The influence of surface interaction on protonic conductivity of heteropolycompounds

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The phosphor-tungsten $H_3[HPW_{12}O_{40}]\cdot nH_2O$, 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: “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 $H_3O^+$. 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 $(NH_4)H[PMO_{12}O_{40}]\cdot nH_2O$, concentration of protons is three times lower, and in $(NH_4)[PMO_{12}O_{40}]\cdot nH_2O$ there are no “acid” protons at all. To explain the phenomenon of high conductivity of neutral salts of heteropolyacids in the work based on NMR-relaxation, a model of “virtual” protons was proposed. This model suggested transport of protons-crystal-hydrates water molecules. Dissociation of water on an anion was proposed in the study. However, in the study 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 randomly blocked sites. 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 $m\leq 12$.

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 in8, and dependencies of conductivity on composition of heteropolycompound — $SnO_2\cdot 1.5H_2O$ in9. Tunneling microscopies surface characterization of these composites showed, 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.

Dependences of conductivity of composite material acid salt $(NH_4)H[PMO_{12}O_{40}]\cdot nH_2O$ — $SnO_2\cdot 1.5H_2O$ 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:

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

8 Atomyman L.O., Ukshe A.E., Leonova L.S., Electrokhimia (Russian), 21 (1985) 946