Preparation and Conductivity of Substituted Germanic Heteropoly Acids Polyethylene Glycol Hybrid Materials

Shouli Zhao,[1] Qingyin Wu,[1] Xuelu Huan,[2] Lichuan Zhao[2]

[1]Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China
[2]College of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

ABSTRACT: In this work, the polyethylene glycol (PEG) hybrid materials composited with substituted germanic heteropoly acids were prepared. Infrared (IR) spectra revealed that the Keggin structure characteristic of the $GeM_{11}VO_{40}^{5-}$ anion were present in the hybrid materials. At room temperature (20°C), the conductivity of the products is 4.07×10^{-3} S cm^{-1} and 2.12×10^{-3} S cm^{-1}, respectively. The results indicated that the conductivity of substituted germanic heteropoly acids PEG hybrid materials is higher than that of the corresponding pure substituted germanic heteropoly acids. According to the experimental results, we proposed a possible mechanism of the proton conduction of the hybrid materials. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2545–2548, 2008

Key words: polyethylene glycol (PEG); tungstovanadogermanic heteropoly acid; decatungstomolybdovanadogermanic 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. Heteropoly acids (HPAs) and their derivatives have been investigated for over a century because of particularly interesting nanosized structures and their potential applications in catalysis, conductivity, photo- 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 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 or polymers.[5,6] A variety of composites based on HPAs dispersed in inorganic–organic matrices have been developed.[7–10]

In this article, the preparation and conductivity of new hybrid materials polyethylene glycol (PEG) composited with substituted germanic heteropoly acids are reported.

EXPERIMENTAL

Characterization

Infrared (IR) spectra were recorded on a Nicolet Nexus 470 FT/IR spectrometer in the wave number range 400–4000 cm^{-1} using KBr pellets. X-ray powder diffraction analysis was obtained on a Bruker AXS D8 ADVANCE X-ray diffractometer using a Cu tube operated at 40 kV and 30 mA in the range of $2\theta = 5–40°$ at a rate of $0.5°$ min^{-1}. Impedance measurements of the products 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 $H_5GeW_{11}VO_{40} \cdot 22H_2O$ (GeW$_{11}$V) and the decatungstomolybdovanadogermanic acid $H_5GeW_{10}MoVO_{40} \cdot 21H_2O$

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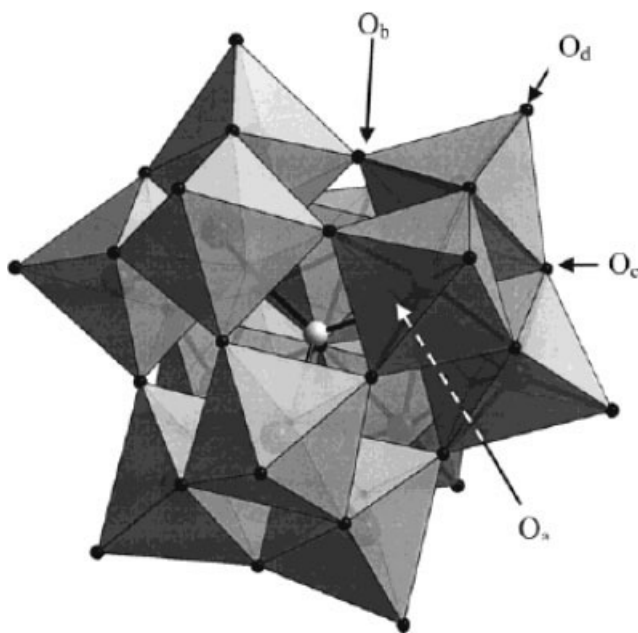
Figure 1 Structure schematic diagram for $GeM_{11}VO_{40}^{5-}$.

(GeMoW$_{10}$V) were prepared according to the litera-tures.[11,12] 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 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. GeMoW$_{11}$V/PEG was obtained using the same process.

RESULTS AND DISSCUSION

Infrared spectra

Figure 1 presents the structure schematic diagram of $GeM_{11}VO_{40}^{5-}$ (M = W or Mo). The Keggin structure of $GeM_{11}VO_{40}^{5-}$ consists of one GeO$_4$ tetrahedron sur-rounded by four M$_3$O$_{13}$ sets formed by three edge-sharing octahedra. The M$_3$O$_{13}$ sets are linked to-gether through oxygen atoms. Thus, there are four kinds of oxygen atoms in $GeM_{11}VO_{40}^{5-}$ four Ge—O$_a$ in which oxygen atom connects with heteroatom, 12 M—O$_b$—M oxygen-bridges (corner-sharing oxygen-bridge between different M$_3$O$_{13}$ sets), 12 M—O$_c$—M oxygen-bridges (edge-sharing oxygen-bridge within M$_3$O$_{13}$ sets) and 12 M—O$_d$ terminal oxygen atoms.[13]

Figure 2 shows the infrared spectra of the pro-ducts. The hybrid materials doped with the substi-tuted germanic heteropoly acids exhibit five charac-teristic peaks of the Keggin anion, which are also observed in the spectra of the pure substituted ger-

manic heteropoly acids. The Keggin characteristic bands of GeM$_{11}$V/PEG are also similar to the pure GeM$_{11}$V. In the IR spectrum of the pure tungstova-nadogermanic heteropoly acid crystal, there are five characteristic bands: 979 cm^{-1}, υ_{as} (M—O$_d$); 888 cm^{-1}, υ_{as} (M—O$_b$—M); 825 cm^{-1}, υ_{as} (Ge—O$_a$); 775 cm^{-1}, υ_{as} (M—O$_c$—M); 463 cm^{-1}, δ (O—Ge—O). The corresponding characteristic bands of the hybrid material are 971 cm^{-1}, υ_{as} (M—O$_d$); 885 cm^{-1}, υ_{as} (M—O$_b$—M); 816 cm^{-1}, υ_{as} (Ge—O$_a$); 773 cm^{-1}, υ_{as} (M—O$_c$—M); 459 cm^{-1}, δ (O—Ge—O). The IR data of the pure decatungstomolybdovanadogermanic are as follows: 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 corre-sponding 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). In addition, a broad peak observed in the high wave number region 3750−3250 cm^{-1} is the characteristic band of water molecules and is due to the O—H stretching, which can be seen from all of the curves. But we cannot exclude the interaction of O—H stretching of PEG. It is most inharmonic and hence usually broad at room temperature. The band of 1630 ∼ 1620 cm^{-1} is attributed to the bending vibration of H—O—H bands. Band at 1110 ∼ 1100 cm^{-1}, is due to the C—O stretching vibrations.

M—O$_d$ vibration is considered as pure stretching vibration, the vibration frequency due to the influ-ence of the anion–anion interactions. M—O$_d$ asym-metrical stretching vibration frequencies decrease from 979 to 971 cm^{-1} (GeW$_{11}$V/PEG) and 978 to 966 cm^{-1} (GeMoW$_{11}$V/PEG), respectively. The decrease of M—O$_d$ asymmetrical stretching frequency of the materials with substituted germanic heteropoly acid 80 wt % is attributed to the weakening of anion–
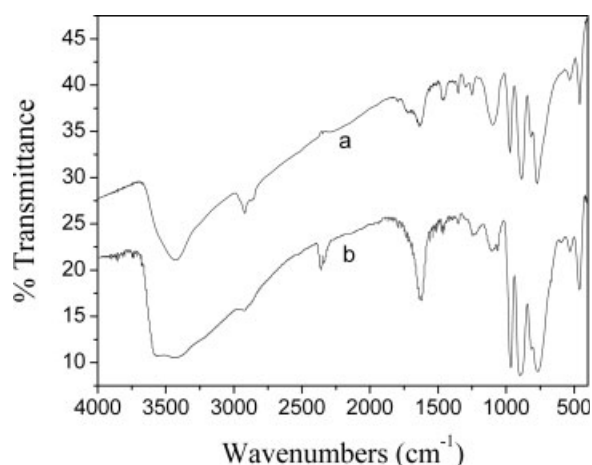
Figure 2 Infrared spectra of the hybrid GeM$_{11}$V/PEG: (a) GeW$_{11}$V/PEG; (b) GeW$_{10}$MoV/PEG.
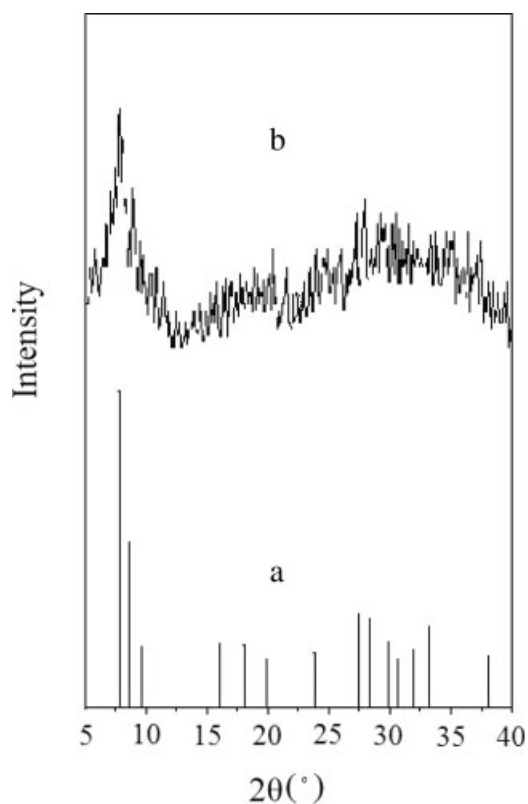
Figure 3 X-ray powder diffraction pattern of pure heteropoly acid $H_5GeW_{10}MoVO_{40}$ (a) and the hybrid PEG by heteropoly acid (b).

anion interactions of the electrostatic type. 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. Because $M—O_b—M$ 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, it may show two different frequency shifts. For $M—O_b—M$ asymmetrical stretching vibrations, the frequency of $GeW_{11}V/PEG$ is decreased from 888 to 885 cm^{-1}, however, that of $GeMoW_{11}V/PEG$ is increased from 877 to 899 cm^{-1}. The $M—O_c—M$ asymmetrical stretching vibrations show no difference between hybrid materials and pure substituted germanic heteropoly acids.

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. The X-ray powder diffraction pattern of $GeW_{11}V/PEG$ is most the same as that of $GeMoW_{11}V/PEG$. This finding proves the existence of Keggin anion in the hybrid materials, which 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 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 network of hydrogen bonds was 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.[14] At 20°C at room humidity, the powders of the $GeW_{11}V/PEG$ and $GeMoW_{11}V/PEG$ were pressed at 20 MPa into pellets 10 mm in diameters, 2.56 and 1.63 mm in thickness, respectively. Figures 4 and 5 show the results of frequency dependent complex impedance measurement of the hybrid PEG by substituted germanic heteropoly acids. We can calculate the conductivity from these results. The conductivity of $GeW_{11}V/PEG$ and $GeMoW_{11}V/PEG$ is 4.07 $\times 10^{-3}$ S cm^{-1} and 2.12 $\times 10^{-3}$ S cm^{-1}, respectively. From the results, we can infer that the conductivity of substituted germanic heteropoly acids PEG hybrid materials is higher than that of the corresponding
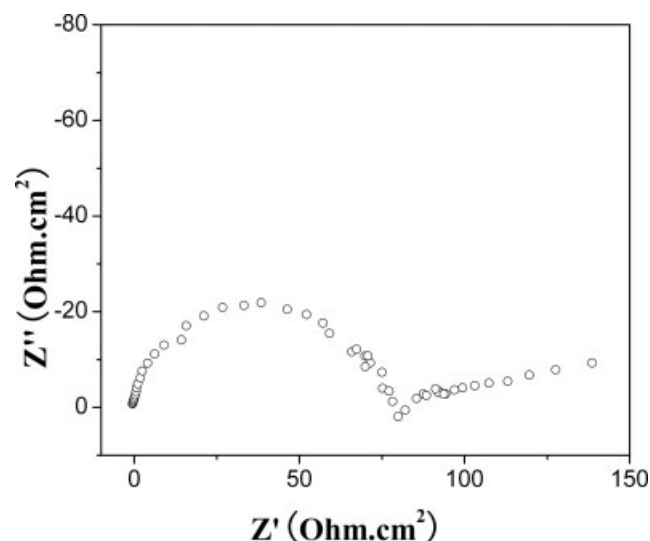
Figure 4 Electrochemical complex impedance of the hybrid $GeW_{11}V/PEG$ at 20°C.
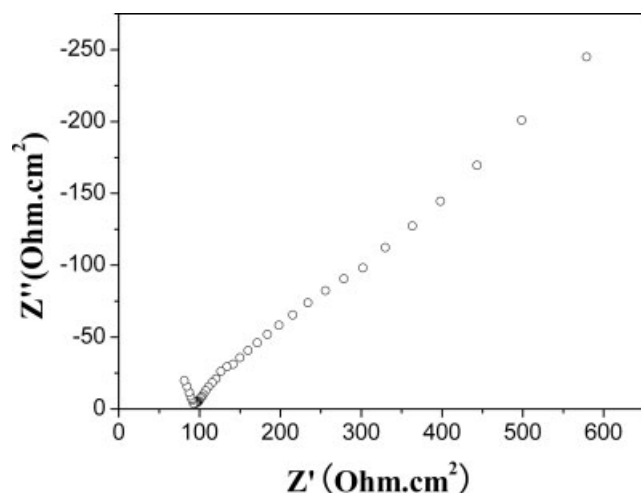
Figure 5 Electrochemical complex impedance of the hybrid $GeW_{10}MoV/PEG$ at 20°C.

pure substituted germanic heteropoly acids (H_5Ge $W_{11}VO_{40} \cdot 22H_2O$: 2.43×10^{-3} S cm^{-1}, $H_5GeW_{10}Mo$ $VO_{40} \cdot 21H_2O$: 3.58×10^{-4} S cm^{-1}).

About the mechanism of proton conduction, there are two principle ones: the vehicle mechanism and the Grotthuss mechanism.[15] 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. Because of 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 materials, there are a number of hydrogen bonds among substituted germanic heteropoly acids, PEG, and water. The volume of $GeM_{11}VO_{40}^{5-}$ 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 spectra and XRD pattern show that $GeM_{11}VO_{40}^{5-}$ anion (Keggin structure) exists in the hybrid materials. It is confirmed that each peak assigned to different vibration modes in the infrared spectra of the products. At room temperature (20°C), the conductivity of hybrid materials is 4.07×10^{-3} S cm^{-1} and 2.12×10^{-3} S cm^{-1}, respectively. The studies on the conductivity of the inorganic–organic hybrid materials indicate that they can be used as promising materials 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 materials.

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