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Research Article

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Preparation of composites from graphene oxide and organic/inorganic complex based-on 2,2'-biimidazole and phosphomolybdic acid and evaluation of their proton conductivity

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ABSTRAT

One composite (denoted as 1–GO2) was prepared from graphene oxide and the organic-inorganic complex $\{H_6[(H_2O)_{1.5}(H_2biim)_2(CH_3OH)]_2[(H_2biim)(CH_3OH)_2][PMo_{12}O_{40}]_2{\cdot}2CH_3CN\}_n$ *(**1**) based-on 2,2'-biimidazole denoted as* H_2biim*) molecules and phosphomolybdic acid. The structure of as-synthesized composites was confirmed by infrared spectrometry and X-ray diffraction. Moreover, the proton conductivity of the synthesized composite was measured by electrochemical impedance spectroscopy in a temperature range of 25 centigrade ~ 100 centigrade and a relative humidity range of 35% ~ 98%. Results indicate that the structure characteristics of complex **1** are retained in two as-synthesized composites. Besides, 1–GO2 exhibits good proton conductivities of 1.26 ~ 2.2 × 10*$^{-3}$ *S cm*$^{-1}$ *in the temperature range of 25 centigrade ~ 100 centigrade under a relative humidity of 98%; and they exhibit good proton conductivity of 0.64 ~ 2.2 × 10*$^{-3}$ *S cm*$^{-1}$ *at 100 centigrade in the relative humidity range of 35% ~ 98%. Moreover, 1–GO2 shows better proton conductivities than complex **1** at the same conditions.*

Keywords: polyoxometalates; graphene oxide; organic-inorganic composites; 2,2'-biimidazole; conducting materials; preparation; proton conductivity

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INTRODUCTION

Graphene oxide (GO) is formed by treating graphite with very strong oxidizing agents, and it has a layered structure and a non-stoichiometric chemical composition. Recently, GO has been used to build various nanocomposites which exhibit enhanced electronic and adsorption properties[1]. The graphene layers of GO are stacked together with an interlayer distance varying from 6 Å to 12 Å depending on the level of hydration[2]. Oxidation of graphite causes the introduction of epoxy and hydroxyl groups into the graphene layers, as well as the introduction of carboxylic groups mainly located on the edges of the layers.

The layered structure of GO as well as an increasing interest for nanocomposite materials has driven several researchers to study the formation of nanocomposites of GO with different compounds, especially in the fields of catalysis and adsorption process[3]. So far, nevertheless, no reports are available about designing excellent proton conductor composed of GO and appropriate organic/inorganic complex. Therefore, in this research we prepare the composites (denoted as 1–GO2) from graphene oxide and the organic-inorganic complex based-on 2,2'-biimidazole (denoted as H_2biim) molecules and phosphomolybdic acid, $\{H_6[(H_2O)_{1.5}(H_2biim)_2(CH_3OH)]_2[(H_2biim)(CH_3OH)_2][PMo_{12}O_{40}]_2{\cdot}2CH_3CN\}_n$ (**1**). This paper reports the syntheses and structure characterization of one synthesized composite as well as the evaluation of their proton conductivity as a function of temperature and relative humidity (RH).

EXPERIMENTAL SECTION

1.1 Materials and instruments

All organic solvents and materials used for synthesis are of reagent grade and used without further purification.

$\{H_6[(H_2O)_{1.5}(H_2biim)_2(CH_3OH)]_2[(H_2biim)(CH_3OH)_2][PMo_{12}O_{40}]_2\cdot 2CH_3CN\}_n$, complex **1**, was synthesized according to a literature method[4]. Graphite oxide was synthesized by oxidation of graphite with Hummer's method[5]. X-ray powder diffraction (XRD) was performed with a Bruker D8 Advance Instrument (Cu-$K\alpha$ radiation). Infrared (IR) spectra were recorded with a VECTOR 22 Bruker spectrophotometer (KBr pellets were used) in the 400 ~ 4000 cm^{-1} region at room temperature. Thermogravimetric (TG) analyses were performed with a Perkin-Elmer thermal analyzer under nitrogen at a heating rate of 10 centigrade·min^{-1}. For electrical conductivity measurements, as-synthesized powder samples were compressed into discs with dimensions of 1.0 ~ 1.2 mm in thickness and 12.0 mm in diameter under a pressure of 12~14 MPa. Alternating current electrochemical impedance spectra (EIS) were measured with a Chi660d (Shanghai Chenhua) electrochemical impedance analyzer equipped with copper electrodes (the purity of Cu is more than 99.8%)[6, 7] over the frequency range from 10^5 Hz to 10 Hz. The conductivity was calculated as $\sigma = (1/R) \times (h/S)$, where R is the resistance, h is the thickness, and S is the area of the tablet (compacted pellets of synthesized powder samples were used for EIS measurements).

1.2 Synthesis of 1–GO2(90 wt.% complex 1 + 10% wt.% GO)

Complex 1 (2.04 g) and GO (227 mg) were dissolved in 40 mL of methanol/acetonitrile/water (volume ratio 1:1:2). Resultant solution was stirred at room temperature for 12 h to afford gray sediment. As-formed gray sediment was immediately washed with water and collected and dried in air to provide 1-GO2 composite as gray powder. IR (KBr) v (cm^{-1}): 803 v(Mo–O_c), 883 v(Mo–O_b), 989 v(Mo–O_t), 1078 v(P–O_a) (four characteristic vibrations of heteropolyanions with Keggin structure; O_t refers to terminal oxygen atoms connecting one Mo atom, O_b refers to atoms located in a shared corner between two Mo_3O_{13} units, and O_c refers to oxygen atoms connecting edge-sharing MoO_6 octahedra in a Mo_3O_{13} unit; 3143 v(N–H), 1718 v(C=N), 1614 v(C=C), and 1255 v(C–N) (vibrations of H_2biim molecules).

RESULTS AND DISCUSSION

2.1 XRD analysis

XRD was used to examine the phase and structure of 1–GO2. Since complex **1** represents the major component of 1–GO2, one would expect a predominance of structure features of complex **1** in terms of the XRD patterns of 1–GO2. Of course, such a predominance should only happen when the synthesis of complex **1** in the presence of GO does not prevent the formation of hydrogen-bonding network constructed by H_2biim molecules ($H_3PMo_{12}O_{40}$) and solvent molecules. As shown in Fig. 1, the XRD patterns of 1–GO2 are essentially similar to that of complex **1**, and in particular, the XRD peaks from complex **1** are preserved. This confirms the aforementioned supposition and suggests that the graphite oxide component does not disturb the crystallization of complex **1**.

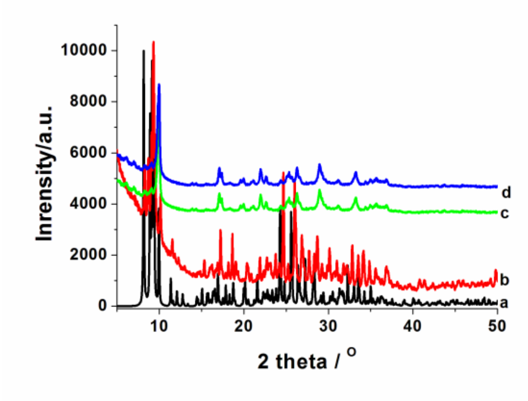

Fig.1 The simulated powder pattern of complex 1(a), the powder of complex 1 before the proton-conductive measurement(b), the powder of 1-GO2 before and after the proton-conductive measurement(c, d).

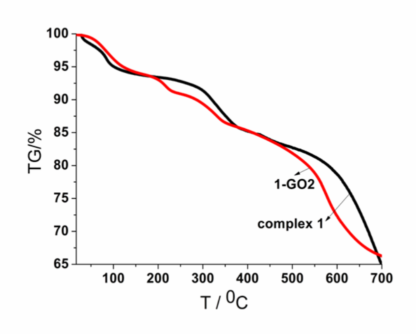

Fig. 2. TGA curves of complex 1 and 1–GO2 in N_2 atmosphere.

1.2 TG analysis

Fig. 2 shows TG analytic results for complex **1** and 1–GO2. Complex **1** exhibits a weight loss of 3.56% in the temperature rang of 20 ~ 300 centigrade, which is attributed to the loss of two acetonitrile molecules, four methanol molecules and three water molecules; and the decomposition of the anhydrous product begins at 300 centigrade[7]. Composites 1–GO2 shows weight losses of about 8.15% in the temperature range (20 ~ 300 centigrade), which is attributed to the evaporation of water molecules contained in 1–GO2. This means that 1–GO2 can potentially be better proton-conducting materials than complex **1**.

1.3 Proton conductivity

Fig. 3 shows some Nyquist plots for 1–GO2. At 25 centigrade under 98% RH conditions, 1–GO2 show proton conductivities of about 8.6 × 10^{-6} S·cm^{-1}; and their proton conductivities reach about 2.2 × 10^{-3} S·cm^{-1} at an elevated temperature of 100 centigrade. Particularly, these proton conductivity values of 1–GO2 is higher than those of complex **1** at the same condition (under 98% RH, complex **1** shows proton conductivities of 5.4 × 10^{-8} S·cm^{-1} at 25 centigrade and 3.1 × 10^{-4} S·cm^{-1} at 100 centigrade), which well conforms to the above mentioned supposition.

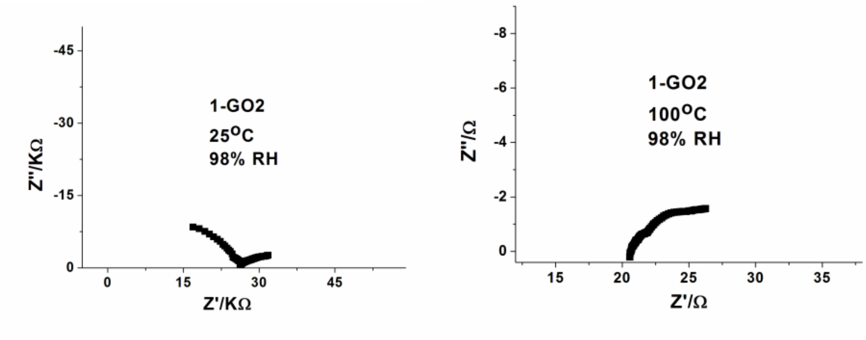

Fig. 3. Some Nyquist plots of 1-GO2

The proton conductivities of 1–GO2 were also measured at 25 centigrade and 100 centigrade in the RH range of 35% ~ 98% with a complex-plane impedance method. Fig. 4 shows the log σ (S·cm^{-1}) versus RH plots of two composites at 25 centigrade and 100 centigrade under 35% ~ 98% RH. The conductivities of 1–GO2 at 25 centigrade and 100 centigrade both increase with rising RH.

Notably, 1–GO2 shows better proton conductivities not only than complex **1** but also than bulk graphite oxide at the same conditions. This means that the high proton conductivities of 1–GO2 is not only due to graphite oxide containing a large number of epoxy, hydroxyl groups and carboxylic groups which may be desirable for excellent proton conductor, but also due to the formation of H-bonding network among the graphene layers, water molecules and complex **1**. Moreover, at the same temperature, 1–GO2 exhibits low proton conductivities at low RH, possibly due to the slow water equilibration between the composites and traces of water vapor. In other words, elevating RH makes water molecules more easily uptaken into the composites, thereby facilitating the proton transport and causing larger proton conductivities.

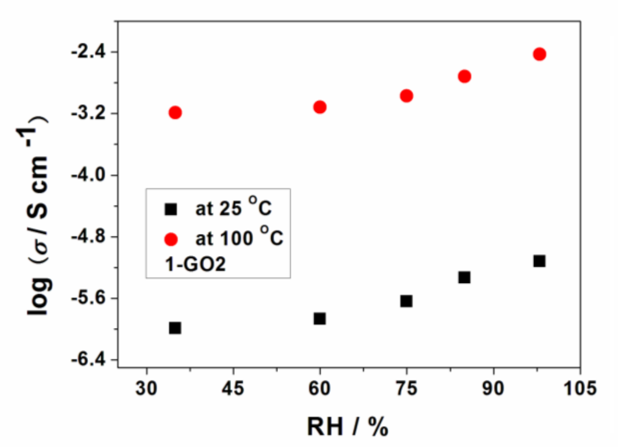

Fig. 4. Log σ (S·cm-1) versus RH plots of and 1–GO2 at 25 centigrade and 100 centigrade

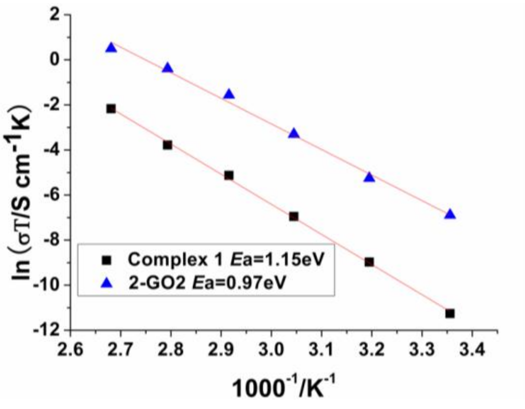

Fig. 5. Arrhenius plots of the proton conductivities of complex 1 and 1–GO2

Fig. 5 shows the Arrhenius plots of the proton conductivities of 1–GO2 in the temperature range of 25 ~ 100 centigrade under 98% RH conditions. As the temperature increases, the proton conductivities increase on a logarithmic scale even with almost saturated humidity. This well conforms to relevant powder XRD data which suggest that the powder samples after proton-conductive measurements have the same supramolecular frameworks as those of 1–GO2. Besides, the lnσT increases almost linearly with elevating temperature from 25 centigrade to 100 centigrade. Corresponding activation energy (E_a) of conductivity for 1–GO2 is estimated to be 0.83 eV and 0.74 eV, respectively, according to the following equation[6,7]:

$$\sigma T = \sigma_0 \exp(-E_a / k_B T) \quad (1)$$

where σ is the ionic conductivity, σ_0 is the preexponential factor, k_B is the Boltzmann constant, and T is the temperature. The E_a values of both composites in the temperature range of 25 ~ 100 centigrade are lower than that of complex **1** (1.17 eV). This is probably due to the fact that protons originated from GO, Keggin-type heteropolyacids and 2,2'-biimidazole molecules need an endothermal process for dissociation yielding hydrated forms such as H^+, H_3O^+ or other proton species[6,7].

CONCLUSION

In summary, the composite was prepared from graphene oxide and the organic-inorganic complex based-on H_2biim molecules and phosphomolybdic acid. It has been found that the structural features of complex **1** is retained in the synthesized composite, which is because the graphite oxide component does not disturb the crystallization of complex **1**. Besides, the synthesized composite shows better proton conductivities than complex **1** at the same conditions, which is due to a large number of epoxy, hydroxyl groups and carboxylic groups of GO and the formation of H-bonding network among the graphene layers, water molecules and complex **1**. In one word, the present approach could provide a new route to increasing proton conductivity of organic-inorganic hybrid materials.

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