Synthesis and Conductivity of High Proton Conductor $H_6GeW_{10}V_2O_{40}{\cdot}22H_2O$

Xiao-Guang Sang and Qing-Yin Wu*
Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

(Received June 17, 2004; CL-040696)

The decatungstodivanadogermanic heteropolyacid $H_6GeW_{10}V_2O_{40}{\cdot}22H_2O$ was synthesized for the first time by the stepwise acidification and the stepwise addition of solutions of the component elements. The product was characterized by means of inductively coupled plasma (ICP), IR, UV, X-ray diffraction and thermal analysis. The results of AC impedance measurement show that its proton conductivity is 1.20×10^{-2} $S{\cdot}cm^{-1}$ at room temperature (16 °C).

Heteropolyacids (HPAs) are of special interest for a long time because they are good proton conductors. Their high proton conductivities at room temperature arise from being strong acids in the solid state.[1,2] Usually, HPAs containing tungsten are of stronger acidity comparing with HPAs containing molybdenum.

We have investigated the synthesis and conductivity of $H_5GeW_{11}VO_{40}{\cdot}22H_2O$.[3] So we tried to synthesize a HPA with more numbers of vanadium for comparison. Here, we originally report the synthesis of $H_6GeW_{10}V_2O_{40}{\cdot}22H_2O$ by the stepwise acidification and the stepwise addition of solutions of the component elements.

$H_6GeW_{10}V_2O_{40}{\cdot}22H_2O$ was synthesized as follows. 0.8 g of GeO_2 was dissolved in a hot solution of 10% NaOH and a solution of 22.8 g of $Na_2WO_4{\cdot}2H_2O$ in 100 mL of hot water was added to get mixture A. The pH of A was adjusted to 6 with HCl (1:1) and heated for 1 h. Then a solution of 7.5 g of Na_2CO_3 dissolved in 25 mL of hot water was added and the pH of mixture A was about 8 then. The mixture was concentrated to 100 mL by heating. 2.4 g of $NaVO_3{\cdot}2H_2O$ and 2.5 g of $Na_2WO_4{\cdot}2H_2O$ were dissolved in 30 mL of hot water, respectively, and the two solutions were mixed to get mixture B. The pH of B was adjusted to 2.5 with H_2SO_4 (1:1). Then A was added dropwise to B, and the pH was kept 2.5 while dropping. After stirring for 3 h at 60°C, the solution was cooled to room temperature. The cooled solution was extracted with ether in sulfuric acid medium and the extractant was dissolved with a small amount of water. After the ether was evaporated, the remaining solution was placed in the desiccator. In this way orange crystals were separated out. The final yield was about 70%.

IR spectrum was recorded on a Nicolet Nexus 470 spectrometer. UV spectrum was measured on a SPECORD 2000 UV spectrophotometer. X-ray powder diffraction analysis was obtained on a Bruker AXS D8 ADVANCE X-ray diffractometer. TG-DSC was carried out on a STA-409 thermal analyzer with a rate of temperature increase of 10 $°C{\cdot}min^{-1}$. Impedance measurements were performed on a M378 electrochemical impedance analyzer with copper electrodes over the frequency range from 0.01 Hz to 99.9 kHz.

Germanium, vanadium and tungsten were analyzed by inductively coupled plasma (ICP) spectrometry. The water content was determined by thermogravimetry. Anal. Calcd. for $H_6GeW_{10}V_2O_{40}{\cdot}22H_2O$: Ge, 2.38; W, 60.18; V, 3.33; H_2O, 12.97, Found: Ge, 2.36; W, 60.03; V, 3.29; H_2O, 12.96%.

At room temperature (16 °C), $H_6GeW_{10}V_2O_{40}{\cdot}22H_2O$ was pressed to a tablet 10 mm in diameter and 1.94 mm in thickness under a pressure of 20 MPa. Two copper sheets were attached to two sides of the tablet. The proton conductivity was measured using a cell: copper | sample | copper.

The number of hydrogen in the HPA and the states of ionization can be determined by potentiometric titration.[4] The potentiometric titration curve (Figure 1) shows that the six protons of $H_6GeW_{10}V_2O_{40}{\cdot}22H_2O$ are equivalent and they are ionized in one step.

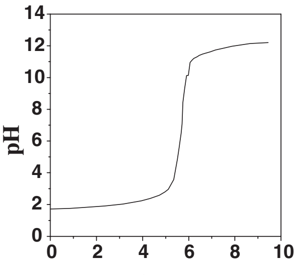

Figure 1. Potentiometric titration curve of $H_6GeW_{10}V_2O_{40}{\cdot}22H_2O$.

The $[GeW_{12}O_{40}]^{4-}$ structure (Keggin structure) consists of one GeO_4 tetrahedron surrounded by four W_3O_{13} sets formed by three edge-sharing octahedra. The W_3O_{13} sets are linked together through oxygen atoms. Thus, there are four kinds of oxygen atoms in $[GeM_{12}O_{40}]^{6-}$ ($M_{12} = W_{10} + V_2$), four Ge–O_a in which oxygen atom connects with heteroatom (Ge), 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.

In the IR spectrum of $H_6GeW_{10}V_2O_{40}{\cdot}22H_2O$, there are five characteristic bands: 965 cm^{-1}, ν_{as} (M–O_d); 883 cm^{-1}, ν_{as} (M–O_b–M); 817 cm^{-1}, ν_{as} (Ge–O_a); 778 cm^{-1}, ν_{as} (M–O_c–M); 462 cm^{-1}, δ (O–Ge–O),[5] all of which correspond to the spectrum of the heteropoly complex of Keggin structure previously reported.[6]

In the high-wavenumber region, there are two other peaks at 3447 and 1619 cm^{-1}. These two peaks are assigned to the stretching vibration of O–H bonds and the bending vibration of H–O–H bonds, respectively.

In the Keggin structure, intense absorption bands at 200 and 260 nm are caused by charge transfer from the terminal oxygen and bridge oxygen to metal atoms, respectively. In the UV spectrum, there are two characteristic bands: 206 nm, $O_d \rightarrow M$; 260 nm $O_b/O_c \rightarrow M$.[7]

X-ray powder diffraction is widely used to study the structural features of HPA and explain their properties.[8] The data

Table 1. Data of X-ray powder diffraction of $H_6GeW_{10}V_2O_{40}\cdot 22H_2O$

$2\theta/°$	9.27	10.34	16.76	18.75	19.10	20.76	25.52
d/nm	0.954	0.855	0.529	0.473	0.465	0.428	0.349
I	95.8	100.0	14.6	25.0	47.9	41.7	45.8
$2\theta/°$	27.09	28.00	29.57	34.70	35.40	36.72	37.79
d/nm	0.329	0.319	0.302	0.259	0.254	0.245	0.238
I	70.8	60.4	27.1	33.3	22.9	35.4	27.1

of X-ray powder diffraction are listed in Table 1.

The result of X-ray powder diffraction of $H_6GeW_{10}V_2O_{40}\cdot 22H_2O$ displays that the diffraction peaks are primarily distributed in four ranges of 2θ which are 7–10°, 16–22°, 25–30° and 33–38°. The positions and intensities of the main peaks are similar to those expected for the Keggin structure.[9] Combined with IR and UV spectra, it is sure that $H_6GeW_{10}V_2O_{40}\cdot 22H_2O$ possesses Keggin structure.

HPA consists of protons, HPA anions and hydration water. Figure 2 is the thermogram of $H_6GeW_{10}V_2O_{40}\cdot 22H_2O$. The TG curve shows that the total percent of weight loss is 12.96%, which indicates that each HPA molecule has 22 molecules of water and there are three steps of weight loss. The first is the loss of 16 molecules of hydration water, the second is the loss of 6 molecules of protonized water and the third is the loss of 3 molecules of structural water. Thus, the accurate molecular formula of the product is $(H_5O_2)_3H_3GeW_{10}V_2O_{40}\cdot 16H_2O$.[10]

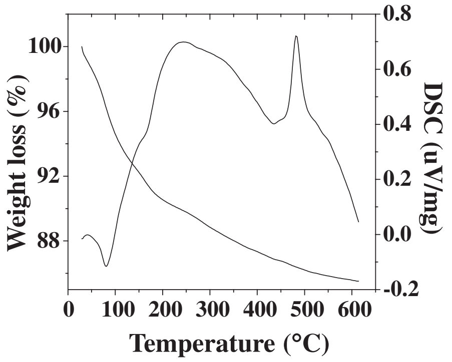

Figure 2. Thermogram of $H_6GeW_{10}V_2O_{40}\cdot 22H_2O$.

In general, we took the temperature of the exothermic peak of DTA curves as the sign of their thermostability.[11] In the DTA curve, there was an exothermic peak at 481.6 °C.

Conductivity is an important parameter. We recorded the results of the complex-impedance measurement of the HPA at room temperature (Figure 3). We can calculate the conductivity from these results. The calculation shows that at room temperature (16 °C), the conductivity of decatungstodivanadogermanic acid $H_6GeW_{10}V_2O_{40}\cdot 22H_2O$ is $1.20 \times 10^{-2}\,S\cdot cm^{-1}$. Its conductivity is higher than that of $H_5GeW_{11}VO_{40}\cdot 22H_2O$ ($2.43 \times 10^{-3}\,S\cdot cm^{-1}$) and $H_4GeW_{12}O_{40}\cdot 14H_2O$ ($3.37 \times 10^{-3}\,S\cdot cm^{-1}$). The conductivity increased with the increase of vanadium content in HPA.

We also have synthesized many HPAs with the structure $H_n[M(H_2O)XW_{11}O_{39}]$, for example $H_6[Al(H_2O)FeW_{11}O_{39}]$ ($4.07 \times 10^{-4}\,S\cdot cm^{-1}$),[12] $H_7[Al(H_2O)CoW_{11}O_{39}]$[13] ($2.74 \times 10^{-4}\,S\cdot cm^{-1}$), and $H_5[Ga(H_2O)ZrW_{11}O_{39}]$[14] ($8.76 \times 10^{-4}\,S\cdot cm^{-1}$). Their conductivities are obviously lower than that of HPAs with Keggin structure.

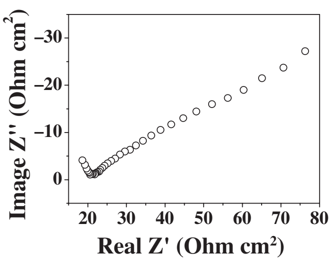

Figure 3. Electrochemical impedance spectrum of $H_6GeW_{10}V_2O_{40}\cdot 22H_2O$.

For comparison with the previous work by O. Nakamura,[15] we also determined the conductivity of 12-tungstophosphoric acid ($H_3PW_{12}O_{40}\cdot 7H_2O$), and it is $3.83 \times 10^{-3}\,S\cdot cm^{-1}$ in the same experiment conditions. So, decatungstodivanadogermanic acid $H_6GeW_{10}V_2O_{40}\cdot 22H_2O$ is a new excellent solid high proton conductor HPA.

In conclusion, decatungstodivanadogermanic heteropolyacid $H_6GeW_{10}V_2O_{40}\cdot 22H_2O$, a new solid high proton conductor, was prepared for the first time and was characterized. We determined the conductivity of $H_6GeW_{10}V_2O_{40}\cdot 22H_2O$ by the complex-impedance measurement. It is $1.20 \times 10^{-2}\,S\cdot cm^{-1}$ at room temperature.

The financial support from the National Natural Science Foundation of China under Grant No. 20271045 and the Foundation of NSFC-RFBR under Grant No. 20411120145 for this work was greatly appreciated.

References

1 W. B. Yang, C. Z. Lu, Q. Z. Zhang, S. M. Chen, X. P. Zhan, and J. H. Liu, *Inorg. Chem.*, **42**, 7309 (2003).
2 D. P. Padiyan, S. J. Ethilton, and R. Murugesan, *Phys. Status Solidi*, **185**, 231 (2001).
3 Q. Y. Wu and G. Y. Meng, *Solid State Ionics*, **136**, 273 (2000).
4 Q. Y. Wu and Y. C. Zhai, *Chin. J. Non-Ferrous Met.*, **8**, 327 (1998).
5 Y. H. Guo, D. F. Li, C. W. Hu, E. B. Wang, Y. C. Zou, H. Ding, and S. H. Feng, *Microporous Mesoporous Mater.*, **56**, 153 (2002).
6 C. Rocchiccioli-Deltchd, M. Fournier, R. Frank, and R. Thouvenot, *Inorg. Chem.*, **22**, 207 (1983).
7 L. Li, L. Xu, and Y. X. Wang, *Mater. Lett.*, **57**, 1406 (2003).
8 Q. Y. Wu, S. K. Wang, D. N. Li, and X. F. Xie, *Inorg. Chem. Commun.*, **5**, 308 (2002).
9 L.-F. Zhong, Y.-M. Zhang, Y. Tang, and Y. Bai, *Polyhedron*, **22**, 2647 (2003).
10 X. E. Cai, D. C. Du, J. P. Ni, Y. M. Jin, J. Zhu, and Y. X. Qian, *Thermochim. Acta*, **292**, 45 (1997).
11 U. B. Mioè, M. R. Todorović, S. M. Uskoković-Marković, M. Davidović, A. Kremenović, A. Spasojević-de Bire, T. Čajkovski, V. Likar-Smiljanić, and R. Biljić, *Solid State Ionics*, **162**, 217 (2003).
12 Q. Y. Wu and X. F. Xie, *Mater. Sci. Eng., B*, **96**, 29 (2002).
13 Q. Y. Wu, *Mater. Lett.*, **42**, 179 (2000).
14 X. G. Sang, Q. Y. Wu, and W. Q. Pang, *Mater. Chem. Phys.*, **82**, 405 (2003).
15 O. Nakamura, T. Kodama, I. Ogino, and Y. Miyake, *Chem. Lett.*, **1979**, 17.

Published on the web (Advance View) October 23, 2004; DOI 10.1246/cl.2004.1518