

Temperature control-type electrolyte based on tungstovanadosilicic heteropoly acid and trioctylmethylammonium chloride

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The material $(\text{TOAME})_5[\text{SiW}_{11}\text{VO}_{40}]$ was synthesized from a heteropoly acid and a simple quaternary ammonium ionic liquid as a new organic-inorganic hybrid material. It has a phase transition and ion conductivity of $\sim 2.03 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at 26 °C.

Heteropoly acids (HPAs) play an important role in materials science, medicine, catalysis, magnetochemistry and electrochemistry^{1–5} because of their excellent properties.^{6–8} Ionic liquids (ILs) are suitable for the composition organic-inorganic hybrid materials preparation.^{9–13} We synthesized a new organic-inorganic product based on the tungstovanadosilicic heteropoly acid ($\text{H}_5\text{SiW}_{11}\text{VO}_{40}$) anion and the trioctylmethylammonium cation (TOAME). This novel material has a high ion conductivity and a low extended melting point. Moreover, it possesses a high conductivity.

The tungstovanadosilicic heteropoly acid $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ was prepared according to a published procedure.^{14,15} $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ and trioctylmethylammonium chloride (TOAMECl) were taken in a molar ratio of 1:5. Then, the organic-inorganic compound was synthesized by the addition of TOAMECl ethanol solution to that of the HPA. The mixture was stirred at room temperature for 12 h. Then, the product was separated and dried.

Figure 1 shows the IR spectra of $(\text{TOAME})_5[\text{SiW}_{11}\text{VO}_{40}]$ and $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$. The characteristic bands of $(\text{TOAME})_5[\text{SiW}_{11}\text{VO}_{40}]$ at 1013, 970, 920, 886 and 801 cm^{-1} correspond to $\delta(\text{O}-\text{Si}-\text{O})$, $\nu_{\text{as}}(\text{M}-\text{O}_{\text{d}})$, $\nu_{\text{as}}(\text{Si}-\text{O}_{\text{a}})$, $\nu_{\text{as}}(\text{M}-\text{O}_{\text{b}}-\text{M})$, and $\nu_{\text{as}}(\text{M}-\text{O}_{\text{c}}-\text{M})$ vibrations, respectively. The corresponding bands of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ are observed at 1018, 981, 924, 880 and 776 cm^{-1} . Thus, the complex anion has the Keggin structure. However, both bands due to $\nu_{\text{as}}(\text{M}-\text{O}_{\text{d}})$ vibrations are shifted to the lower wavenumber.¹⁶ This phenomenon is more significant in $(\text{TOAME})_5[\text{SiW}_{11}\text{VO}_{40}]$ because the size of the trioctylmethylammonium cation is larger

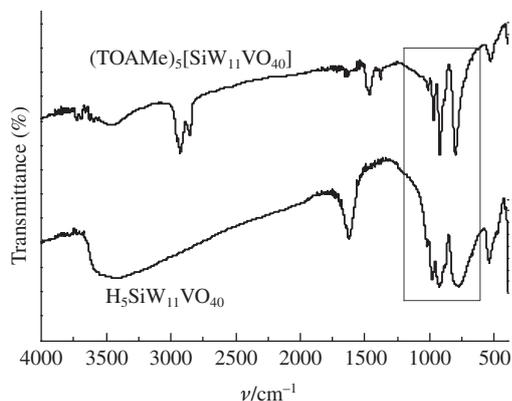


Figure 1 IR spectra of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ and $(\text{TOAME})_5[\text{SiW}_{11}\text{VO}_{40}]$.

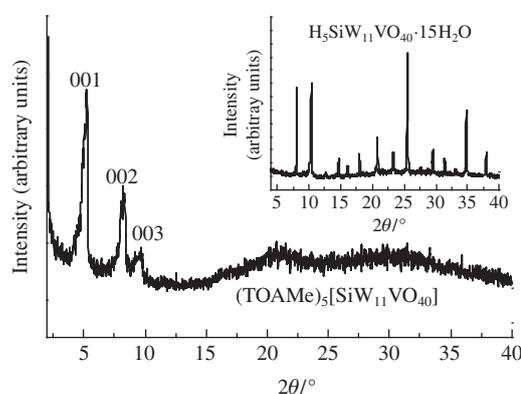


Figure 2 XRD patterns of $(\text{TOAME})_5[\text{SiW}_{11}\text{VO}_{40}]$ and $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$.

than that of hydrated protons, which causes the shift of the distance among the HPA anions. In addition, the bands at 1382, 1465, 2856 and 2926 cm^{-1} of $(\text{TOAME})_5[\text{SiW}_{11}\text{VO}_{40}]$ are assigned to the TOAME ion (bending and stretching vibrations of CH_n groups).

Figure 2 shows the XRD pattern of $(\text{TOAME})_5[\text{SiW}_{11}\text{VO}_{40}]$. It apparently differs from the XRD pattern of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$. The Keggin structure of $(\text{TOAME})_5[\text{SiW}_{11}\text{VO}_{40}]$ anion can also be confirmed due to the sharp peaks at $2\theta = 5.24, 8.32$ and 9.64° , which are in the region of $2\theta = 7-11^\circ$.¹⁷ These reflecting peaks arise from the regular arrangement of the molecules in layers. According to these data, the distances between the layers are equal to 1.684, 1.061 and 0.916 nm, respectively.¹⁸ Moreover, in the wide-angle region, a wide diffraction peak indicates that a smectic phase exists in this compound.¹⁹

The TG and DTA curves of $(\text{TOAME})_5[\text{SiW}_{11}\text{VO}_{40}]$ are shown in Figure 3. In the TG curves, an apparent weight loss can be seen at about 280 °C, which is related to the dehydration and decomposition of the TOAME cation.

The measurements revealed that $(\text{TOAME})_5[\text{SiW}_{11}\text{VO}_{40}]$ possesses a high conductivity as a new kind of ionic liquid. Its conductivity amounts to $2.03 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at 26 °C and 50% relative humidity. Although this compound contains no water molecules, the ionic liquid plays a part of transfer medium in the material. The Arrhenius plot of the $(\text{TOAME})_5[\text{SiW}_{11}\text{VO}_{40}]$ proton conduction is shown in Figure 4. The activation energy E_a of proton conductivity is 22.9 kJ mol^{-1} .

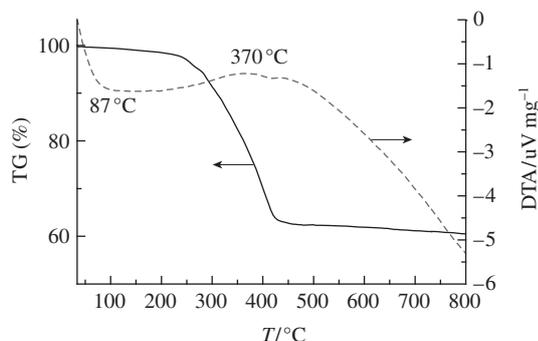


Figure 3 TG and DTA curves of $(\text{TOAMe})_5[\text{SiW}_{11}\text{VO}_{40}]$.

In conclusion, a new kind of HPA-type ionic liquids, $(\text{TOAMe})_5[\text{SiW}_{11}\text{VO}_{40}]$, has been synthesized and characterized by XRD, IR spectroscopy, thermogravimetry and impedance spectroscopy. It has a high ion conductivity and low activation energy. This work provides the basis for the research and progress of HPA–IL hybrid materials. $(\text{TOAMe})_5[\text{SiW}_{11}\text{VO}_{40}]$ can be useful for the liquid crystalline or homogeneous catalysis due to its low melting point.

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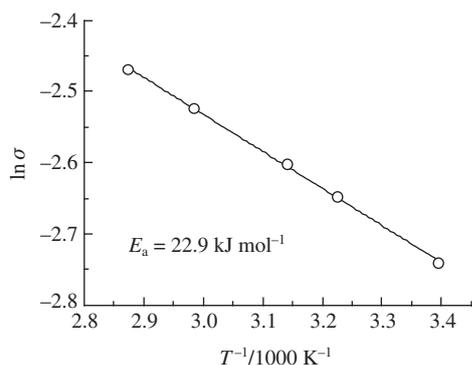


Figure 4 Arrhenius plot for the $(\text{TOAMe})_5[\text{SiW}_{11}\text{VO}_{40}]$ ion conductivity.

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