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Preparation and conductivity of decatungstomolybdovanadogermanic acid polyethylene glycol (PEG) hybrid material

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Rapid development of science and technology requires the discovery of new materials [1]. The conductive polymers and inorganic/organic solid materials are receiving increasing interest in materials science [2].

Heteropoly acids (HPAs), a class of molecularly defined inorganic metal-oxide clusters, possess intriguing structures and diverse properties and attract increasing attention worldwide [3]. It is well known that HPAs are superior protonic conductors at room temperature, and, therefore, they are promising materials for potential applications as solid electrolytes in sensors, electrochromic displays, and so on. But it is also well known that these compounds are sensitive to surrounding conditions, partial pressure of hydrogen and temperature [4].

In order to improve the mechanical properties and thermal stability, HPAs are mixed with inorganic oxides (silica) or polymers. A variety of composites based on HPAs dispersed in inorganic or inorganic–organic (SiO_2-PEO, SiO_2-PBI) matrices have been developed [5, 6].

In this paper, the preparation and conductivity of a new hybrid material polyethylene glycol (PEG) composited with decatungstomolybdovanadogermanic heteropoly acid are reported.

The decatungstomolybdovanadogermanic heteropoly acid $H_5GeW_{10}MoVO_{40}\cdot 21H_2O$ ($GeW_{10}MoV$) was prepared according to the literature [7]. The purity of PEG (20000) is more than 99.0%. The synthesis of $GeW_{10}MoV$/PEG is described as follows: PEG (0.25 g) was dissolved in 20 ml of boiling water, then $GeW_{10}MoV$ (1.00 g) was added to the solution, and the mixture was stirred strongly until complete dissolution of HPA powder. The solution was vaporized at 50 °C. Finally, the viscous solution was kept in the oven at 40 °C and dried in constant temperature and lapped to powders. The whole process was carried out in the dark.

Fig. 1 shows the infrared spectrum of the sample. The hybrid material doped with the decatungstomolybdovanadogermanic acid exhibits five characteristic peaks of the Keggin anion, which are also observed in the spectrum of the pure decatungstomolybdovanadogermanic acid crystal. The Keggin structure $[GeW_{10}MoV]^{5-}$ consists of one GeO_4 tetrahedron surrounded by four M_3O_{13}($M = W$, Mo or V) sets formed by three edge-sharing octahedra. The M_3O_{13} sets are linked together through oxygen atoms. Thus, there are four kinds of oxygen atoms in $[GeW_{10}MoV]^{5-}$, 4 Ge–O_a in which oxygen atom connects with heteroatom, 12 M—O_b—M oxygen-bridges (corner-sharing oxygen-bridge between different M_3O_{13} sets), 12 M—O_c—M oxygen-bridges (edge-sharing oxygen-bridge within M_3O_{13} sets). and 12 M—O_d terminal oxygen atoms [8]. In the IR spectrum of the pure decatungstomolybdovanadogermanic heteropoly acid crystal, there are five characteristic bands: 978 cm^{-1}, υ_{as} (M—O_d); 877 cm^{-1}, υ_{as} (M—O_b—M); 816 cm^{-1}, υ_{as} (Ge—O_a); 767 cm^{-1}, υ_{as} (M—O_c—M); 458 cm^{-1}, δ (O—Ge—O). The corresponding characteristic bands of the hybrid material are 966 cm^{-1}, υ_{as}(M—O_d); 899 cm^{-1}, υ_{as} (M—O_b—M); 809 cm^{-1}, υ_{as} (Ge—O_a); 766 cm^{-1}, υ_{as} (M—O_c—M); 462 cm^{-1}, δ (O—Ge—O).

M—O_d vibration is considered as pure stretching vibration, the vibration frequency due to the influence of the anion–anion interactions. The decrease of M—O_d asymmetrical stretching frequency of the films with decatungstomolybdovanadogermanic acid wt% 80% is attributed to the weakening of anion–anion interactions of the electrostatic type. M—O_d asymmetrical stretching vibration frequencies decrease from 978 to 966 cm^{-1}. We assumed that the anion–anion interactions are weakened due to the influence of PEG, which leads to the lengthening of the anion–anion distances. M—O_b—M is different from M—O_d stretching, and they are not pure and cannot be free from bending character; there is a competition of the opposite effects. The decrease in electrostatic anion–anion interactions leads to a decrease in the stretching frequencies, but they lead to an increase in the bending vibrations and, moreover, to a perturbation due to a decrease in the frequencies of vibration. In general, vibration frequencies increase from 877 to 899 cm^{-1} [9].

Although the intensities are changed due to the influence of PEG, the characteristic diffraction peaks of crystal were still observed in the X-ray powder

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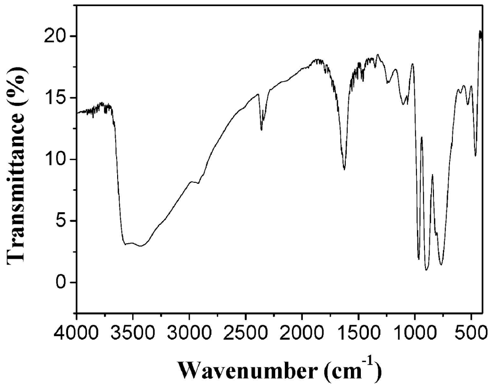

Figure 1 Infrared spectrum of the hybrid PEG by heteropoly acid.

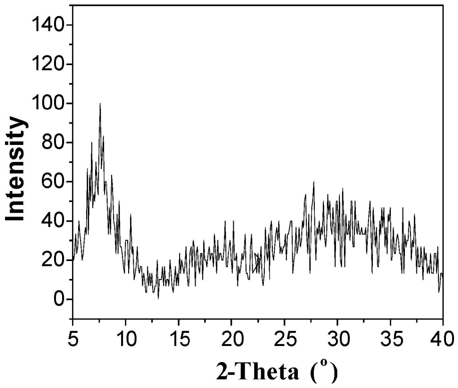

Figure 2 X-ray powder diffraction pattern of the hybrid PEG by heteropoly acid.

diffraction. This finding proves the existence of Keggin anions in the PEG, and is in accordance with the infrared spectra data [10]. The XRD pattern (Fig. 2) shows that the HPA in hybrid materials is amorphous; the most intense peak exists at about 7.5 °.

In the studied material, there are a number of hydrogen bonds among $H_5GeW_{10}MoVO_{40}\cdot 21H_2O$, PEG, and water. The volume of $[GeW_{10}MoVO_{40}]^{5-}$ is so big that the anions cannot move as a result of the strength of hydrogen bonds, but its protons can transfer along these hydrogen bonds. So, the material is a proton conductor.

The conductivity is a function of the movement of protons. It is known that heteropoly acids are sensitive to surrounding conditions such as temperature, relative humidity, and content of crystal water. For example, the research on $H_3PW_{12}O_{40}\cdot nH_2O$ and $H_3PMo_{12}O_{40}\cdot nH_2O$ shows that a mass of hydrogen bonds was produced when the content of crystal water had increased, and at the same time the conductivity increased.

At room temperature (20 °C), the powder of the product was pressed at 20 MPa into a tablet 10 mm in diameters and 1.63 mm in thickness. Two copper sheets were attached to two sides of the tablet. The proton conductivity was measured using a cell: copper |sample| copper over the frequency ranges from 12 Hz to 100 kHz. Fig. 3 shows the result of frequency-dependent complex impedance measurement of the hybrid PEG by decatungstomolybdovanadogermanic heteropoly acid. We can calculate the conductivity from these results. The conductivity of the product is 2.12×10^{-3} S·cm^{-1}, which is much higher than that of the pure PEG (1.86×10^{-9} S·cm^{-1}) and pure decatungstomolybdovanado-germanic heteropoly acid. The results indicate that the PEG hybrid material composited with decatungstomolybdovanadogermanic acid is a new kind of excellent high-proton conductor.

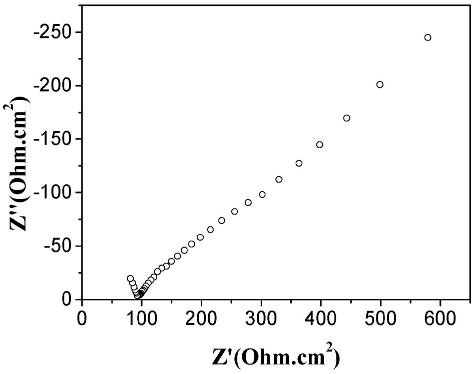

Figure 3 Electrochemical complex impedance of the hybrid PEG by heteropoly acid at 20 °C.

In conclusion, the polyethylene glycol (PEG) hybrid material composited with decatungstomolybdovanadogermanic heteropoly acid was prepared in this work. Infrared (IR) spectrum revealed that the Keggin structure characteristic of the $[GeW_{10}MoV]^{5-}$ anion was present in the PEG hybrid material. At room temperature (20 °C), the conductivity of the sample is 2.12×10^{-3} S·cm^{-1}. The results indicate that it is a new kind of excellent high-proton conductor and can be used as a promising material in the coming future.

Acknowledgments

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