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*K.M. Sukhyy^a, Yu.P. Gomza^b, E.A. Belyanovskaya^a, V.V. Klepko^b, O.A. Shilova^c, M.P. Sukhyy^a,
A.V. Gavrilko^a*

PROTON-CONDUCTING ORGANIC-INORGANIC SILICOPHOSPHATES DOPED BY POLYIONENES

^aState Higher Education Institution «Ukrainian State University of Chemical Engineering»,
Dnipropetrovsk, Ukraine

^bInstitute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine

^cGrebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, St. Petersburg, Russia

The technological principles for the process control of the sol-gel synthesis of a new class of organic-inorganic nanostructured materials on the basis of tetraethoxysilane and polyionenes doped by orthophosphoric acid are developed in this work. The chemical compositions improvement is based on the results of complex investigation of morphology, physical and chemical properties. The rate of hydrolytical polycondensation reaction of tetraethoxysilane increases with the addition of polyionenes. The gelling rate increases with polyionene molecular weight. The polyionenes in silicophosphate sols are revealed to prevent crystallization processes which occur in silicophosphate xerogels with silica phosphates and pyrophosphates; this hinders the transport processes. The hybrid organic-inorganic silicophosphates doped by polyionenes exhibit higher proton conductivity than that of the initial nanocomposites. This influence may be improved by the ultrasonic treatment of the sol.

Keywords: organic-inorganic silicophosphates; sol-gel synthesis; tetraethoxysilane; polyionenes; phosphoric acid; proton conductivity.

Introduction

Nanocomposites obtained by sol-gel method are perspective material for heat storage materials, gas-diffusion electrodes, membranes, water-repellent coatings and electrochemical sensors. Their electronic conductivity is negligible, whereas the ionic conductivity can be as high as 10^{-1} S/cm. Increased interest in conducting dielectric is predominantly caused by the possibility of their use as proton-conducting membranes in fuel cells and electrochemical sensors [1]. The known proton-conducting polymer membranes cannot be used in the temperature range 100–200°C, which is most favorable for operating fuel cells that ensures a maximum efficiency of platinum catalysts. Silicophosphate membranes synthesized by the sol-gel method can operate at temperatures higher than 100°C [2,4].

However, their low hydrolytic resistance, a high corrosivity, and a tendency to crystallization at high temperatures prevent the commercial introduction. At present, attempts have been made to search for ways of improving these characteristics due to the modification of silicophosphate compounds with organic and inorganic additives (boric acid, boric acid esters, aluminum alkoxides, elastomers, epoxy

resins) [4,5].

Sol-gel technology allow incorporating organic molecules into an inorganic network, so that they can be combined virtually at any ratio on the molecular level with the formation of hybrid organic-inorganic nanocomposite materials [5]. The mechanical properties of such materials can vary from brittle and hard to rubbery depending on the content of organic modifiers in the inorganic network.

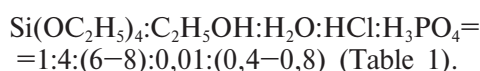
In our earlier works we studied the influence of the introduction of small amounts of organic modifiers into silicophosphate matrix which improved the ionic conductivity and operating characteristics of membranes. For this purpose, we used oligomeric alkylaromatic quaternary ammonium salts, i.e., polyionenes [6]. These compounds are appeared to be appropriate for the use in sol-gel processes, because they dissolved in water without breaking the homogeneity of the sol-gel system. These modifiers favor the formation of a xerogel that can be subsequently compacted.

The aim of the present work is to develop the sol-gel synthesis technology of nanocomposite based on hydrolyzed tetraethoxysilane (TEOS), orthophosphoric acid, and a number of polyionenes, as well as to investigate of physicochemical properties

of the sol-gel systems and the prepared hybrid silicophosphate materials with the use of different methods (viscometry, derivatography, X-ray analysis, IR-spectroscopy).

Experimental

Silicophosphate sol-gel systems synthesized from tetraethoxysilane $\text{Si}(\text{OEt})_4$, orthophosphoric acid H_3PO_4 , ethanol EtOH (as a solvent), and hydrochloric acid HCl (as a catalyst of hydrolysis process) were the objects of investigation. The basic reactants were introduced in following mole ratio with variation of concentration of water and orthophosphoric acid:



A large array of organic-inorganic nanocomposite was studied in present work. Therefore, sufficient rational marking by content of water (W_{mol}) and orthophosphoric acid (PA_{mol}), type of organic modifier and order of component mixing was suggested. Polyionenes (Table 2) were dissolved in water previously, and then introduced into sol comprising TEOS, ethanol, hydrochloric and orthophosphoric acid portionwise. Some sols were exposed to ultrasonic treatment (44 kHz, 20 min) after that. Then, sols were retained in closed vessels until formation of gel which dried at vacuum during 8 h until coarse-grained powder formation. For investigation this powder was grinded in agathic mortar. Solid films for tests were formed on teflon substrates by watering method with following centrifugation.

The viscosity of the sols was measured on a Höppler rheoviscometer. Thermal analysis (DTA,

DTG, TG) was performed on a Paulik–Paulik–Erdey derivatograph. X-ray powder diffraction analysis was carried out on a Siemens D-500 X-ray diffractometer. IR-spectra were registered on IR-Fourier spectrometer Perkin-Elmer 1760X in transmission regime with resolution of 4 cm^{-1} and averaging of 50 spectra in spectral range of $0-4000 \text{ cm}^{-1}$.

Broadband isothermal dielectric relaxation spectroscopy (DRS) measurements were carried out in the frequency range $10^{-1}-10^6 \text{ Hz}$ and the temperature range from 173 to 293 K, using a frequency response analyzer (Schlumberger SI 1260) supplemented by a buffer amplifier gain (Chelsea Dielectric Interface). The samples were placed between gold-coated brass electrodes.

Results and discussion

Mechanical strength is one of important parameters of organic-inorganic membranes. Their significant characteristic is thermodynamic flexibility of macromolecular chain of polymer used as organic modifier. A mechanical strength is equilibrium characteristic, it being determined by chemical structure of molecules and realized as a result of heat motion of chain segments. Heterochains containing atoms of sulphur and oxygen are known to be most flexible [7]. The cause of anomalous high flexibility is related to freedom of rotation of atoms around bonds without substituents. A chain flexibility decreasing is result from occurrence of cycles and coupling of atoms being part of main chain. However, occurrence of cycles in a chain is not necessarily the case for considerable stiffening effect in itself.

It could be prevented by flexible bridges between cycles or absence of coupling between them, for example, as occurred in polyionenes. The double-

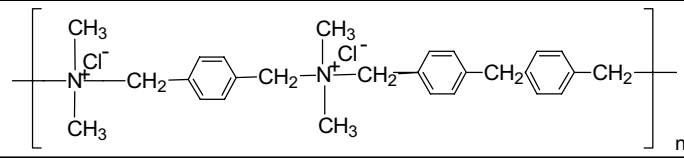
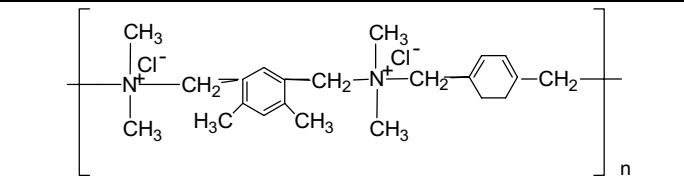
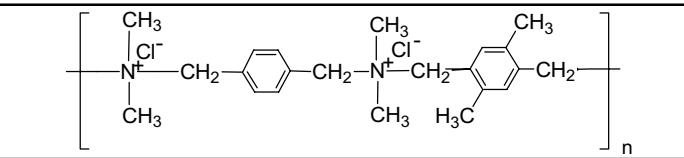
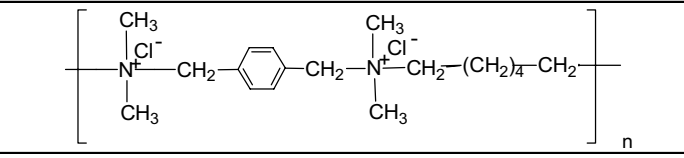
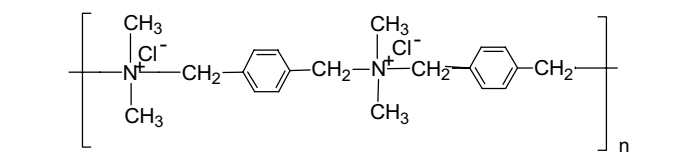
Table 1

Reactants ratio and sol-gel system state during silicophosphate and hybrid nanocomposite synthesis

marking	Molar concentration of components, mole/mole TEOS						Gel formation time, day	Mixing order
	TEOS No 1	$\text{C}_2\text{H}_5\text{OH}$ No 2	H_2O No 3	HCl No 4	H_3PO_4 No 5	Modifier No 6		
$\text{PA}_1\text{-W}_8$	1	4	8	0,01	1.00	–	6	1,2,4,5,3
$\text{W}_8\text{-PA}_1$			8		1.00	–	6	1,2,3,4,5
$\text{PA}_{0,5}\text{-W}_8$			8		0.50	–	8	1,2,4,5,3
$\text{W}_8\text{-PA}_{0,5}$			8		0.50	–	8	
$\text{W}_2\text{-PA}_{1,5}$			2		1.50	–	1	1,2,3,4,5
$\text{W}_2\text{-PA}_{2,2}$			2		2.20	–	0	
$\text{W}_8\text{-PA}_1\text{-I-1}$			8		1.00	I-1 $8 \cdot 10^{-4}$	3	
$\text{W}_8\text{-PA}_1\text{-I-1us}$			8		1.00	I-1 $8 \cdot 10^{-4}$	3	
$\text{W}_{16}\text{-PA}_1\text{-I-1us}$			16		1.00	I-1 $8 \cdot 10^{-4}$	3	
$\text{W}_2\text{-PA}_{0,1}\text{-I-2}$			2		0.12	I-2 $9 \cdot 10^{-4}$	14	1,2,3,4,5,6
$\text{W}_{24}\text{-PA}_{0,1}\text{-I-2}$			24		0.12	I-2 $2 \cdot 10^{-4}$	14	
$\text{W}_8\text{-PA}_{1,5}\text{-I-3us}$			8		0.12	I-3 $1.2 \cdot 10^{-4}$	39	
$\text{W}_8\text{-PA}_{1,5}\text{-I-4us}$			8		0.12	I-4 $1.2 \cdot 10^{-4}$	21	
$\text{W}_8\text{-PA}_{1,5}\text{-I-5us}$			8		0.12	I-5 $1.2 \cdot 10^{-4}$	33	

Table 2

Polyionenes structural formula

Logical number	Structural formula	Molecular weight
I-1		5900
I-2		7200
I-3		8400
I-4		6100
I-5		5600

stranted polysiloxanes forming results in insufficient membranes strength apparently.

Processes of sols structuring are accelerated by an addition into sol $PA_{0,1}-W_8-NH_4OH$ of small amount of polyionenes I-2, I-4 ($TEOS:I=1:1.2 \cdot 10^{-4}$) as ammonia. Their gelation is completed more rapidly on 20 and 30 day. The polyionenes occurrence in sols is revealed to be able to promote both coagulation process and sol stabilization. In that case, introducing $8 \cdot 10^{-4}$ mole I-2 per 1 mole TEOS into sol decreases an aggregative stability of sols. Examples of sols stability increasing when polyionenes involved will be shown below. The state of sol-gel system is affected appreciably by component mixing order (Table 1). Homogeneous or heterogeneous (with precipitate) sol-gel systems form depending on it.

An appearance and properties of xerogel obtained is affected by order of water introducing (before or after H_3PO_4). The addition of water at the end of the process after the mixing of all the other components drying transforms into the xerogel in the form of an easily friable virtually dry powder. The introduction of water at the initial stage of the sol-gel process results in the formation of the opalescent solution which over a period from six to eight days transforms into a wet gel that is poorly amenable to drying. So, the structure and, possibly,

composition of the prepared gels depend substantially on the order of mixing of the components (Table 1). The incomplete removal of water during drying of the gel is associated with the increase in the rate of hydrolytic splitting of ethoxy groups with the formation of free silanol groups $Si-OH$, which form hydrogen bonds with excess water molecules. It leads to formation of xerogels with different porosities. A decrease in the porosity hinders the removal of sorbed water. It is noted [8] that the use of a base catalyst (NH_4OH) results in a fast anhydrocondensation of silanol groups with the formation of SiO_2 particles [9].

Time dependences of the structural viscosity for the base sol without organic modifier (W_8-PA_1), sol containing polyionenes (W_8-PA_1-I-1) and sol including ammonia ($W_8-PA_1-NH_4OH$) are plotted on Fig. 1. The processes of gels structuring during the sol-gel synthesis are substantially affected by the amount of water and the catalysts due to the acceleration of the hydrolytic polycondensation of TEOS [10,11].

It can be seen from Fig. 1 that rather fast gelation process followed by ripening period when structural viscosity of all the sols increases monotonically. The initial sol W_8-PA_1 gelation is finished for six days. The polyionenes introducing

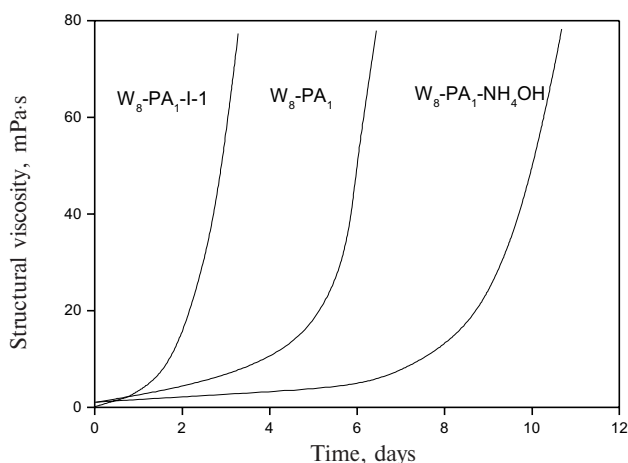


Fig. 1. Time dependences of structural viscosity of sols based on TEOS and orthophosphoric acid

accelerates structure formation completed in 3 days. By contrast, ammonia increases gelation (11 days).

Generally, the drying of the prepared gels under vacuum at 80°C for 5 h results in coarse-grained white powders formation. The heat treatment of the gels in air at 200°C leads to formation of coarsely crystalline brown powders. In this case, the colour of the powders becomes more intense when organic modifier used. A number of derivatograms for these xerogels are shown in Fig. 2.

All the DTA curves of unmodified sols exhibit endothermal effects at temperatures of 160–280°C. These effects are accompanied by the weight loss (Table 3) due to the removal of water and ethanol both adsorbed and formed as a result of thermal destruction of the products of the sol-gel process [12,13].

A little exo-effect resulted from removing remained etoxygroups is observed at 400°C for DTA curve of sol modified with ammonia (PA_{0,1}-W₈-NH₄OH).

Table 3
Thermogravimetric analysis results

Marking	Temperature range, °C			
	0–200	200–400	400–600	600–1000
	Mass loss, %			
PA _{0,1} -W ₈ -NH ₄ OH	14	5	2	2
PA ₁ -W ₈	6	8	3	2
W ₈ -PA ₁	15	13	1	1
PA _{0,5} -W ₈	18	5	1	1
W ₈ -PA _{0,5}	15	17	1	1
W ₂ -PA _{1,5}	6	11	2	2
W ₈ -PA ₁ -I-1	11	9	3	2
W ₈ -PA ₁ -I-1us	10	10	2	1
W ₁₆ -PA ₁ -I-1us	20	9	3	1

Xerogels PA₁-W₈ and W₈-PA₁ with the same ratio H₃PO₄:TEOS=1:1 but different component

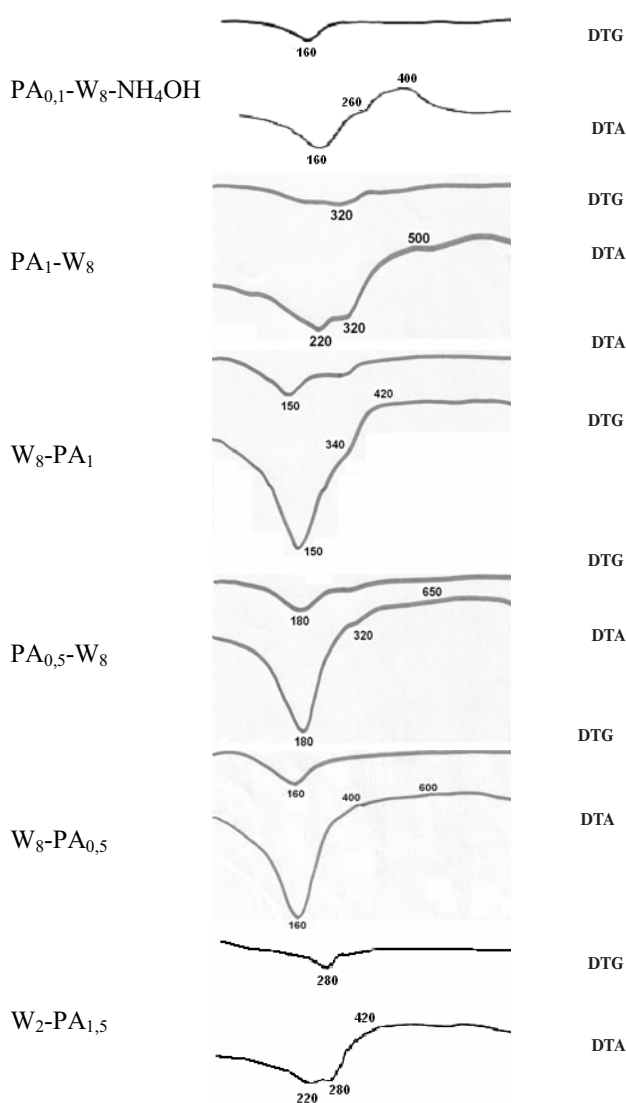


Fig. 2. DTA and DTG curves of unmodified xerogels

mixing order exhibit various characteristics of DTA curves. The composition PA₁-W₈ obtained when water introduced at the end of process in strongly acidic mixture of ether and acid shows two endo-effects at 220 and 320°C and considerably less mass loss at 400°C then for xerogel W₈-PA₁ prepared when water added at the middle of synthesis (Table 1). At that, one endo-effect is revealed at noticeably less temperature (150°C). Physical processes for compositions PA_{0,5}-W₈ and W₈-PA_{0,5} (Table 1) with less by half media acidity (H₃PO₄:TEOS=1:0,5) and as consequence DTA curves characteristics are lesser affected by components mixing order. For xerogel W₈-PA_{0,5} (water added at the middle of synthesis) endo-effect is observed at 160°C, but for xerogel (water introduced at the end of process) it is shown at 180°C.

Mass loss at that as in first case is appeared more high for xerogel W₈-PA_{0,5} with endo-effect at lesser temperature (Table 3). Hence, it could be

concluded that in more acid media hydrolysis and polycondensation run more complete, strong bonds Si—O—Si being formed on condition that water added into acidified system. If water is introduced into ether-alcohol mixture, in first formation of monodisperse siliceous particles with size of several nm began at that. When acid is added, precipitation of electrolyte ions occurred on surface of these particles. It leads to increasing their size that becomes apparent by opalescence.

DTA curve of xerogel W_2 -PA_{1,5} by quantity of H_3PO_4 greater exhibits two adjacent endo-effects at 220 and 280°C. On condition that water was not added into sols, this endo-effects can be attributed to process of removal of ethanol and sol-gel synthesis products formed as a result of thermal destruction.

As for unmodified xerogels (Fig. 3), endo-effect at 160–180°C is typical for all DTA curves of xerogels with organic modifiers. These endo-effects are accompanied with mass loss (Table 2), that being conditioned by removal of water and ethanol both adsorbed and resulted from thermal destruction sol-gel synthesis products.

It can be seen as compared with DTA curves of samples with identical composition W_8 -PA₁-I-1 and W_8 -PA₁-I-1us (sol W_8 -PA₁-I-1us was exposed to ultrasonic treatment (44 kHz, during 15 min)) that endo-effect at 160°C (W_8 -PA₁-I-1) is deposed on 20°C (180°C for W_8 -PA₁-I-1us). The mass changing characteristics is practically identical at that. Possibly, ultrasonic influence increases a number of Si—O—Si bonds, that is, it promotes more complete polycondensation and more closed shielding of bound-free water and hydroxyl groups.

At the introducing of a large quantity of water (W_{16} -PA₁-I-1) into silicophosphate system (base sol W_8 -PA₁-I-1) for producing a large number of free

hydronium ions and protons one endo-effect at 160°C accompanied with mass loss twice as many in first two cases is revealed on DTA curve of xerogel W_{16} -PA₁-I-1. However, mass loss at temperature increasing to 400°C is the same as first two samples. It indicates that water excesses are not accumulated in the gel breakable pores and can be extracted easily.

According to shielding extent in three-dimensional structure of ethyl silicate gel and bonding strength in silica structure burning of organic components formed at ethyl and ethoxy groups decomposition occur at different temperature.

Phase composition of silicophosphate obtained was determined by the X-ray powder diffraction analysis. The xerogels heat treated at a temperature of 250°C were studied. Typical X-ray powder diffraction patterns of xerogel studied are shown on Fig. 4. The sample W_8 -PA₁ (like other unmodified xerogels with composition ratio H_3PO_4 :TEOS=1:1) X-ray powder diffraction pattern involves the reflections corresponding to $Si(PO_4)_4$. X-ray powder diffraction pattern of xerogel W_2 -PA_{1,5} synthesized with raised content of orthophosphoric acid (H_3PO_4 :TEOS=1,5:1) and vacuum dried at 80°C after heat treatment at 250°C diffraction maxima is revealed that is known to be typical for SiP_2O_7 and $SiHP_3O_{10}$ compounds.

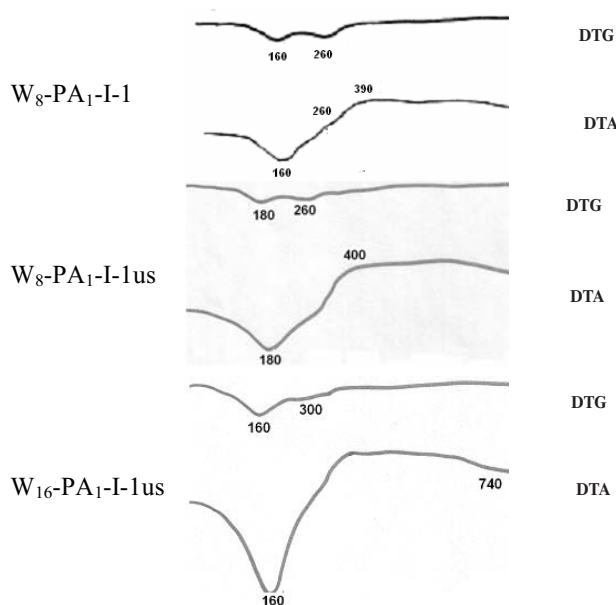


Fig. 3. DTA and DTG modified xerogels

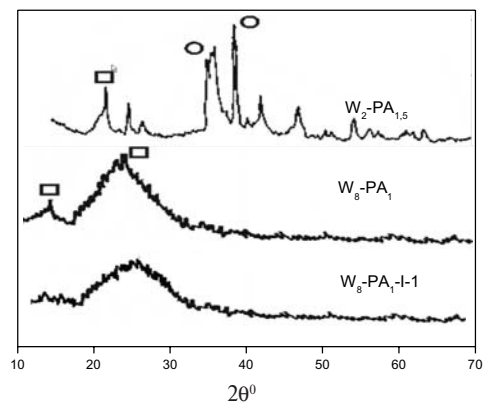
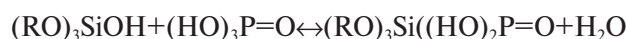


Fig. 4. X-ray powder diffraction patterns of a samples heat treated at 250°C: □ — $Si(PO_4)_4$; ○ — SiP_2O_7

In silicophosphate xerogels heat treated at 250°C occur solid products of variable composition $nSiO_2 \cdot mP_2O_5 \cdot xH_2O$. In water-alcohol solutions, the intermediate products of the TEOS hydrolysis react according to the scheme



X-ray powder diffraction revealed that the crystalline phase $Si_5O(PO_4)_6$ is generated in the material with ratio P:Si=0.5 and more after heat treating. $Si(PO_4)_4$ forming occurred at temperatures above than 250°C is regarded as undesirable for membrane proton-conducting materials because of

low proton conductivity of such xerogels. It is explained that surface groups P–OH are conduction source in silicophosphate nanocomposites.

Diffraction maxima are absent for all modified xerogels. So, they are X-ray amorphous that is associated with the influence of the modifier polyionene on structuring processes.

The typical IR-transmission spectrums of nanocomposites studied are shown on Fig. 5.

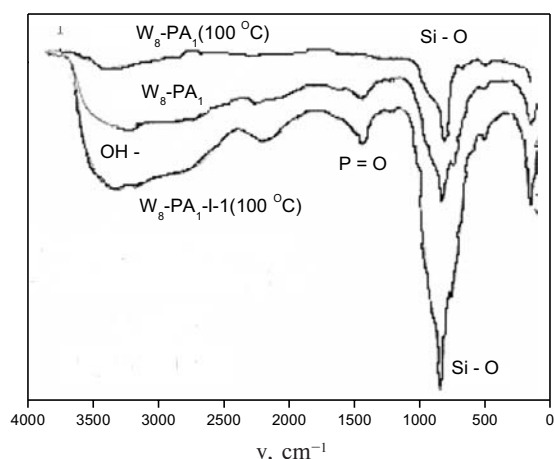


Fig. 5. IR-transmission spectrums nanocomposite studied

Intensive bands of hydronium ions, oscillations of groups of Si–O, Si–OH and P=O ionized are revealed on IR-spectra of silicophosphate xerogel W₈-PA₁-I-1 prepared with modifier I-1. Qualitative changings are not noticed after heat treatment of this nanocomposite at 100°C. However, changing are good visible after heat treatment of unmodified composite W₈-PA₁. The absorption band according to Si–O-groups oscillation disappears, and absorption band of OH-groups becomes hardly noticeable.

The vibrations accorded to P=O group are typical for the sample W₈-PA₁-I-1 (both before and after heat treatment at 100°C) and W₈-PA₁ before heat treatment. They are appeared at 1350–1175 cm⁻¹ (Table 4). This band is deposed on 50–80 cm⁻¹ because molecule contains groups OH or =NH, they being able for hydrogen bonds forming with P=O group. For phosphorus compounds containing >P(O)–OH group where hydrogen bond is more strong than, for example, in carboxylic acids the corresponding band of OH-oscillations (wide and

blurred) appears in the range of 2700–2560 cm⁻¹. It is an evidence of ionized state of orthophosphoric acid.

The curves of the samples prepared with use of organic modifier reveal more intensive absorption band than the curves of samples obtained without modifier.

These differences are agreed with small-angle X-ray scattering (SAXS) curves and TEM images of aggregation forming of nanocomposites. For example, nanocomposite W₈-PA₁-I-1 reveals formation surface fractal with smoother surface as compared with initial W₈-PA₁ synthesized without polyionenes [14]. Ultrasonic treatment of organic-inorganic nanocomposite leads to decreasing of sizes of particles on the first, second and third structural levels.

These results are correlated with conductivity data (Fig. 6). The organic-inorganic nanocomposites (W₈-PA₁-I-1 and W₈-PA₁-I-1us) have a higher protonic conductivity and a lesser activation energy of conductivity as compared with the base silicophosphate nanocomposite W₈-PA₁. A protonic conductivity increasing on order is resulted from a sol ultrasonic treatment (W₈-PA₁-I-1us).

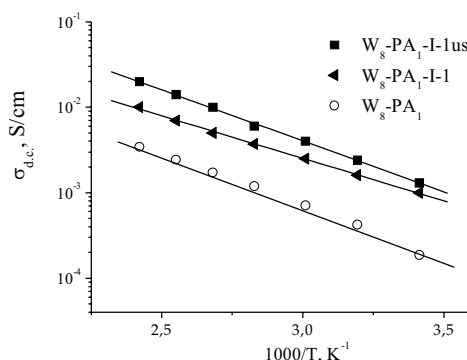


Fig. 6. Arrhenius' dependencies of conductivity on direct current σ_{dc} for nanocomposites W₈-PA₁, W₈-PA₁-I-1 and W₈-PA₁-I-1us in the temperature range of 20 to 140°C.

Solid lines are approximating curves

Conclusions

The process control of sol-gel synthesis of new class of organic-inorganic nanostructured materials on basis of tetraethoxysilane and polyionenes doped by orthophosphoric acid are developed. The chemical compositions improvement is based on results of

Table 4

Characteristics of IR-spectra of nanocomposite studied

Marking	t, °C	Absorption bands maximums, cm ⁻¹				
		Si–O	Valence vibrations of various hydroxide groups: Si–OH	Si–O–Si	P=O	OH–
W ₈ -PA ₁ -I-1	–	2000–1800, 1250, 750	790–800	886	1350–1175	2700–2560
W ₈ -PA ₁ -I-1	100	2000–1800, 1250, 750	790–800	886	1350–1175	2700–2560
W ₈ -PA ₁	–	2000–1800, 1250, 750	790–800	886	1350–1175	2700–2560
W ₈ -PA ₁	100	750	790–800	886	–	3000

complex investigation of morphology, physicochemical properties. The rate of hydrolytical polycondensation reaction of tetraethoxysilane is increased by polyionenes. The gelation process is accelerated with polyionene molecular weight. The polyionenes added in silicophosphate sols ($8 \cdot 10^{-4}$ mole polyionenes per mole $\text{Si}(\text{OEt})_4$) are stated by X-ray analysis to prevent crystallization processes occurred in silicophosphate xerogels with silicon phosphates and pyrophosphates. Doping silicophosphate sols with polyionenes enhances their protonic conductivity. This effect is improved with sol ultrasonic treatment.

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PROTON-CONDUCTING ORGANIC-INORGANIC SILICOPHOSPHATES DOPED BY POLYIONENES

K.M. Sukhyy^a, Y.P. Gomza^b, E.A. Belyanovskaya^a, V.V. Klepko^b, O.A. Shilova^c, M.P. Sukhyy^a, A.V. Gavrilko^a

^aUkrainian State University of Chemical Technology, Dnipropetrovsk, Ukraine

^bInstitute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine

^cGrebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, St. Petersburg, Russia

The technological principles for the process control of the sol-gel synthesis of a new class of organic-inorganic nanostructured materials on the basis of tetraethoxysilane and polyionenes doped by orthophosphoric acid are developed in this work. The chemical compositions improvement is based on the results of complex investigation of morphology, physical and chemical properties. The rate of hydrolytical polycondensation reaction of tetraethoxysilane increases with the addition of polyionenes. The gelling rate increases with polyionene molecular weight. The polyionenes in silicophosphate sols are revealed to prevent crystallization processes which occur in silicophosphate xerogels with silica phosphates and pyrophosphates; this hinders the transport processes. The hybrid organic-inorganic silicophosphates doped by polyionenes exhibit higher proton conductivity than that of the initial nanocomposites. This influence may be improved by the ultrasonic treatment of the sol.

Keywords: organic-inorganic silicophosphates; sol-gel synthesis; tetraethoxysilane; polyionenes; phosphoric acid; proton conductivity.

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