150°C. The ionic conductivity of the xerogels and IR transmission of the films were examined.

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The development of hydrogen power engineering, which attracts steadily increasing attention, requires a solution of a number of accompanying problems should be solved. One of problems of this kind consists in development of proton-conducting materials for membranes and catalytic systems. For example, to improve the efficiency of the new generation of catalysts based on an amorphous carbon–platinum composite produced by magnetron cosputtering, it is necessary to impart proton conductivity to thin catalytic layers with thicknesses of several hundred nanometers [1–5]. The pore sizes in these layers are on the order of 10 nm, and, therefore, Nafion cannot be used to impart proton conductivity because large Nafion molecules are not able to penetrate into the pores so small. In addition, Nafion markedly diminishes the catalytic activity of catalysts of this kind, which can be attributed to blocking of active centers on the platinum surface by adsorbed molecules of the polymer, as well as to its gas-impermeability [6, 7].

Silicophosphate gels are a material promising in this regard. Variation of the synthesis conditions of sol-gel systems praides a control over their chemical and component composition, degree of amorphization, fraction of the finely crystalline phase, specific surface area, cluster size, pore size, and gas-permeability. An advantage of systems of this kind is their porous structure. The presence of pores provides access of gases to the catalyst surface. Modification of sol-gel systems based on tetraethoxysilane with sulfur and copper compounds is intended to improve and stabilize the performance of structural elements of a fuel cell (membranes or catalytic layers) by primarily providing a high proton conductivity on the order of magnitude of $10^{-3}$–$10^{-2}$ S cm$^{-1}$ at room and, especially, elevated tempera-tures (60–140°C) [8–13].

The aim of this study was to examine the effect of modifying compounds, orthophosphoric and sulfuric acids, on the structure and proton conductivity of materials formed by the sol-gel method. This study is the first in a series of systematic studies of processes used to create proton-conducting materials based on silica gels.

## EXPERIMENTAL

As objects of spectroscopic studies served films and xerogels formed from tetraethoxysilane-based silica sols modified with orthophosphoric and sulfuric acids. The sols were synthesized by successive mixing of components at a molar ratio $Si(OC_2H_5)_4$ : $C_2H_5OH$ : $H_2O$ : HCl : $H_3PO_4$ : $H_2SO_4$ = 1.0 : 4.4 : 5.7 : 0.02 : 0.2 : 0.4. The molar ratio of the reagents was chosen on the basis of experimental data on sol-gel synthesis of silicophosphate systems [8–10, 12]. To determine the role of the acids, three more sols were prepared in a similar way with almost the same composition

differing in that no acids ($H_3PO_4$ or $H_2SO_4$) or each acid separately were contained. The modified silica sols were kept at room temperature for several hours prior to further use.

Films were formed from the sols by centrifugation at 3000 rpm on wafers of single-crystal KEF-15 silicon (*n*-Si: P with a resistivity of 15 ohm m), polished on both sides, and then were dried in air at room temperature. To reveal an effect of the thermal treatment on the structure of the films, a part of samples were dried in air at 100–150°C for 15 min. This temperature was chosen because the material under study is intended for low-temperature fuel cells working in the temperature range 20–150°C. The time of 15 min is considered sufficient for a thermodynamic equilibrium to be attained in thin layers.

Xerogels were obtained by natural aging of the sols at room temperature in a closed vessel. The thermal treatment of the xerogels was also performed in the temperature range 100–150°C, but for 10 h, because removal of volatile components (water, ethanol) from the xerogels (bulk material) requires a longer time than that from thin layers.

The proton conductivity was studied by impedance spectroscopy [14, 15] with a Z-500PX impedance meter, using a two-electrode scheme in the frequency range 500 kHz–0.06 Hz on 2-cm-thick pellets compacted from the xerogels at room temperature. The electrical conductivity was found from the intercept on the real impedance axis in the high-frequency range.

The composition of the materials formed was analyzed by IR spectroscopy on film samples. IR transmission spectra of the films at 400–4000 $cm^{-1}$ were measured with a Shimadzu FTIR-8400S Fourier spectrophotometer with a resolution of 8 $cm^{-1}$ and number of scans equal to 100.

Figure 1 shows the transmission spectrum of a silicon wafer polished on both sides, a substrate for the films, with which the spectra under study were compared. The bands associated with the lattice absorption of silicon were used as bands with standard frequencies and intensities.

The rough data on the proton conductivity of the xerogels, obtained in the study, indicate that its levels are rather high at room temperature (9.3 10–3 S $cm^{-1}$) for samples modified with orthophosphoric and sulfuric acids, whereas for sample modified with only orthophosphoric acid, the conductivity is 6 10–4 S $cm^{-1}$.

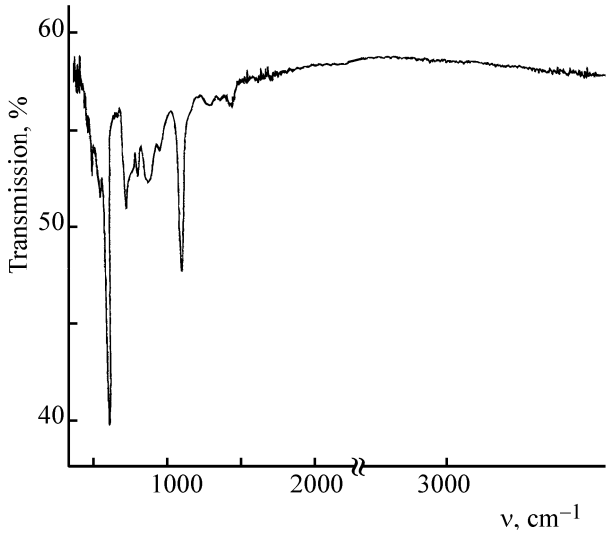


**Fig. 1.** Transmission spectrum of a silicon wafer serving as substrate for films formed from sols; (ν) is wave number; the same for Figs. 2–4.

Presumably, this result can be accounted for by the different first-stage dissociation constants of the acids (it is substantially higher for $H_2SO_4$). In addition, in the course of a possible thermal treatment, ortho-

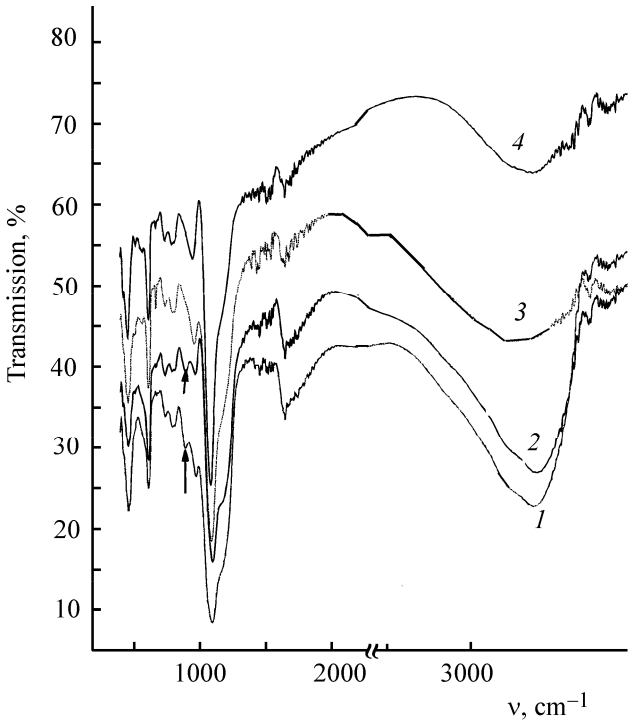


**Fig. 2.** Transmission spectra of films formed from sols with modifying acids (*1*) $H_3PO_4$, (*2*) $H_2SO_4$, (*3*) $H_2SO_4$, and (*4*) without modifying acids and dried at room temperature. The arrows point to bands associated with modi-fication of a film with sulfuric acid; the same for Figs. 3, 4.

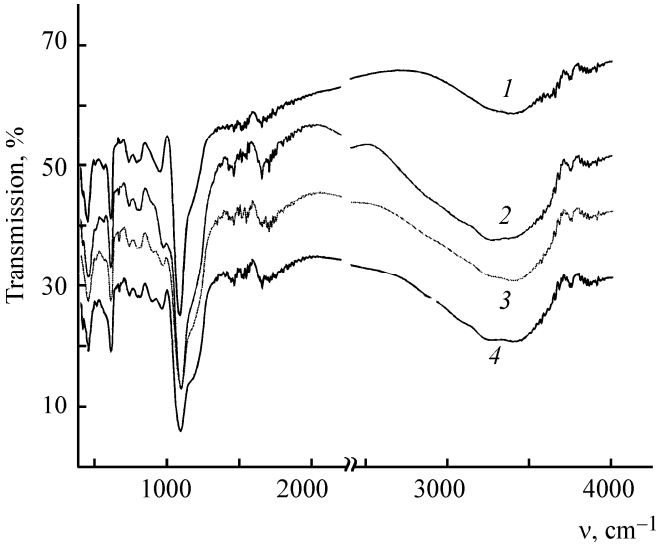


**Fig. 3.** Transmission spectra of films formed from sols (*1*) without modifying acids and (*2–4*) with modifying acids: (*2*) $H_3PO_4$, (*3*) $H_3PO_4 + H_2SO_4$, and (*4*) $H_2SO_4$, and dried at 150°C.

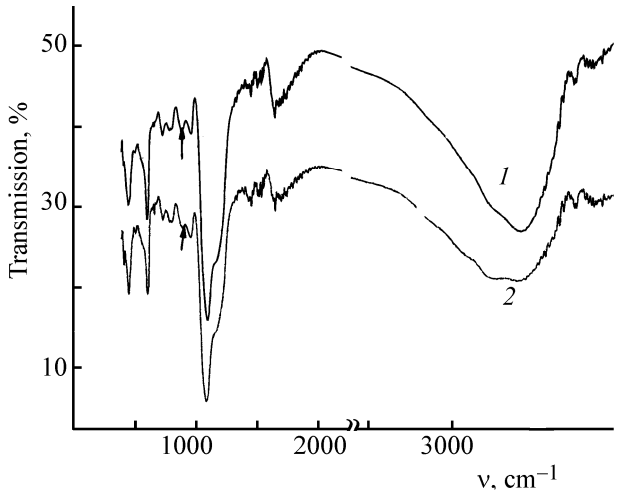


**Fig. 4.** Transmission spectra of films formed from sols modified with sulfuric acid and dried at (*1*) room temperature and (*2*) 150°C.

phosphoric acid partly interacts with the matrix, whereas sulfuric acid is retained in the matrix by the host–guest mechanism. The formation of such a structure in the course of structuring is confirmed by IR spectroscopic data. Figures 2–4 show IR spectra of the films synthesized by the sol-gel method.

The spectra of the films from sols unmodified with acids contain the following features:

Spectral range 4000–3300 cm$^{-1}$, region of absorption by water adsorbed on the surface. Narrow absorption bands coincide with the bands observed for silicon wafers serving as substrates for the films in the spectral positions of the bands, but differ in intensity. The intensity of the bands is approximately 10 times higher for samples fabricated at room temperature (Fig. 2) and 8 times higher for samples thermally treated at 150°C (Fig. 3). Thus, the absorption intensity by hydroxy groups adsorbed on the surface is lower for a film dried at a higher temperature.

Spectral range 2800–3700 cm$^{-1}$. A broad absorption band with minimum transmission at 3400 cm$^{-1}$ is observed. This band is associated with stretching vibrations of hydroxy groups formed in synthesis of silicic acid in hydrolysis of tetraethoxysilane in the silicon dioxide structure [16]. The band is absent in the spectra of silicon. The intensity of this band is somewhat lower for samples thermally treated at 150°C (Fig. 3).

Spectral range 1800–2000 cm$^{-1}$. The same narrow absorption bands as those for the silicon sample are observed.

Spectral range 1600–1800 cm$^{-1}$. The same narrow bands as those for silicon are observed with a somewhat higher intensity, but on the background of a broader band with minimum transmission at about 1650 cm$^{-1}$. This band is due to absorption by molecular water, associated with bending vibrations of hydrogen atoms within the plane of water molecules [17]. The intensity of this band somewhat decreases as the sample treatment temperature is raised.

Spectral range 1300–1600 cm$^{-1}$. The same narrow bands as those for silicon, associated with bending vibrations of hydroxy groups, are observed for samples fabricated at different temperatures.

Spectral range 1300–1000 cm$^{-1}$. A deep band with minimum transmission at 1080 cm$^{-1}$ and weak shoulder at 1180 cm$^{-1}$, associated with longitudinal, transverse, and mixed vibrations of Si–O–Si bonds, is observed [18]. Its intensity exceeds that for silicon and is higher for a sample dried at room temperature (Fig. 2), compared with that thermally treated at 150°C (Fig. 3). The shoulder at ~1180 cm$^{-1}$ has a frequency close to that of an absorption band in the spectrum of thermally oxidized silicon [18], observed in the case of an oblique incidence of light. However, as noted in [18, 19], this band can also be observed under normal

incidence for a disordered network thin films of amorphous $SiO_2$.

Spectral range 400–1000 $cm^{-1}$. The bands observed here are due to vibrations of various Si–O and Si–OH bonds. These bands differ only slightly for films obtained at room temperature (Fig. 2) and at 150°C (Fig. 3).

The spectra of the films produced from sols modified with orthophosphoric acid and dried both at room temperature (Fig. 2, spectrum *3*) and at 150°C (Fig. 3, spectrum *2*) reproduce, with minor differences in band intensities, the results obtained for films formed from sols unmodified with acids.

An absorption band appears at ~890 $cm^{-1}$ in the spectra of films produced from sols modified with sulfuric acid (Fig. 4) and with sulfuric and orthophosphoric acids (Figs. 2, 3; spectra *4*), in contrast to the spectra of films produced from sols unmodified with acids. It can be assumed that the appearance of this band is due either to distortions of the $SiO_2$ network, or to an increase in strains at pore boundaries in amorphous $SiO_2$, caused by appearance of sulfate ions at interstitial sites of the $SiO_2$ network. This assumption seems to be even more realistic because the characteristic frequencies of a free $SO_4^{2-}$ anion are 1105 and 611 $cm^{-1}$, and the characteristic frequencies of sulfates lie at 1080–1130, 1150–1230, and 1350–1440 $cm^{-1}$, i.e., far from 890 $cm^{-1}$ [20, 21].

Upon generalization of the results obtained, it can be concluded that modification of silicophosphate sol-gel systems with sulfuric acid makes it possible to obtain a higher proton conductivity in the materials formed. The stability of the system against free $H_2SO_4$ is provided by sulfate ions retained by the host–guest mechanism in the structure of the silicate matrix formed.

## CONCLUSIONS

(1) The impedance and IR spectroscopies were used to study films and xerogels formed by the sol-gel method. The ionic conductivity of the silicophosphate materials is on the order of $10^{-4}$ S $cm^{-1}$. Introduction of sulfuric acid can raise the conductivity to $9\times10^{-3}$ S $cm^{-1}$ at room temperature.

(2) An absorption band associated with the presence of $H_2SO_4$ and caused by distortions of the silica matrix upon modification was found in IR spectra of the films.

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