The influence of surface interaction on protonic conductivity of heteropolycompounds

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The phosphor-tungsten $H_3[PW_{12}O_{40}] \cdot nH_2O$, and phosphor-molybdenum $H_3[PMo_{12}O_{40}] \cdot nH_2O$ acids and their salts belong to heteropolycompounds with high proton conductivity in solid state. The structures of both acids are equal[1]: "acid" protons are not connected with oxygen atoms of Keggin anions but located in an external sphere between water molecules, thus forming cation associates of the type $H_5O_2^+$. It is generally accepted that the conductivity of these compounds is determined by the presence of continuous hydrate polyoxone medium with hydrogen bonds and high proton concentration. Proton concentration in acids is really high; there is 3 "acid" protons for $n=6...30$ water molecules. However, in acid salts, such as $(NH_4)_2H[PW_{12}O_{40}] \cdot nH_2O$, concentration of protons is three times lower, and in $(NH_4)_3[PW_{12}O_{40}] \cdot nH_2O$ there are no "acid" protons at all. To explain the phenomenon of high conductivity of neutral salts of heteropolyacids in the work[2] based on NMR-relaxation, a model of "virtual" protons was proposed. This model suggested transport of protons of crystal-hydrates water molecules. Dissociation of water on an anion was proposed in the study[3]. However, in the study[4] of IR-spectra it was demonstrated that there is no direct dissociation of water molecules, however, sufficient amount of permanent extrinsic protons is left in crystals.

Conductivity of an acid is lower than that of an acid salt, has higher activation energy and fast decrease with reduction of amount of crystalline water. Probably, not all protons in acids can concurrently participate in proton conductivity. This may be a result of correlation effects in the protonic lattice gas in framework system, which can be described as motion in framework containing randomly blocked sites[5]. As it was previously shown by computer simulation [6,7], if occupation of conductivity channels network is equal to 3, than loading more than 20% sites by mobile particles leads to very strong correlation effect and mutual ion-transport blocking. Most likely, it is the phenomenon which is observed in heteropolyacids with amount of crystalline water $n \leq 12$.

As an illustration, we can reveal the change of conductivity of phosphor-molybdenum and phosphor-tungsten acids and ammonia salts of the last as a result of surface modification in contact with poly(ethylene)oxide and hydrated tin dioxide in microcomposites.

Composites with poly(ethylene)oxide was studied in[8], and dependencies of conductivity on composition of heteropolycompound — $SnO_2 \cdot 1.5H_2O$ in[9]. Tunneling microscopies surface characterization of these composites shown, that they may be described as random mixture of spherical particles with close diameters as 10 nm.
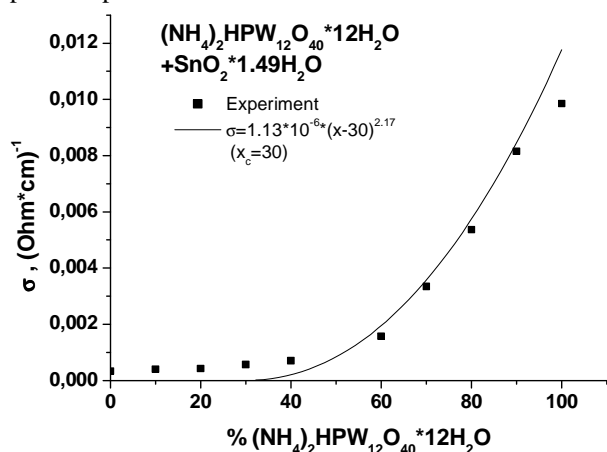

Fig. 1. Conductivity of composite with acid salt.

Dependencies of conductivity of composite material acid salt $(NH_4)_2H[PW_{12}O_{40}] \cdot nH_2O$ — $SnO_2 \cdot 1.5H_2O$ and acid $H_3[PMo_{12}O_{40}] \cdot nH_2O$ — PEO on composition is shown at fig.1. They satisfy to percolation theory equation:

$$\sigma = \sigma_0 (x - x_c)^p \qquad (1)$$

with percolation threshold $p = 33$,
i.e. these composites correspond to the model of non-interaction particles and there is no any surface modification.
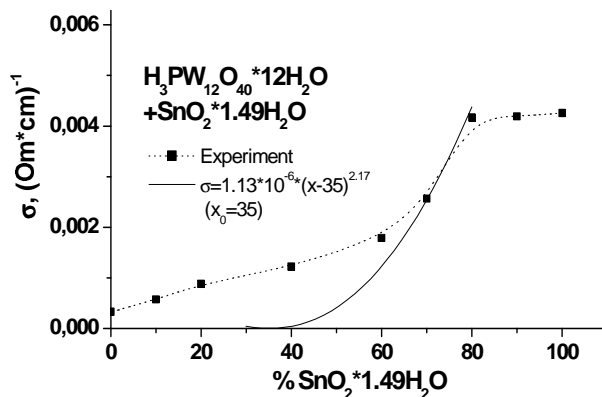

Fig.2. Conductivity of composite with heteropolyacid.

For the system $H_3[PW_{12}O_{40}] \cdot nH_2O$ — $SnO_2 \cdot 1.5H_2O$ there is observed a plateau up to 20% SnO_2 at the curves of conductivity versus composition. I.e. decreasing of high conductivity component $H_3[PW_{12}O_{40}] \cdot nH_2O$ and changing it by $SnO_2 \cdot 1.5H_2O$, which conductivity less about 20 times, does not lead to increasing of conductivity. We suppose, that due to amphoterism of tin dioxide some "acid" protons enter into neutralization reaction with hydroxyl groups of tin hydroxide. In other words, some curriers begin be bound with $SnO_2 \cdot 1.5H_2O$ and do not take part in proton transport in acid. The conductivity of acid yet increasing, approaching to conductivity of acid salt, because there go away " excess" protons, which impede of transport.

Proton conductivity of neutral salt $(NH_4)_3[PW_{12}O_{40}] \cdot nH_2O$, on the contrary, very fast falls at addition of $SnO_2 \cdot 1.5H_2O$. The percolation threshold is about 20% SnO_2, i.e. 80% of salt! Moreover, activation energy for proton transport synchronously increases at this threshold. Within the bounds of our model one can suppose, that neutralization of extrinsic protons by tin hydroxide lead to extremely decrease of conductivity of $(NH_4)_3[PW_{12}O_{40}] \cdot nH_2O$. The additional argument is the fact, that the curves of conductivity vs composition for this system cannot be approximated by law (1).

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