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Short Communication

A Novel Molybdotungstosilicate Gel Electrolyte with Wide Electrochemical Stability Window

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New hybrid gel electrolyte $[MIMPS]_4SiW_{11}MoO_{40}$ (IL-SiW_{11}Mo) has been synthesized from the heteropoly acid $H_4SiW_{11}MoO_{40}$ and 1-(3-sulfonic group) propyl-3-methyl imidazolium (abbreviated as MIMPS). The results of FTIR and XRD reveal that the synthesized polyoxometalate-based gel electrolyte possesses lamellar structure and exhibits the characteristic thermo-tropic liquid-crystalline behavior, which can undergo a phase transformation from a viscous gel state to liquid state below 100 ^{o}C. Its ionic conductivity of up to ~10^{-3} S cm^{-1} was observed above the phase transformation temperature. The electrochemical stability potential window (ESW) of IL-SiW_{11}Mo was found to be about 4V at room temperature. The electrochemical impedance spectroscopy (EIS) was carried out to study the capacitance and ion mobility of IL-POM used as electrolyte. The results show that IL-SiW_{11}Mo has high capacitance and fast ion mobility.

Keywords: polyoxometalates; structural; ionic conductivity; amorphous materials; electrochemical stability potential window.

1. INTRODUCTION

Hybrid inorganic-organic compounds have drawn constant attention in the fields of modern materials chemistry and technology, due to their unique and excellent structure and performance. By assembly of hybrid inorganic-organic materials, novel functional materials with relevant physical and chemical properties have obtained great development [1-3]. Different methods have been used to prepare hybrid inorganic-organic materials, which have maintained the functional properties of both inorganic and organic species [4]. Polyoxometalates (POMs), which belong to a large family of metal-oxygen clusters of the early transition metals, have been of longstanding interest to the investigators due to their diverse structures and versatile chemical and physical properties [5-9]. Materials derived from polyoxometalates (POMs) usually demonstrate better properties than the pristine acids in the particular fields of applications. Hence, lots of effort has been taken to broaden the tactics for the design and synthesis of POM-based derivatives by incorporating heteropolyanions into organic matrices through chemical and physical approaches [10-12]. Particularly, POM-based materials with ionic liquids have become a hot spot of research as electrolytes for electrochemical energy storage and conversion devices [13].

Ionic liquids (ILs) are a type of compounds that keep liquid at low temperature. In recent years, they are of growing interest owing to the various attractive properties, such as high ionic conductivity, high electrochemical stability potential window (ESW), good thermal and chemical stability, and negligible vapor pressure [14-16]. These ionic liquids that possess functional groups are chosen to modify the heteropolyanions and tune their physical and chemical performances [17]. In fact, different organic cations have significant impact on the micro structure and properties of hybrid inorganic-organic complexes. According to recent studies, the combination of POMs with some organic cations can lead to some interesting structural compounds like gel-type hybrid materials [18,19]. These POM-based gel-type hybrid materials possess the significant physical characteristics like temperature-responsive behavior, which show a quasi-solid state at room temperature, while heated to about 100°C, they will change to liquid state. Consequently, these gel-type hybrid materials demonstrate higher ionic conductivity than that of other solid conductors, and have advantages over both solid electrolytes and liquid electrolytes [20].

Herein, we chose a different monosubstituted heteropoly anions ($SiW_{11}MoO_{40}^{4-}$) and a type of SO_3H-functionalized imidazolium cation 1-(3-sulfonic group) propyl-3-methyl imidazolium ($MIMPS^+$) to prepare a novel temperature-dependent POM-based gel electrolyte $[MIMPS]_4SiW_{11}MoO_{40}$. The hybrid gel-type electrolyte $[MIMPS]_4SiW_{11}MoO_{40}$ exhibits high ionic conductivity of $\sim 10^{-3}$ S cm^{-1} above the phase transition temperature, and shows electrochemical stability potential window (ESW) of ~ 4V at room temperature.

2. EXPERIMENTAL SECTION

2.1 Synthesis of gel electrolyte

Solid acid of the nominal chemical composition $H_4SiW_{11}MoO_{40}$ ($HSiW_{11}Mo$) was synthesized by a modified method according to the literature [21]. 1-(3-sulfonic group) propyl-3-methyl imidazolium (MIMPS) was synthesized as reported in the literature [11]. $[MIMPS]_4SiW_{11}MoO_{40}$ (IL-

$SiW_{11}Mo$) was synthesized by taking 4:1 mol ratio of MIMPS and $HSiW_{11}Mo$. MIMPS (0.04 mol) was added to 25mL aqueous of $HSiW_{11}Mo$ (0.01 mol) under constant stirring at room temperature for 24 hours. water was first removed by a water bath of 45 °C. Then, the formed pseudo-solid state matter was washed with ethanol and dried under vacuum to get the target hybrid gel product.

2.2 Instruments and reagents

FTIR spectra were recorded using a NICOLET NEXUS470 FT/IR spectrometer over the wavenumber range 400-4000 cm^{-1} by mixing the product with dry KBr, and the resolution for IR is 4 cm^{-1}. Powder X-ray diffraction (XRD) patterns were recorded on a BRUKER D8 ADVANCE X-ray diffractometer (Cu K_α, 40 kV, 40 mA) in the range of 2θ = 3-40° at the rate of $0.02°\cdot s^{-1}$. The conductivity measurements of the product were obtained using a DDS-11A conductivity meter. The investigation of cyclic voltammetry (CV) was performed with a CHI660E electrochemical workstation. The electrochemical impedance spectroscopy was carried on a VMP2 Multichannel potentiostat electrochemical impedance analyzer over a frequency range from 9.99×10^4 to 0.01 Hz.

All reagents were of analytical grade.

3. RESULTS AND DISCUSSION

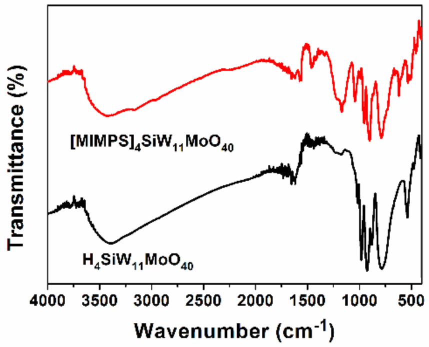
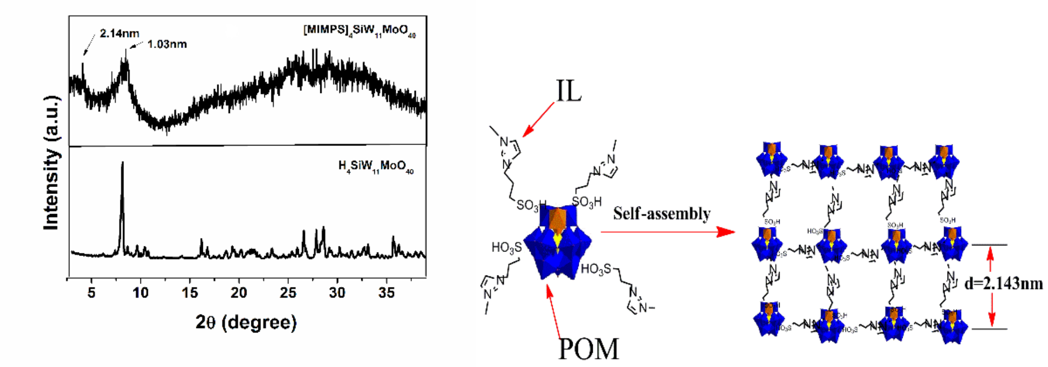


Figure 1. FT-IR spectra of $[MIMPS]_4SiW_{11}MoO_{40}$ and $H_4SiMo_{11}WO_{40}$.

Fig.1 presents the FT-IR spectra of the gel-type electrolyte IL-$SiW_{11}Mo$ and its precursor. The characteristic vibration corresponding to heteropoly anions with Keggin structure exist in the region of 1100-700cm^{-1} [22]. The spectrum of IL-$SiW_{11}Mo$ was found to be similar to the relevant pristine solid acid $H_4SiW_{11}MoO_{40}$, which verify that the Keggin units of the heteropoly anions has been retained. Slight shifts of vibration bands of the synthesized POM-ILs have occurred owing to the interaction of heteropoly anions and MIMPS cations [23]. The FT-IR spectra of IL-$SiW_{11}Mo$ also exhibit the feathered peaks of organic cations functional groups. The bands at 1226 cm^{-1} and 1461 cm^{-1}, assigned to the S=O and imidazole ring stretching vibration, confirm the existence of sulfonic functional group in the products.

XRD is an effective method to investigate the phase and structure of POM-based derivatives. Fig.2(a) depicts the XRD patterns of IL-POM and its parent acid. The XRD patterns of POM-IL display very broad diffraction peaks in the region of 2θ = 15-40°, indicating that the synthesized gel-type electrolyte doesn't have an identified shape like the pristine acid, but a smectic phase instead [24]. The results suggest that the cations have great influence on the secondary structure of POMs derivatives. IL-$SiW_{11}Mo$ shows another Bragg reflection at $2\theta = 4.41^{\circ}$, with d-spacing of 21.42 Å. Using the size of Keggin-type POMs (10.40 Å), the vertical height of MIMPS cations was estimated to be 10.91Å [25]. The diffraction peak of 21.42Å possibly suggests that MIMPS cations and heteropoly anions can be combined regularly by the self-assembly process, which leads to formation of layered super structure. The corresponding d-spacing distances of IL-$SiW_{11}Mo$ is 2.143nm. Schematic of the layered structure of hybrid gel-type electrolyte is shown in the Fig. 2(b).



(a) (b)

Figure 2. (a) Powder XRD patterns of IL-$SiW_{11}Mo$ and pristine acid; (b) Scheme of layered structure of hybrid gel-type electrolyte.

The electrochemical stability potential window (ESW) of the synthesized IL-POM was characterized by the cyclic voltammetry (CV) using a Pt as counter electrode and Ag/AgCl as reference electrode at the different scan rates of 50 mV/s. The Fig. 3(a) shows the cyclic voltammetry curve of $[MIMPS]_4SiW_{11}MoO_{40}$ at room temperature. The ESW of IL-$SiW_{11}Mo$ is up to ~4V. Compared to other common IL electrolytes, these IL-POM shows much higher electrochemical stability potential window [26]. What is worthy to explain is that the redox peaks of early transition metal in the POM anions are not apparently observed in the CV curve, which may result from a high background current due to the fast ionic conductivity of POM-IL gel electrolytes. Fig.3(b) describes the ionic conductivity of IL-$SiW_{11}Mo$ at different temperature and various phases. The endothermic peak of DTA curve indicates that the gel electrolyte can undergo a phase transformation at 83 °C. It is observed that ionic conductivity would increase sharply to 10^{-3} $S \cdot cm^{-1}$ at high temperature, owing to the enhanced ionic mobility from viscous gel state to liquid state [27, 28].

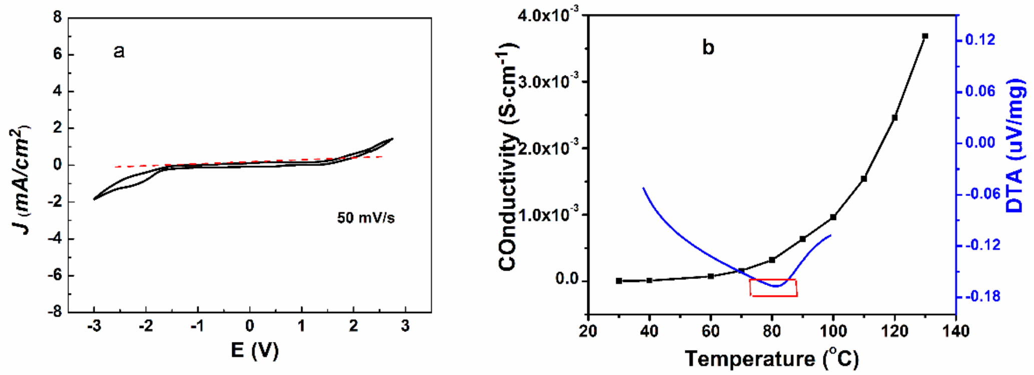


Figure 3. (a) The CV curve (black) of $[MIMPS]_4SiW_{11}MoO_{40}$ under the scan rates of 50 mV/s at room temperature with red level line for comparison; (b) DTA and conductivity-temperature plots of $[MIMPS]_4SiW_{11}MoO_{40}$.

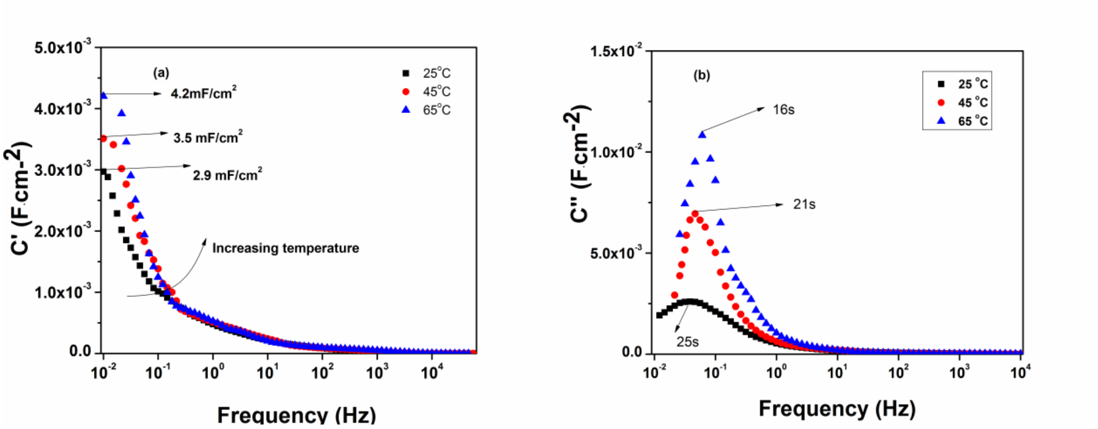


Figure 4. The evolution of (a) real part and (b) imaginary part capacitance vs frequency for the assembled cell using two steel foils of 1 cm^2 as electrodes and $[MIMPS]_4SiW_{11}MoO_{40}$ (IL-$SiW_{11}Mo$) as the electrolyte.

The electrochemical impedance spectroscopy was performed to investigate the capacitance when the IL-POMs were used as the electrolytes in the capacitors. According to the approach in the literature [29], we separated the real part capacitance (C′) from its imaginary part (C″) and plotted them as a function of frequency. As shown in Fig. 4, C′ represents the accessible capacitance of the device vs frequency, and C″ is related to the energy dissipation of an irreversible process [30]. Fig. 4(a) shows the C′ values of different temperatures at very low frequency. At low frequency, when the frequency decreases, C′ sharply increases, then tend to be a constant value and less frequency dependent. With higher temperature, the real part capacitance (C′) of the cell system increases from 2.9 mF·cm^{-2} to 4.2·mF cm^{-2}. Fig. 4(b) exhibits the imaginary part capacitance (C″) of the cell system. The peaks of the C″ vs frequency curves represent a time constant (τ_0= 1/f_0) from resistive to capacitive behavior and reflect the ion mobility rates of electrolyte, IL-$SiW_{11}Mo$. It shows highest ion mobility at the temperature of 65 °C due to the lowest constant time.

4. CONCLUSIONS

In this work, we have successfully synthesized a novel gel-type electrolyte based on the heteropoly anion with Keggin structure and 1-(3-sulfonic group) propyl-3-methyl imidazolium (MIMPS) cation. The gel-type compound possesses lamellar structure and can undergo a phase transformation from gel-state to liquid-state under 100 °C. The electrolyte shows excellent electrochemical properties with high ionic conductivity of up to ~10^{-3}·S cm^{-1} at high temperature and wide electrochemical stability potential window (ESW) of about 4V. The cell system assembled with IL-$SiW_{11}Mo$ electrolyte shows high capacitance and faster ion mobility. With excellent electrochemical properties, these hybrid materials can be potential used as electrolyte materials for developing advanced electrochemical devices.

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