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

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Abstract In this work, the polyethylene glycol (PEG) hybrid material composited with tungstovanadogermanic heteropoly acid was prepared. Infrared (IR) spectrum revealed that the Keggin structure characteristic of the $GeW_{11}VO_{40}^{5-}$ anion was present in PEG hybrid material. At room temperature (20°C), the conductivity of the sample is $4.07 \times 10^{-3} \text{ S cm}^{-1}$. The results indicated that it is a new kind of excellent high-proton conductor. According to the experimental results, we proposed a possible mechanism of the proton conduction of the hybrid materials.

Keywords Inorganic–organic · Polyethylene glycol (PEG) · Tungstovanadogermanic heteropoly acid · Conductivity · Mechanism

Introduction

Inorganic–organic hybrid heteropoly acids (HPAs)-based materials have been of considerable interest in recent years due to their versatile properties [1]. The design, synthesis and structural characterization of new hybrid materials, of which many applications can be predicted, through the assembly of organic and inorganic building blocks, is a highly visible research area [2]. A current development in this area is to design new materials that combine properties.

HPAs and their derivatives have been investigated for more than a century because of particularly interesting

nanosized structures and their potential applications in catalysis, conductivity, photochromic and electrochromic devices, and molecular electronics [3]. Interest in their use as proton conductors began in late 1970s, when their excellent proton conductivity was first reported [4]. In the past, polyoxometalate based hybrid compounds have been constructed either by creation of electrostatic interactions between the inorganic and organic components or of by formation of covalent bonds between the organic and inorganic moieties. To improve the mechanical properties and thermal stability of the electrolytes, HPAs are mixed with inorganic oxides (silica) or polymers [5, 6]. A variety of composites based on HPAs dispersed in inorganic–organic matrices have been developed [7–10].

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

Materials and methods

Characterization

Infrared (IR) spectrum was recorded on a Nicolet Nexus 470 FT/IR spectrometer in the wave number range 400–4,000 cm^{-1} using KBr pellets. Impedance measurements of the samples were performed on a M273 electrochemical impedance analyzer with copper electrodes over the frequency range from 12 to 100 kHz.

Synthesis

The tungstovanadogermanic heteropoly acid $H_2GeW_{11}VO_{40} \cdot 22H_2O$ ($GeW_{11}V$) was prepared according to the literature [11]. The purity of PEG (20,000) is more than 99.0%. The synthesis of $GeW_{11}V/PEG$ is described as follows: PEG (0.25 g) was dissolved in 20 ml of boiling water, then $GeW_{11}V$ (1.00 g) was added to the solution, and the mixture was stirred strongly until complete dissolution of HPA powder. The solution was vaporized

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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.

Results and discussion

Infrared spectrum

Figure 1 presents the structure schematic diagram of $GeW_{11}VO_{40}^{5-}$. The Keggin structure of $GeW_{11}VO_{40}^{5-}$ consists of one GeO_4 tetrahedron surrounded by four M_3O_{13} ($M=W$ or V) sets formed by three edgesharing octahedra. The M_3O_{13} sets are linked together through oxygen atoms. Thus, there are four kinds of oxygen atoms in $GeW_{11}VO_{40}^{5-}$, four $Ge-O_a$ in which oxygen atom connects with heteroatoms, twelve $M-O_b-M$ oxygen-bridges (corner-sharing oxygen-bridge between different M_3O_{13} sets), twelve $M-O_c-M$ oxygen-bridges (edge-sharing oxygen-bridge within M_3O_{13} sets), and twelve $M-O_d$ terminal oxygen atoms [12].

Figure 2 shows the infrared spectrum of the sample. The hybrid material doped with the tungstovanadogermanic acid exhibits five characteristic peaks of the Keggin anion, which are also observed in the spectrum of the pure tungstovanadogermanic acid crystal. In the IR spectrum of the pure tungstovanadogermanic heteropoly acid crystal, there are five characteristic bands: 979.0 cm^{-1} , $\nu_{as}(M-O_d)$; 888.0 cm^{-1} , $\nu_{as}(M-O_b-M)$; 825.0 cm^{-1} , $\nu_{as}(Ge-O_a)$; 775.0 cm^{-1} , $\nu_{as}(M-O_c-M)$; and 463.0 cm^{-1} , $\delta(O-Ge-O)$ [11]. The corresponding characteristic bands of compounds are 970.9 cm^{-1} , $\nu_{as}(M-O_d)$; 885.2 cm^{-1} , $\nu_{as}(M-O_b-M)$; 815.7 cm^{-1} , $\nu_{as}(Ge-O_a)$; 773.3 cm^{-1} , $\nu_{as}(M-O_c-M)$; and 459.0 cm^{-1} , $\delta(O-Ge-O)$.

$M-O_d$ 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 tungstovanadogermanic acid 80 wt.% is attributed to the weakening of anion-anion interactions of the electrostatic type. $M-O_d$

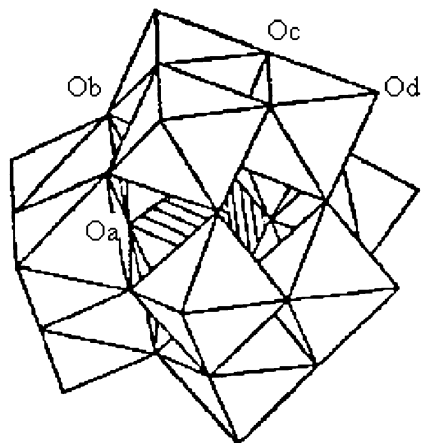


Fig. 1 Structure schematic diagram for $GeW_{11}VO_{40}^{5-}$

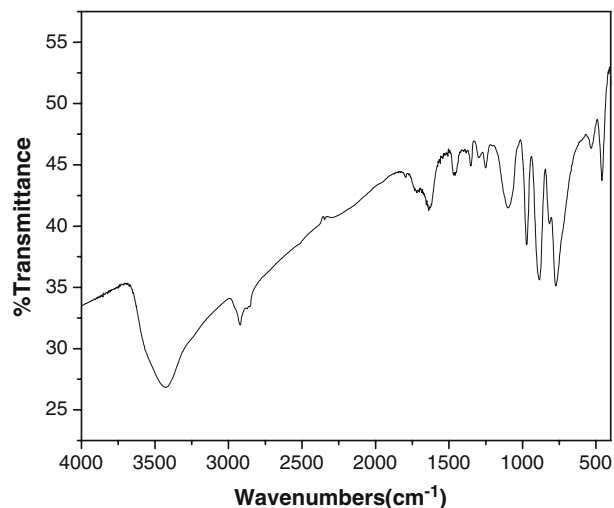


Fig. 2 Infrared spectrum of the hybrid PEG by heteropoly acid

asymmetrical stretching vibration frequencies decrease from 979.0 to 970.9 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. The stretching involving O_b or O_c atoms are different from $M-O_d$ stretching and they present some bending character. This can be inferred from geometrical considerations. The wave number of the $M-O_b-M$ asymmetrical stretching vibrations decreases from 888.0 to 885.2 cm^{-1} and that of the $M-O_c-M$ asymmetrical stretching vibrations decreases from 775.0 to 773.3 cm^{-1} . Because $M-O_b-M$ and $M-O_c-M$ vibrations are not pure and cannot be free from bending character, there is a competition of the opposite effects. The electrostatic anion-anion interactions lead to an increase in the stretching frequencies, but they lead to a decrease in the bending vibrations. In the competition of the opposite effects, the decreasing effect is stronger than the increasing one, but not for $M-O_b-M$. So, $M-O_c-M$ asymmetrical stretching frequencies are decreasing functions of anion-anion interaction.

X-ray powder diffraction

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 diffraction. This finding proves the existence of Keggin anions in the PEG, and is in accordance with the infrared spectra data. The XRD pattern (Fig. 3) shows the HPA in hybrid materials is amorphous; the most intense peak exists at about 7.5° .

Conductivity

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

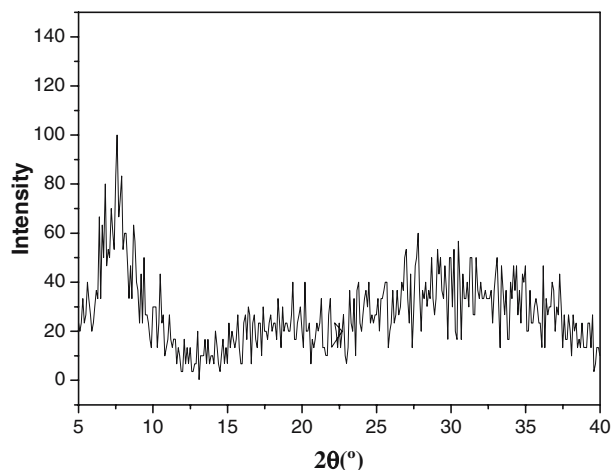


Fig. 3 X-ray powder diffraction pattern of the hybrid PEG by heteropoly acid

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 were produced when the content of crystal water had increased, and at the same time the conductivity increased. The conductivity was calculated as $\sigma = (1/R) \cdot (h/S)$, where R is the resistance, h is the thickness, and S is the area of the tablet [13]. At room temperature ($20^\circ C$), the powder of the product was pressed at 20 MPa into a tablet 10 mm in diameters and 2.56 mm in thickness. Figure 4 shows the result of frequency-dependent complex impedance measurement of the hybrid PEG by tungstovanadogermanic heteropoly acid. We can calculate the conductivity from these results. The conductivity of the product is $4.07 \times 10^{-3} \text{ S cm}^{-1}$ (Fig. 4), which is much higher than that of the pure PEG ($1.86 \times 10^{-9} \text{ S cm}^{-1}$) and pure tungstovanadogermanic heteropoly acid ($2.43 \times 10^{-3} \text{ S cm}^{-1}$). The results indicated that the PEG hybrid material

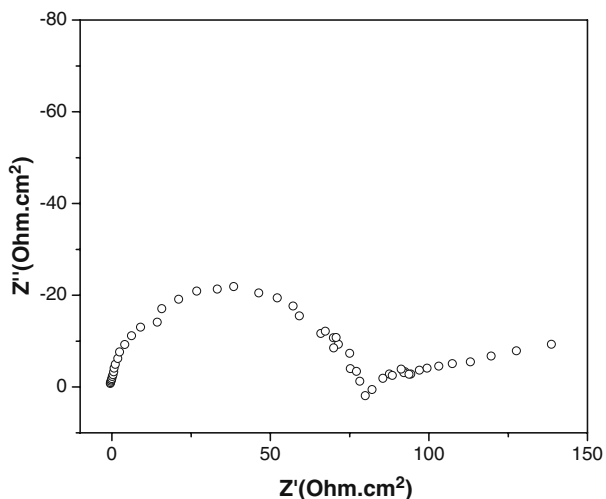


Fig. 4 Electrochemical complex impedance of the hybrid PEG by heteropoly acid at $20^\circ C$

composited with tungstovanadogermanic acid is a new kind of excellent high-proton conductor.

About the mechanism of proton conduction, there are two principle ones: the vehicle mechanism and the Grotthuss mechanism [14]. In the vehicle mechanism, the protons attach themselves to a vehicle (a solvent such as water), and the vehicles diffuse through the medium, carrying the protons along with them. Due to the buildup of “vehicle” molecules on one side of the medium, a concentration gradient is generated, driving vehicular counter diffusion in the opposite direction. This results in the net transfer of protons through the medium. The rate of proton transfer via this mechanism is a strong function of the rate of vehicular diffusion. On the other hand, the Grotthuss mechanism involves stationary vehicle molecules (no translational motion of the vehicle molecules), with the proton itself moving from molecule to another molecule, a process known as “hopping”.

In the studied material, there are a number of hydrogen bonds among tungstovanadogermanic heteropoly acid, PEG, and water. The volume of $GeW_{11}VO_{40}^{5-}$ is so big that the anions cannot move as a result of the strength of hydrogen bonds, but the protons can transfer within these hydrogen bonds from one molecule to the other. The addition of the hydrophilic components (such as PEG in this work), which after sufficient swelling, leads to the diminishing of the capacitance characteristic, which can be attributed to homogenization of the medium through which protons transport, then results in the formation of an uninterrupted trajectory for proton migration. This suggests the Grotthuss mechanism plays a vital role in proton conduction.

Conclusions

IR spectrum and XRD pattern show that $GeW_{11}VO_{40}^{5-}$ anion (Keggin structure) exists in the hybrid material. In the infrared spectrum of the sample, each peak assigned to the different vibration modes is confirmed. The conductivity of material doped with 80% tungstovanadogermanic heteropoly acid is $4.07 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature ($20^\circ C$). The studies on the conductivity of the inorganic–organic hybrid material indicate that it can be used as a promising material in the coming future. An analysis of the data allows us to suggest that the Grotthuss mechanism is responsible for proton conduction in the hybrid material.

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