Polymer Bulletin 56, 95–99 (2006)
DOI 10.1007/s00289-005-0469-z

Polymer Bulletin

Preparation and conductivity of organic-undecatungstochromoindic heteropoly acid hybrid materials

Shouli Zhao, Qingyin Wu (✉), Zhiwei Liu

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China
E-mail: mqywu@sohu.com

Received: 24 June 2005 / Revised version: 28 October 2005 / Accepted: 31 October 2005

Summary

Hybrid organic-inorganic proton conductors (PEG/ $InCrW_{11}$ and PVP/ $InCrW_{11}$) were prepared by polyethylene glycol (20000) or polyvinylpyrrolidone (38000) and undecatungstochromoindic heteropoly acid ($InCrW_{11}$). The hybrid materials were characterized by the infrared (IR) spectra and the impedance spectra. The results reveal that the conductivity of hybrid materials is 2.23×10^{-3} and 1.25×10^{-3} $S{\cdot}cm^{-1}$ at room temperature, respectively. According to the experimental results, we proposed a possible mechanism of the proton conduction of the hybrid materials.

Introduction

In recent years, polyoxometalates (POMs) have been widely studied due to their attractive electronic and molecular properties, which give rise to a variety of applications in catalysis, biomedicine, and materials science. An aspect of the research in materials science has been the preparation of hybrid materials either as crystalline phases containing POMs and organic conducting donors of the tetrathiafulvalene family or as thin films by the entrapment of POMs into conducting organic polymers, such as polythiophene, polyaniline, polypyrrole (Ppy), and some of their derivatives [1]. By virtue of the chemical and structural modifications, it is possible to design specific properties and produce novel materials with both inorganic and organic characteristics [2]. But POMs used as inorganic building blocks were not used until last decade [3]. The difficulty to prepare such molecular materials from POM's, mainly due to their high charges and sizes, may explain this late research. Nevertheless, POM's present some unique properties that make them very good and suitable candidates to be used as inorganic building blocks in the preparation of multifunctional molecular materials: (1) In many cases it is possible to change the anionic charge of the POM's while keeping unchanged their structures. This fact confers POM's a rare ability for the study of the role of the anionic charge on the structure and properties of the resulting materials and enables the control and tuning of the physical properties in some cases. (2) POM's also present highly symmetrical shapes that may induce highly symmetrical structures with high dimensionalities. (3) POM's can be solubilized in aqueous and nonaqueous solutions while maintaining their structure in solution and in solid state. This property allows the use of many different synthetic conditions and techniques to prepare the desired molecular materials [4].

The preparation and properties of organic-POMs hybrid materials have been reported [5-13]. But there are little reports about the hybrid from POMs and the bad conducting organic polymer. In the present work, we report the preparation and conductivity of polyethylene glycol (PEG) or polyvinylpyrrolidone (PVP) and undecatungstochromo-indic heteropoly acid ($InCrW_{11}$).

Experimental

Materials

$In(NO_3)_3$ was prepared from indium dissolved in HNO_3, polyethylene glycol (PEG), polyvinylpyrrolidone (PVP), the molecular weight of the PEG and PVP is 20000 and 38000, respectively, the purity of them is more than 99.0%. All other reagents are analysis grade.

Instruments

FT/IR spectra were recorded on a Nicolet Nexus 470 FT/IR spectrometer in the range of 4000-400 cm^{-1} using KBr pellets. Conductivity was determined by complex impedance spectroscopy using a M273 electrochemical impedance analyzer with copper electrodes over the frequency range from 99.9 kHz to 12 Hz at room temperature.

Preparation of hybrid materials

The undecatungstochromoindic heteropoly acid $H_6[CrW_{11}O_{39}In(H_2O)]\cdot 14H_2O$ ($InCrW_{11}$) was prepared according to our previous paper [14]. The two kinds of hybrid materials were obtained using the following process: The polymer (0.25g) was dissolved in 20ml of boiling water, $InCrW_{11}$ (1.00g) was added to the solution, and the mixture was stirred strongly until complete dissolution of HPA powder. The solution was vaporized at given temperature (PEG: 50°C, PVP: 45°C). Finally the viscous solution was kept in the oven at 45°C and dried in constant temperature, crushed to powders. The whole process was carried out in the dark.

Results and discussion

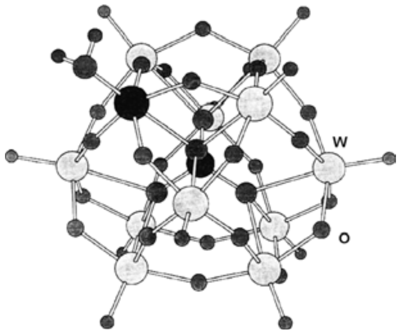

Fig.1 Schematic diagram of the triheteropolyacid structure $H_6[CrW_{11}O_{39}In(H_2O)]\cdot 14H_2O$. The In (III) ion, which is in the upper left hand corner, is depicted as a darker sphere with a terminally coordinated H_2O molecule. The Cr (III) heteroatom resides in a central pseudotetrahedral hole of the structure, and it is the dark central atom.

Infrared spectra

Fig. 1 presents the schematic diagram of $[CrW_{11}O_{39}In(H_2O)]^{6-}$. There are four kinds of oxygen atoms in $[CrW_{11}O_{39}In(H_2O)]^{6-}$, four Cr-$O_a$ in which oxygen atom connects with heteroatom (Cr), twelve W-O_b-W oxygen-bridges (corner-sharing oxygen-bridge between different W_3O_{13} sets), twelve W-O_c-W oxygen-bridges (edge-sharing oxygen-bridge within W_3O_{13} sets) and eleven W-O_d terminal oxygen atoms [15].

IR spectra of the two hybrid materials and pure $InCrW_{11}$ are shown in figure 2. In addition, a broad peak observed in the high wave number region 3690-2990 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 in curve a. It is most anharmonic and hence usually broad at room temperature. The band of 1643 cm^{-1} is attributed to the bending vibration of H-O-H bands. Band at 1106 cm^{-1}, which is only observed for PEG/$InCrW_{11}$, is due to the C-O stretching vibrations.

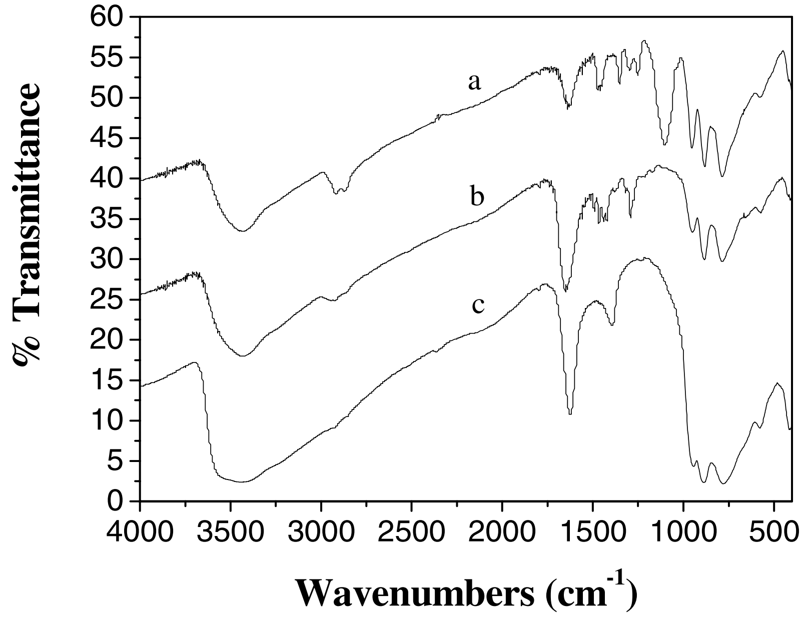

Fig.2 IR spectra of PEG/$InCrW_{11}$ (a), PVP/$InCrW_{11}$ (b) and pure $InCrW_{11}$ (c).

It is clearly for both of the hybrid materials that there are frequency shift compared with pure $InCrW_{11}$ from Fig.2. The positions of vibration modes of all W-O bonds are strongly affected by interactions of neighboring anions and solvents. The stretching involving O_b or O_c atoms are different because of the mixed bending-stretching character. This can be inferred from geometrical considerations. Due to W–O_b–W and W–O_c–W vibrations 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. As a result, the frequency shifts of W–O_b–W and W–O_c–W may show different change direction. The wave number of the W–O_b–W asymmetrical stretching vibrations decreases from 885 cm^{-1} to 882 (PEG), 884 cm^{-1} (PVP), and that of the W–O$_c$–W asymmetrical stretching vibrations increases from 781 cm^{-1} to 786 (PEG), 788 cm^{-1} (PVP).

Conductivity

Conductivity, being a fundamental property of the heteropoly acid, is measured in these hybrid materials. The measurements were made with a two-electrode configuration at room temperature. Pellet shape samples were sandwiched between two copper electrodes in a measurement cell. The conductivity was calculated as $\sigma = (1/R) \cdot (h/S)$, where h is the pellet thickness, and S is the area of the pellet [16]. Fig.3 show the results of frequency dependent complex impedance measurements of the hybrid materials PEG/InCrW$_{11}$ (a) and PVP/InCrW$_{11}$ (b). At room temperature, the powders of the PEG/ InCrW$_{11}$ and PVP/InCrW$_{11}$ were pressed at 20 MPa into pellets 10 mm in diameters, 2.60 and 1.78mm in thickness, respectively. According to the formula, we can calculate conductivity from the complex impedance measurements (Fig.3, 4). The conductivity of hybrid materials is 2.23×10^{-3} and 1.25×10^{-3} S•cm^{-1} at room temperature, respectively.

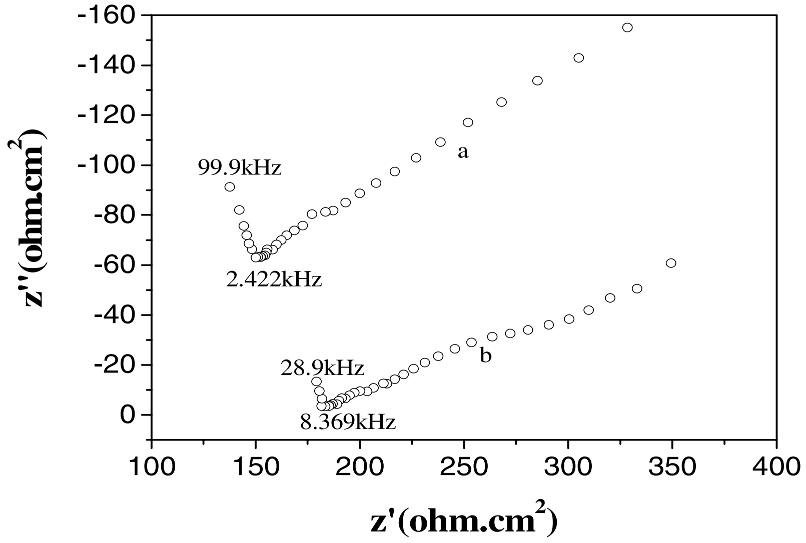

Fig.3 Electrochemical complex impedance of PEG/InCrW$_{11}$ (a), PVP/InCrW$_{11}$ (b) at 20°C.

About the mechanism of proton conduction, there are two principle ones: the vehicle mechanism and the Grotthuss mechanism [17]. 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 molecule, a process known as “hopping”.

In the studied materials, there are a number of hydrogen bonds among $InCrW_{11}$, PEG (or PVP), and water. The volume of $[CrW_{11}O_{39}In(H_2O)]^{6-}$ 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 molecular to the other. The addition of the hydrophilic components (such as PEG, PVP), 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 mechanism is frequently termed the Grotthuss mechanism.

Conclusion

IR spectra confirm the existence of Keggin anions in the hybrid materials. The high conductivity values achieved for the organic-undecatungstochromoindic heteropoly acid hybrid materials investigated in this study make them promising materials for application in electrochemical devices such as solid electrolytes in sensors. An analysis of the data allows us to suggest that the Grotthuss mechanism is responsible for proton conduction in these hybrid materials.

Acknowledgements. The financial support from the National Natural Science Foundation of China under Grant No. 20271045, the Foundation of International Cooperation Project of the Ministry of Science and Technology under Grant No. 014-08 and SRTP Foundation of Zhejiang University for this work is greatly appreciated.

References

[1] Otero TF, Cheng SA, Coronado E, Ferrero EM, Gómez-García CJ (2002) Chem Phys Chem 9:808
[2] Xu L, Li MQ, Wang EB (2002) Mater Lett 54:303
[3] Coronado E, Gómez-García CJ (1998) Chem Rev 98:273
[4] Clemente-León M, Coronado E, Gómez-García CJ, Ferrero EM (2002) J Cluster Sci 13:381
[5] Cheü ckiewicz K, Zú ukowska G, Wieczorek W (2001) Chem Mater13:379
[6] Gong J, Yang JH, Cui XJ, Wang SG, Su ZM, Qu LY (2002) Synth Met 129:15
[7] Cheng SA, Otero TF, Coronado E, Gómez-García CJ (2002) J Phys Chem: B 106:7585
[8] Li L, Xu L, Wang YX (2003) Mater Lett 57:1406
[9] Gong J, Li XD, Ding B, Lee DR, Kim HY (2003) J Appl Polym Sci 89:1573
[10] Cui YL, Mao JW, Wu QY (2004) Mater Chem Phys 85:416
[11] Stangar UL, Orel B, Vince J, Jovanovski V, Spreizer H, Vuk AS, Hocevar S (2005) J Solid State Electrochem 9:181
[12] Wu QY, Sang XG, Deng LJ, Pang WQ (2005) J Mater Sci 40:1771
[13] Lu M, Xie BH, Kang JH, Chen FC, Yang Y, Peng ZH (2005) Chem Mater 17:402
[14] Wu QY, Sang XG, Liu B, Ponomareva VG (2005) Mater Lett 59:123
[15] Wu QY, Sang XG, Shao F, Pang WQ (2005) Mater Chem Phys 92: 16
[16] Jin HX, Wu QY, Pang WQ (2004) Mater Lett 58:3657
[17] Ramani V, Kunz HR, Fenton JM (2004) J Membr Sci 232:31