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Preparation and Performance of High-Proton Conductive Silica Gels Containing Molybdotungstovanadogermanic Heteropoly Acid

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The silica gel containing molybdotungstovanadogermanic acid was prepared by means of the sol–gel method. SEM and infrared spectra revealed that the Keggin structure characteristic of the $GeW_9Mo_2VO_{40}^{5-}$ anion was presented in the silica gel skeleton. The regularity of the change of characteristic peaks in the infrared spectra was investigated. The XRD pattern of the gel was amorphous. The TG curve showed three steps of weight loss. The DTA curve showed that the thermal stability of the gel is lower than that of the pure molybdotungstovanadogermanic acid. The gel exhibited considerably high proton conductivity, which increased with the increase of the molybdotungstovanadogermanic acid content. The proton conductivity of the gel containing 71 wt% molybdotungstovanadogermanic acid is 1.86×10^{-3} S cm^{-1} at 18°C. © 1999 Academic Press

INTRODUCTION

Since exceptionally high proton conductivities of heteropoly acids (HPA) at room temperature were discovered 20 years ago (1), the research in this field has been very active. Their potential application as solid electrolyte attracts a lot of attention, especially their applications in hydrogen–oxygen fuel cells, sensors, electrochromic displays, etc. (2). However, it is well known that these compounds are sensitive to surrounding conditions such as temperature, relative humidity, and the partial pressure of hydrogen (3, 4).

The sol–gel syntheses offer new possibilities in the field of solid state ionics by increasing the stability and conductivity of various inorganic materials on gel matrices. The gel materials prepared using the sol–gel method, which are evidently solid state, contain a large number of micropores and mesopores filled with "liquid" which can be utilized for fast proton transport (5–8). A large number of silanol (Si–OH) groups presented in the gel skeleton may also be desirable for designing an excellent proton conductor composed of the silica gel as a host material and an appropriate proton conductor as a guest material.

Silica gels doped with 12-molybdophosphoric acid and 12-tungstophosphoric acid have been almost thoroughly investigated. In the present paper, we report the preparation of silica gel containing molybdotungstovanadogermanic acid by the sol–gel method. The results of AC impedance measurement show that the silica gel doped with molybdotungstovanadogermanic acid is a new kind of excellent high-proton conductor.

EXPERIMENTAL

Synthesis

Molybdotungstovanadogermanic acid $H_5GeW_9Mo_2VO_{40} \cdot 22H_2O$ was prepared according to the literature (9) as follows. GeO_2, 1.6 g, was dissolved in a hot solution of 10% NaOH. $Na_2WO_4 \cdot 2H_2O$, 45.6 g, was dissolved in 100 ml hot water and was added to the former solution. The pH of the mixture was adjusted to 6 with HCl (1:1), and the mixture was heated for 1 h. After the heating, a solution of Na_2CO_3 (15 g Na_2CO_3 was dissolved in 50 ml hot water) was added. The mixture (pH was about 8) was concentrated to 100 ml by heating, stirred at constant temperature (70–80°C), cooled, and finally several ml ethanol was added. Then white precipitate appeared. After being kept in a refrigerator for 1 day, the mixture was filtered. By desiccating the precipitate, $Na_{10}GeW_9O_{34} \cdot 15H_2O$ was obtained. $Na_{10}GeW_9O_{34} \cdot 15H_2O$, 18.6 g, was dissolved in 100 ml water, and 1.2 g $NaVO_3 \cdot 2H_2O$ was added to the solution. Its pH was adjusted to 1.5 with H_2SO_4 (1:1). After the solution had been boiled for 30 min, it was kept for 24 h. Then 3.7 g $Na_2MoO_4 \cdot 2H_2O$ was added to the solution and H_2SO_4 (1:1) was added to adjust it to pH 1.5. The solution had been boiled for 2 h. After the solution was kept for two days, the required substance was extracted from H_2SO_4 solution by ether. A small amount of water was added to the etherate. After the ether was evaporated, the remaining solution was placed in the desiccator. In this way orange

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polyhedral crystals of $H_5GeW_9Mo_2VO_{40}\cdot 22H_2O$ were produced.

Tetraethoxysilane ($Si(OEt)_4$:TEOS) was diluted with EtOH and was hydrolyzed with the H_2O containing an appropriate amount of $H_5GeW_9Mo_2VO_{40}\cdot 22H_2O$. The molar ratio of $TEOS/EtOH/H_2O = 1/4/5$. After about 3 h of stirring, a homogeneous, transparent sol was obtained. Then the sol was kept at 40°C until it was transferred to gelation.

Three different compositions of the gel were prepared, 45, 59, and 71 wt%. Transparent gels were obtained for each composition.

Experimental Technique

The samples' morphology was investigated with a scanning electron microscope (SEM), Hitachi X-650. IR spectra were recorded on a Bruker VECTOR-22 FT/IR spectrometer in the range 400–4000 cm^{-1} using KBr pellets. X-ray powder diffraction analysis was carried out with an Y-4Q diffractometer, using a Cu tube operated at 40 kV and 30 mA. Diffraction data were collected in the 2θ angle range 5–40° with a scan speed of 0.06 deg/sec. The thermal stability of the samples was checked with differential thermal analysis (DTA) and simultaneous thermogravimetry (TG) between room temperature to 600°C. Measurements were performed using a Shimadzu 50 thermal analyzer, with a scanning rate of 10°C/min. Impedance measurements of pellet samples were performed on a Genrad 1689 Precision RLC Digibridge with copper electrodes over the frequency range from 12 Hz to 100 kHz. The powder was pressed at 8.9×10^8 Pa into compact pellets with a diameter of 13 mm. The thicknesses of the gel pellets were as follows: 45 wt%, 2.86 mm; 59 wt%, 2.98 mm; 71 wt%, 3.18 mm.

RESULTS AND DISCUSSION

Preparation of Silica Gels Doped with Molybdotungstovanadogermanic Acid

A hydrolysis catalyst like HCl or HNO_3 is usually used in the preparation of silica gels. But we found that no catalyst was required in the preparation of silica gels doped with molybdotungstovanadogermanic acid, probably because the molybdotungstovanadogermanic acid can work as a hydrolysis catalyst. Silica gels containing molybdotungstovanadogermanic acid, and in the case of catalyst addition, showed no marked difference in gelation time, appearance of gel products, etc.

SEM

The morphology of the pure molybdotungstovanadogermanic acid crystal and the gels was observed by SEM, Fig. 1. As shown in Fig. 1a, the pure molybdotungstovanadogermanic acid crystal exhibits a polyhedron appearance. In Figs. 1b and 1c, the big transparent sheets of silica gel and small polyhedron crystal of molybdotungstovanadogermanic acid can be identified. Two phases are evident, and the proportion of molybdotungstovanadogermanic acid crystal decreases with the decrease of the content.

Infrared Spectra

Figure 2 compares the infrared (IR) spectra of the gels with different compositions and the $H_5GeW_9Mo_2VO_{40}\cdot 22H_2O$ crystal.

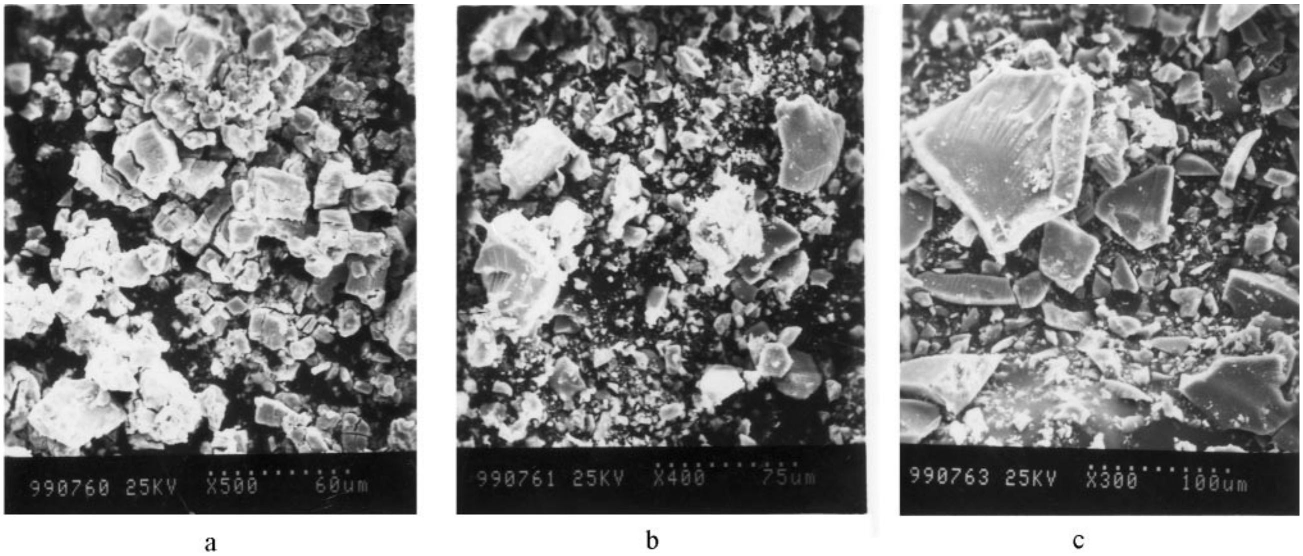

FIG. 1. SEM photomicrographs: (a) pure HPA; (b) doped silica 71 wt% HPA; (c) 45 wt% HPA.

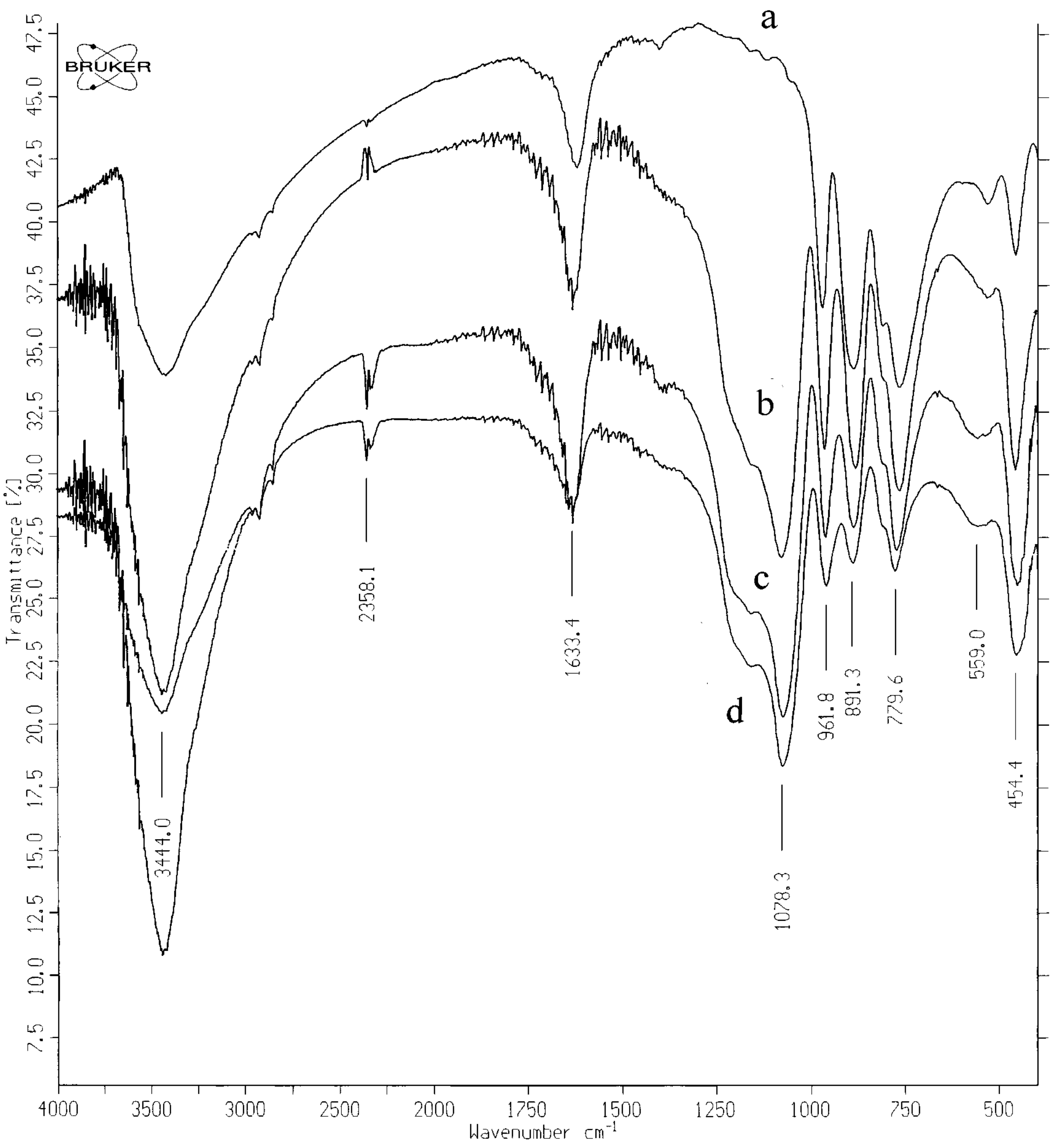

FIG. 2. IR spectra of samples: (a) pure HPA; (b) doped silica 71 wt% HPA; (c) 59 wt% HPA; (d) 45 wt% HPA.

Generally, in the wavenumber range from 700 to 1200 cm^{-1}, pure silica gel exhibits three characteristic peaks at around 1130, 950, and 790 cm^{-1}. The peak at about 1130 cm^{-1} is a broad shoulder peak, which is actually composed of two peaks. The peak at about 1130 cm^{-1} is assigned to the Si–O stretching; the peaks at about 950 and 790 cm^{-1} are assigned to the Si–OH stretching (10). The silica gels doped with the molybdotungstovanadogermanic acid exhibits five characteristic peaks of the Keggin anion, which are also observed in the spectrum of the pure molybdotungstovanadogermanic acid crystal. The Keggin structure of $GeM_{12}O_{40}^{5-}$ (M = W, Mo, or V) consists of one GeO_4 tetrahedron surrounded by four M_3O_{13} 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 $GeM_{12}O_{40}^{5-}$, four Ge–Oa in which an oxygen atom connects with a heteroatom, twelve M–Ob–M oxygen-bridges (corner-sharing oxygen-bridges between different M_3O_{13} sets), twelve M–Oc–M oxygen-bridges (edge-sharing oxygen-bridges within M_3O_{13} sets), and twelve M–Od terminal oxygen atoms (11). In the IR spectrum of the pure molybdotungstovanadogermanic acid crystal, there are five characteristic bands: 977 cm^{-1}, v as (M–Od); 883 cm^{-1}, v as (M–Ob–M); 810 cm^{-1}, v as (Ge–Oa);

767 cm^{-1}, v as (M–Oc–M); 459 cm^{-1}, δ (O–Ge–O) (12). In the spectra of silica gels doped with the molybdotungstovanadogermanic acid, only one characteristic peak at about 1130 cm^{-1} of silica gel was observed. The other two were hidden by the more intense peaks of the Keggin anion.

In the high wavenumber region, each spectrum of the gels exhibits two other peaks at around 3444 and 1633 cm^{-1}, while the spectrum of the pure molybdotungstovanadogermanic acid crystal exhibits two peaks at 3420 and 1622 cm^{-1}. These peaks are assigned to the stretching vibration of O–H bonds and the bending vibration of H–O–H bonds, respectively. The wavenumbers of both peaks of the pure molybdotungstovanadogermanic acid crystal are lower than that of doped silica gels.

Due to the influence of the molybdotungstovanadogermanic acid, the characteristic peak of the Si–O stretching vibration is split with the decrease of the content of the molybdotungstovanadogermanic acid. It is obvious in the IR spectra of gels containing 45 and 59 wt% molybdotungstovanadogermanic acid. With the wt% decreases, the wavenumber of Si–O stretching vibration decreases: 71%, 1080 cm^{-1}; 59 and 45%, 1078 cm^{-1}.

Generally, the M–O_d stretching can be considered as pure vibration and is an increase function of the anion–anion interaction. The M–O_d asymmetrical stretching frequency of the silica gels decreases from 966 to 962 cm^{-1} with the decrease of the molybdotungstovanadogermanic acid wt% from 71 to 45%. This is attributed to the weakening of anion–anion interactions of the electrostatic type. We assumed that due to the influences of silica such as the lengthening of the anion–anion distances, the anion–anion interactions are weakened. The stretchings involving O_b or O_c atoms are different from M–O_d stretching and they present some bending characteristics. This can be assumed from geometrical considerations. Because M–O_b–M and M–O_c–M vibrations are not pure and cannot be free from bending characteristics, there is 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. Moreover, perturbations due to water molecules and anion–cation interactions lead to a decrease in the frequencies of vibrations and can strengthen the decreasing effect of anion–anion interactions. In the competition of opposite effects, the decreasing effect is stronger than the increasing one. So M–O_b–M and M–O_c–M asymmetrical stretching frequencies are decrease functions of anion–anion interaction. With the decrease of the molybdotungstovanadogermanic acid wt% from 71 to 45%, the M–O_b–M and M–O_c–M asymmetrical stretching frequencies increase from 884 to 891 cm^{-1} and 769 to 780 cm^{-1}, respectively. With the increase of the content of the molybdotungstovanadogermanic acid, the characteristic peak of the Ge–Oa stretching vibration was changed to a shoulder peak. The wavenumber of the O–Ge–O bending vibration increases from 454 to 459 cm^{-1} with the increase of the molybdotungstovanadogermanic acid wt%.

X-ray Powder Diffraction

X-ray powder diffraction (XRD) patterns of gels are shown in Fig. 3. The XRD pattern of the silica gel containing the molybdotungstovanadogermanic acid shows low crystallinity. The characteristic peak of the pure silica gel XRD is at about 20° (13) with a characteristic peak of heteropoly acid at about 7.2°. Comparing the XRD patterns of the samples with different compositions, we found that with the increase of the molybdotungstovanadogermanic acid content, the crystallinity increases.

TG-DTA

Figure 4 is the thermogram of the gel containing 71 wt% $H_5GeW_9Mo_2VO_{40} \cdot 22H_2O$. The TG curve shows that there are three steps of weight loss. Before 111.3°C it is the loss of zeolite water; between 111.3 to 228.6°C it is the loss of protonized water; after 228.6°C it is the loss of structural water. In general, we take the temperature of the exothermic peak of DTA curves as the sign of their thermostability (14). In the DTA curve, there are two endothermic peaks and one exothermic peak. The process of dehydration occurs at 47.2°C, which is an endothermic peak. The other endothermic peak at 515.9°C is caused by the melting of decomposed products. The exothermic peak at 436.2°C is due to the decomposition of molybdotungstovanadogermanic acid, which is lower than that of the pure molybdotungstovanadogermanic acid; i.e., the thermal stability of the gel is lower than that of pure molybdotungstovanadogermanic acid, so the interaction between molybdotungstovanadogermanic acid and silica gel is further proved.

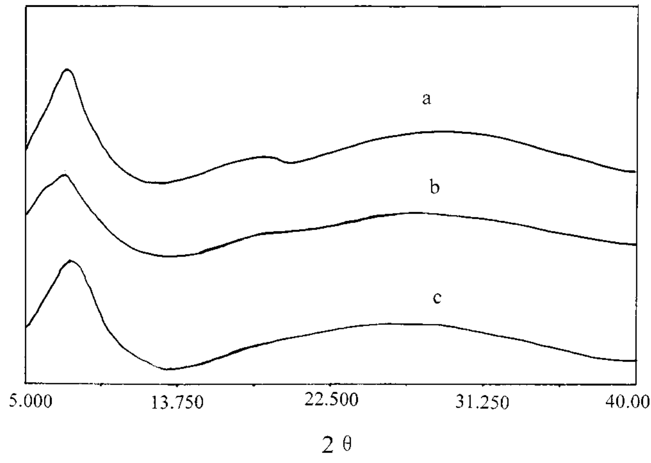

FIG. 3. XRD patterns: (a) doped silica 71 wt% HPA; (b) 59 wt% HPA; (c) 45 wt% HPA.

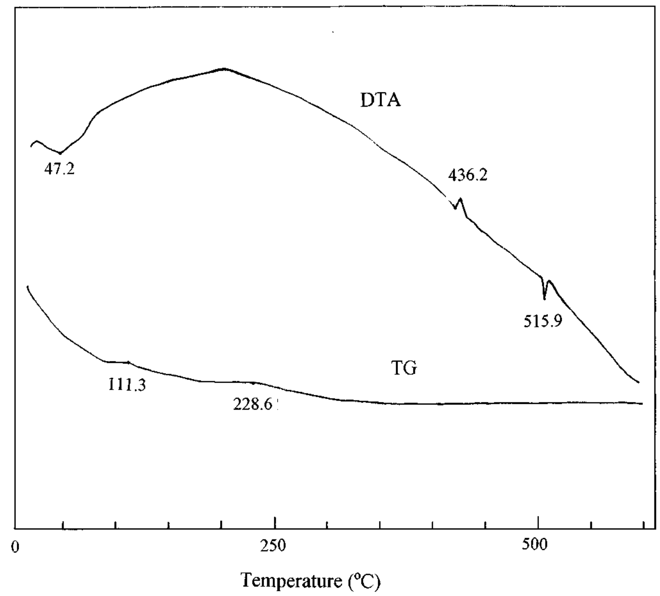

FIG. 4. The thermogram of silica gel containing 71 wt% HPA.

Conductivity

Figure 5 shows the result of the frequency-dependent complex impedance measurement of the silica gel containing 71 wt% molybdotungstovanadogermanic acid at 18°C. The calculation from this result shows that the conductivity of silica gel containing 71 wt% of the molybdotungstovanadogermanic acid is 1.86×10^{-3} S cm^{-1} at 18°C. We also investigated the relation between conductivity and the content of the molybdotungstovanadogermanic acid at 18°C. Figure 6 shows that the conductivity obviously increases from 3.42×10^{-4} to 1.86×10^{-3} as the molybdotungstovanadogermanic acid content increases from 45 to 71 wt%.

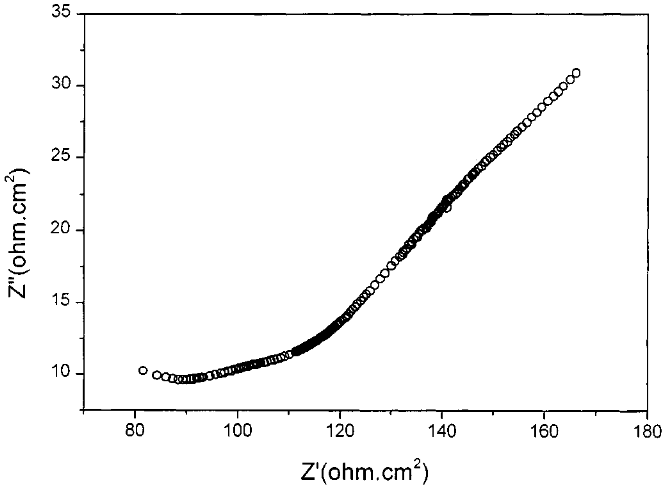

FIG. 5. The impedance spectra of the silica gel containing 71 wt% of the HPA at 18°C.

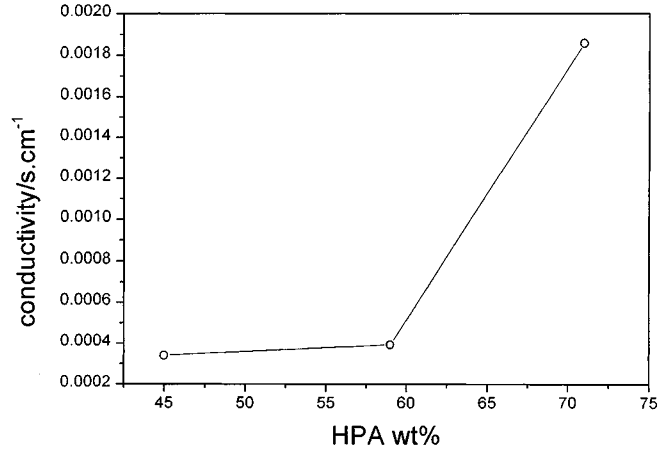

FIG. 6. The relation between conductivity and HPA wt%.

CONCLUSION

Silica gels composited with molybdotungstovanadogermanic acid were prepared by the sol–gel method. Their SEM and IR spectra confirm the existence of Keggin anions in the silica gels. The regularity of the change of the characteristic peaks in the infrared spectra was investigated. XRD patterns of the gels show low crystallinity. The TG curve shows that there are three steps of weight loss. The DTA curve shows that the thermal stability of the gels is lower than that of the pure molybdotungstovanadogermanic acid. The gels exhibit excellent proton conduction. The proton conductivity of the gel containing 71 wt% molybdotungstovanadogermanic acid is 1.86×10^{-3} S cm^{-1} at 18°C. The conductivity increases with the increase of the molybdotungstovanadogermanic acid content.

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