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Preparation and conductivity of a hybrid material based on tungstovanadosilicic acid polyvinylpyrrolidone

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The Keggin structure and its amorphous phase were detected in the title material. The proton conductivity of the PVP/$H_5SiW_{11}VO_{40}$ hybrid material is 1.39×10^{-2} S cm^{-1} at 18 °C or 1.78×10^{-2} S cm^{-1} at 59 °C and 50% relative humidity, and its activation energy is 11.34±0.03 kJ mol^{-1}.

Heteropoly acids (HPAs) and polyoxometalates (POMs) are formed by inorganic metal-oxygen cluster anions.[1] Because of their unique structures and tunable acidic and redox properties, they can be used in catalysis, biochemical processes and materials science.[2–4] Nakamura first reported the high proton conductivity of $H_3PM_{12}O_{40}\cdot29H_2O$ (M = Mo, W), which is highly sensitive to ambient temperature and humidity. Moreover, HPAs can be incorporated into various matrices to form hybrid materials. HPAs have been explored as additives to materials like Nafion to increase their proton density and water retention at high temperatures.[5,6] There are more negative charge carrier concentrations in $SiW_{11}VO_{40}^{5-}$ in comparison with $PW_{11}VO_{40}^{4-}$ and $SiW_{12}O_{40}^{4-}$. Here, we report the preparation and conductivity of a hybrid material based on polyvinylpyrrolidone (PVP) and tungstovanadosilicic heteropoly acid ($H_5SiW_{11}VO_{40}$) with the Keggin structure.†

Figure 1 shows the anion structure of $SiW_{11}VO_{40}^{5-}$. The Keggin structure of $SiW_{11}VO_{40}^{5-}$ consists of one SiO_4 tetrahedron surrounded by four M_3O_{13} (M = W or V) sets formed by three edge-sharing octahedrons. The M_3O_{13} sets are linked together through oxygen atoms. Thus, there are four kinds of oxygen atoms in $SiW_{11}VO_{40}^{5-}$, four Si–O_a, in which the oxygen atom is bound to a heteroatom, 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.

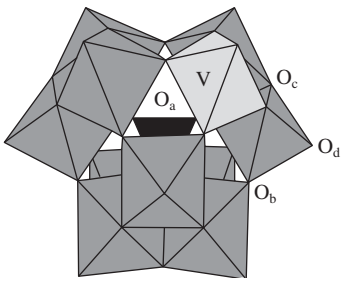

Figure 1 Schematic diagram of the $SiW_{11}VO_{40}^{5-}$ anion structure.

† $H_5SiW_{11}VO_{40}\cdot15H_2O$ ($SiW_{11}V$) was synthesized by the stepwise acidification and addition of metal salt solutions. PVP (0.5 g) and as-synthesized $SiW_{11}V$ (2.0 g) were dissolved in 10 ml portions of boiling water; then, the two solutions were mixed and stirred for 6 h. The mixture was evaporated at 50 °C, dried at 45 °C in an oven and, finally, ground to powders. The resulting material had the empirical formula 0.982 $SiW_{11}V\cdot nH_2O\cdot0.018$PVP.

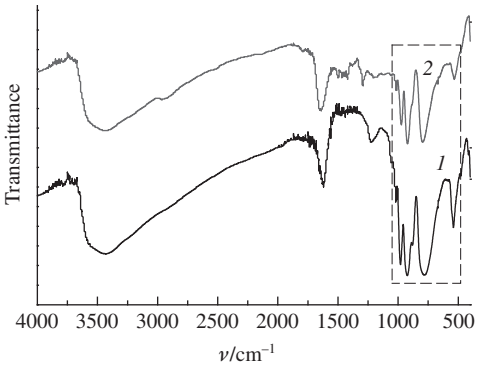

Figure 2 FT-IR spectra of (*1*) pure $SiW_{11}V$ and (*2*) PVP/$SiW_{11}V$.

The FT-IR spectra of HPA and its hybrid material are shown in Figure 2. In the region of 700–1100 cm^{-1}, the spectrum of PVP/$SiW_{11}V$ exhibits five characteristic peaks of the Keggin anion, which are also observed in the spectrum of a pure tungstovanadosilicic acid crystal. The FT-IR spectra confirm the existence of $SiW_{11}V$ in the hybrid material. The M–O_d vibration is red-shifted from 980 to 972 cm^{-1} and the stretching vibration frequency of M–O–M is blue-shifted from 784 to 795 cm^{-1} due to the weakening of anion-anion interactions. The results indicated that interactions between the HPA and PVP take place in the hybrid material.

In the high-wavenumber region, two characteristic vibration frequencies of water molecules manifest themselves, including the stretching vibration of O–H bonds around 3450–3600 cm^{-1} and the bending vibration of H–O–H bonds at 1610–1650 cm^{-1}. The bands observed at 2960, 1264 and 1470 cm^{-1} in PVP-containing material are ascribed to the stretching, twisting and scissoring –CH_2–CH_2– vibrations of organic polymers, respectively.[7] The characteristic band centered at about 1641 cm^{-1} is involved in the C=O vibrations of PVP.[8]

Figure 3 depicts the X-ray diffraction patterns of HPA, PVP and the hybrid material. For the pure $SiW_{11}V$ (Figure 3, curve *1*), there were four peak groups in the 2θ ranges of 5–10°, 17–22°, 25–30° and 31–37°, corresponding to the characteristic reflec-

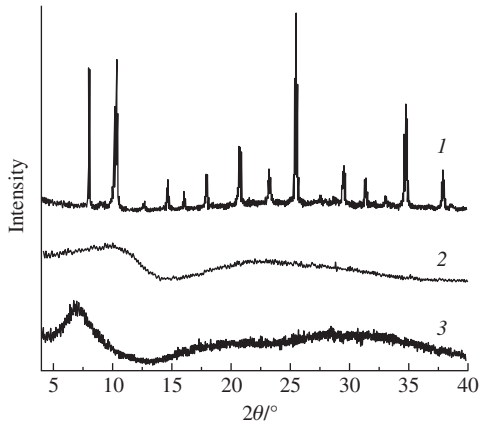

Figure 3 XRD patterns of (*1*) pure $SiW_{11}V$, (*2*) PVP and (*3*) PVP/$SiW_{11}V$.

tions of the Keggin structure. The PVP (Figure 3, curve *2*) presented a typical wide amorphous halo. However, the HPA lost its long-range order after incorporation into a PVP matrix (Figure 3, curve *3*). It had a distinct peak at 7° and a broad band at 17–38°, indicating that the hybrid material is amorphous.[9]

The electrochemical impedance spectra (EIS) of PVP/$SiW_{11}V$ were measured at a 50% relative humidity (RH). Figure 4 shows the Arrhenius plots of the proton conduction of pure $SiW_{11}V$ and the PVP/$SiW_{11}V$ hybrid material. The proton conductivity of the composite material increases from 1.39×10^{-2} S cm^{-1} at 18 °C up to 1.78×10^{-2} S cm^{-1} at 59 °C. These values can be described by the Arrhenius equation. The activation energy of conductivity can be evaluated using the relation

$$\sigma = \sigma_0 \exp(-E_a/kT),$$

where E_a is the activation energy of conductivity, σ_0 is the pre-exponential factor, and k is the Boltzmann constant. The activation energy of proton conductivity of PVP/$SiW_{11}V$ (11.34±0.03 kJ mol^{-1}) is lower than that of $SiW_{11}V$ (21.59±0.06 kJ mol^{-1}). This indicates

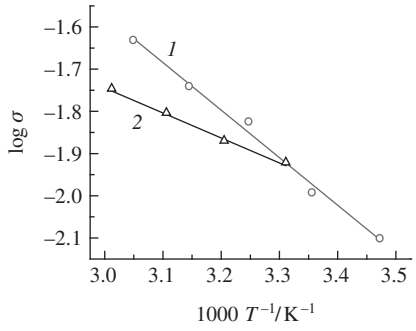

Figure 4 Arrhenius plots of the proton conductivity of (*1*) $SiW_{11}V$ and (*2*) PVP/$SiW_{11}V$.

that the conductivity most likely occurs by the Grotthuss mechanism due to proton migration along $H_3O^+(H_2O)_n$ chains, including proton hydrates $[H(H_2O)_n]^+$ and water molecules.[10,11]

PVP is a water-soluble polymer with high polarity and low conductivity. In a composition with $SiW_{11}V$, H-bonds can be formed. Due to the large volume of the Keggin anion and the hydrogen bond formation, it cannot move but its protons transfer along these hydrogen bonds system. At a low temperature, the proton conductivity is higher than the conductivity of $SiW_{11}V$. It can be explained by additional defect formation on the grain boundaries or by polymer chains participation in proton migration processes.[12]

In conclusion, the PVP/$SiW_{11}V$ hybrid material exhibits excellent proton conductivity up to 1.78×10^{-2} S cm^{-1}. Its activation energy is 11.34±0.03 kJ mol^{-1}. The low activation energy for PVP/$SiW_{11}V$ suggests that the proton transport occurs *via* a Grotthus-like mechanism.

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