

# Organic–inorganic composites based on room temperature ionic liquid and 12-phosphotungstic acid salt with high assistant catalysis and proton conductivity

Zhiying Li<sup>a</sup>, Qian Zhang<sup>b</sup>, Hongtao Liu<sup>a</sup>, Ping He<sup>a</sup>,  
Xiudong Xu<sup>a</sup>, Jinghong Li<sup>a,b,\*</sup>

<sup>a</sup> State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry,  
Chinese Academy of Sciences, Changchun 130022, China

<sup>b</sup> Department of Chemistry, Tsinghua University, Beijing 100084, China

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## Abstract

Proton-conducting composite material was synthesized from 1-butyl-3-methyl-imidazolium chloride (BMIImCl) and 12-phosphotungstic acid (PWA). The structure, assistant catalytic effect and ionic conductivity of the composites for the as-synthesized, 200 and 400 °C annealed samples were studied, respectively. The as-synthesized salt was crystal and kept Keggin structure even being annealed at 400 °C, but the organic part was partly decomposed with increasing of the annealing temperature. The partly decomposed BMIIm/PWA salt formed by annealing at 400 °C associated with Pt catalyst had excellent assistant catalytic effect on methanol electro-oxidation and displayed a high proton conductivity of 2 mS cm<sup>-1</sup> at 30 °C under 96% relative humidity condition.

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## 1. Introduction

Polyoxometalates (POMs), although having a long history, continue to attract significant attention in the fields of catalyst [1], photo- and electrochromism [2], magnetic [3], fuel cells [4,5], and others [6]. The primary structure of polyoxometalate anions such as 12-phosphotungstic acid (PWA) has the Keggin structure, and the Keggin anions are interconnected with hydrogen-bonded water molecules. Actually, PWA molecule can contain up to a maximum 29 water molecules, whereas reducing the number of water molecules by equilibrated to lower water activities resulted in four different hydrate phases ( $n=29, 21, 13-14, 6$ ). This variety of interactions gives a possibility of forming different protonic species and hydrogen bonds of different strengths [1]. The consequence is high proton conductivity at room temperature thus hydrated PWA has been extensively stud-

ied as proton-conducting electrolytes for low-temperature fuel cells [7,8]. However, the application of PWA is limited by the extreme sensitivity of their conductivity to the relative humidity of the surrounding atmosphere, in addition to that the PWA is soluble in water and the risk of its continuous leakage during cell operation is high. To overcome the stability problems and to increase the lifetime of the cell, a novel synthetic route has been continuously investigated to enable fast ionic conduction in the hybrid materials through the molecular modification of organic ligand to inorganic structures for the fuel cells application. Attempts have been made to immobilize the PWA in silica gel [9], ammonium salt [10], to disperse them in an organically modified membrane [11] and organic/inorganic hybrid membranes [12–15].

The introduction of organic groups to POMs is an efficient way to allow the development of organic–inorganic hybrid materials, and thus to expand their properties [16]. By replacing a certain number of protons in heteropolyacids with cations, it is possible to obtain different salts of heteropolyacids [8,17,18]. According to literatures [19–22], the nature of the cations has

\* Corresponding author. Tel.: +86 10 62795290; fax: +86 10 62795290.  
E-mail address: [jhli@mail.tsinghua.edu.cn](mailto:jhli@mail.tsinghua.edu.cn) (J. Li).

a great influence on the dynamic equilibrium of the protonic species, the secondary structure of heteropoly compounds, and the characteristics of HPA salts. The cation characteristics affect indirectly the general properties of heteropoly compounds: their conductive, catalytic, biochemical and biomedical activity. Such salts are more stable systems, and less sensitive to humidity and temperature than the acids themselves. Also, they are good proton conductors [23].

From the point of view of a catalyst, HPAs and their salts are oxidation catalysts for various reactions and they are found in several industrial applications [24]. One of the applications is to be as assistant catalyst for the electrochemical oxidation of methanol associated with platinum catalyst [25,26]. Platinum film/nanoparticle is of particular interest, as it is known to be one of the most important catalysts for methanol oxidation in fuel cell. A critical problem with platinum-based catalysts is their prohibitive cost. To date, efforts have focused on the development of techniques to produce platinum catalysts with high utilization efficiency and low platinum loading [27].

This work is to find the composite of 12-phosphotungstic acid combined with room temperature ionic liquid (RTIL) as a stable proton conducting substrate. RTILs have attracted intensive interest in recent years as replacements for classical molecular solvents in fundamental research and applications, including electrochemistry [28–30], organic synthesis [31,32], and separations [33]. The advantages of RTILs include good chemical and thermal stability, almost negligible vapor pressure, good electrical conductivity, and a wide electrochemical window. Combining heteropolyacids with RTILs should provide some interesting materials. Antonio et al. [34] reported the preparation of the solid salts of  $[C_n\text{Mim}]_3[\alpha\text{-PW}_{12}\text{O}_{40}]$  (for  $n = 2$  and 5) and only the redox chemistry of the Keggin phosphotungstate anion in ionic liquids had been investigated. In this paper, we synthesized the compound from 12-phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ : PWA) and 1-butyl-3-methyl-imidazolium chloride  $[\text{C}_8\text{H}_{15}\text{N}_2\text{Cl}]$ : BMImCl] ionic liquid and characterized its structure, assistant catalysis on electrochemical oxidation of methanol, and proton conducting properties, etc.

## 2. Experimental

### 2.1. Chemicals

1-Butyl-3-methyl-imidazolium chloride (BMImCl) was synthesized and purified according to literature [35]. Phosphotungstic acid (PWA) and chloroplatinic acid were from Beijing Chemical Reagent Factory and used as received. All reagents were of reagent grade in this work.

### 2.2. Measurements

Cyclic voltammetry was carried out on a CHI630A electrochemical workstation (CH Instruments, USA). A three-electrode electrochemical configuration, i.e., a glassy carbon (GC) disk working electrode ( $\Phi$  3 mm), a Pt counter electrode, and an Ag/AgCl (sat. KCl) reference electrode, was adopted. The

electrocatalytic oxidation measurements were carried out in a solution of 0.5 mol L<sup>-1</sup> methanol and 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 100 mV s<sup>-1</sup>.

The elemental analyses were performed on an elemental analysis FLASH-EA-1112-Series.

Fourier transform infrared spectroscopy (FT-IR) was conducted at FTS135 infrared spectroscopy (Bio-Rad, USA). FT-IR transmission spectra of the compounds were obtained by forming thin transparent KBr pellet containing the interesting materials.

The X-ray diffraction (XRD) pattern was recorded with a Philips Analytical X-ray Diffractometer using a Cu K $\alpha$  radiation (1.5406 Å) of 40 kV and 30 mA.

The thermal gravimetry analysis (TGA) and differential thermal analysis (DTA) were carried out using a Perkin-Elmer thermal analysis TG/DTA system. Measurements were made heating from 20 to 700 °C, at a heating rate of 10 °C min<sup>-1</sup> under dry air.

The ionic conductivity of the composite electrolyte was evaluated using electrochemical impedance spectra in the temperature range of 18–50 °C. The impedance measurements were carried out on a Solartron 1255B Frequency Response Analyzer and a Solartron 1470 Battery Test Unit (Solartron Inc., UK) coupled with a computer. For the powder samples, the compact discs were prepared by pressing at 6 MPa. The disc samples with 1 cm in diameter were sandwiched between two stainless steel blocking electrodes and the measurements were conducted as a function of both relative humidity (RH) and temperature. The samples were allowed to equilibrate at the desired RH for 48 h inside a sealed chamber containing saturated solutions of salts: K<sub>2</sub>SO<sub>4</sub> for the 96–97%, NaCl for the 75–76%, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O for the 48–53%, MgCl<sub>2</sub>·6H<sub>2</sub>O for the 32–33%, LiCl·xH<sub>2</sub>O for the 11–12% [36]. The impedance spectra were recorded with the help of ZPlot/ZView software (Scribner Associates Inc.) under an ac perturbation signal of 10 mV over the frequency range of 1 MHz to 1 Hz.

### 2.3. Synthesis

The BMIm/PWA compound was synthesized by dissolving 12-phosphotungstic acid in deionized water and BMImCl was directly added into the PWA solution at room temperature, and the resulting precipitate was filtered. The white product was washed with deionized water and dried at room temperature. Samples were heat-treated under atmosphere (air) for 6 h at a temperature range of 200–400 °C, respectively, and kept in room temperature for further characterization.

Anal. Calcd for the as-synthesized C<sub>24</sub>H<sub>45</sub>O<sub>40</sub>N<sub>6</sub>PW<sub>12</sub>: C, 8.7%; H, 1.4%; N, 2.5%. Found: C, 9.4%; H, 1.4%; N, 2.5%. Anal. Calcd for the 200 °C annealed C<sub>24</sub>H<sub>45</sub>O<sub>40</sub>N<sub>6</sub>PW<sub>12</sub>: C, 8.7%; H, 1.4%; N, 2.5%. Found: C, 9.2%; H, 1.4%; N, 2.5%. Elemental analyses found results for the 400 °C annealed C<sub>24</sub>H<sub>45</sub>O<sub>40</sub>N<sub>6</sub>PW<sub>12</sub>: C, 0.6%; H, 0.4%; N, 0.5%. From these results, it was speculated that the formulas of BMIm/PWA compounds for as-synthesized, 200 and 400 °C annealing were  $[(\text{C}_8\text{H}_{15}\text{N}_2)_3 \cdot (\text{PW}_{12}\text{O}_{40})]$ ,  $[(\text{C}_8\text{H}_{15}\text{N}_2)_3 \cdot (\text{PW}_{12}\text{O}_{40})]$  and  $[\text{N}(\text{CH}_3)_x\text{H}_{4-x}]_3 \cdot (\text{PW}_{12}\text{O}_{40})$  structures, respectively.

The composite Pt/salt catalyst was prepared by the reduction of chloroplatinic acid with sodium borohydride in the presence of BMIm/PWA compound. Definitely, the BMIm/PWA compound was added into a solution of chloroplatinic acid and stirred for 15 min before the addition of nine-fold excess sodium borohydride reductant. The resultant solution quickly turned dark, and it was further stirred for several hours. The crude product was separated and dried at 120 °C for 1 h. Glass carbon electrode (GC,  $\Phi$  3 mm), polished to a 0.05  $\mu\text{m}$  mirror finish (alumina, Buehler) before each experiment, and served as substrate for the Pt/BMIm/PWA catalyst. Aqueous suspensions of 2 mg mL<sup>-1</sup> catalyst were produced by ultrasonically dispersing and 20  $\mu\text{L}$  suspension was pipetted onto the glass carbon electrode. After evaporation of the water droplet, 20  $\mu\text{L}$  of a Nafion solution (5 wt.%, Aldrich) was put on the modified electrode surface [37].

### 3. Results and discussion

Fig. 1 shows the infrared absorption spectra of the samples for (a) as-synthesized BMIm/PWA, (b–d) the same annealed at 200, 350 and 400 °C, respectively, (e) pure PWA and (f) pure BMImCl. Keggin-type HPAs are known to clearly show four typical peaks, referred as fingerprint, in the range of 1100–700 cm<sup>-1</sup> of their FT-IR spectra [8,12,38,39]. Herein, the absorption peaks of PWA Keggin clusters of the as-synthesized BMIm/PWA and the same annealed at 200–400 °C agreed well with those of pure PWA. This meant that the PWA Keggin structure was retained in these samples. The minor peak shifts of 2–6 cm<sup>-1</sup> comparing with the spectra of pure PWA indicated chemical interaction between the PWA anion and the BMIm cation. Correspondingly, the peaks of the heterocyclic structure of the as-synthesized and the sample annealed at 200 °C had a shift of 3–7 cm<sup>-1</sup> comparing with the spectra of pure BMImCl (curve f) [40,41].

On the contrary, the imidazolium heterocycle was destroyed with the increase of annealing temperature and disappeared at

the annealing temperature of 350 and 400 °C (curves c and d). Moreover, the composites annealed at 350 and 400 °C showed new bending mode 1410 cm<sup>-1</sup> of [N–H (NR<sub>x</sub>H<sub>4-x</sub><sup>+</sup>)] [42] and the peak of H<sub>2</sub>O (1627 cm<sup>-1</sup>) appeared again after 350 and 400 °C annealing. Although it was difficult to get specific information of C–H vibration in the samples annealed at 350 and 400 °C due to the low sensitivity (in the case of few contents) of IR, it showed carbon ingredient by CHN analysis. The composites annealed at 350 and 400 °C did not show the peaks of the imidazolium heterocycle, and the appearance of 1410 cm<sup>-1</sup> suggests that [N(CH<sub>3</sub>)<sub>x</sub>H<sub>4-x</sub>]<sup>+</sup> ions were present in the materials. Unfortunately, the baseline of the spectra drifted due to the carbonization of the samples annealed at 350 and 400 °C, and it was hard to distinguish the stretch bands of the adsorbed water.

Fig. 2 shows the TGA and DTA results of the as-synthesized BMIm/PWA (a), the samples annealed at 200–400 °C respectively (b–c), and pure PWA (d). In curve a, the weight loss of the as-synthesized BMIm/PWA sample around 180 °C corresponding to the endothermic peak in DTA was due to the loss of the structural water; two high weight losses corresponding to the exothermic peaks in DTA at 400–650 °C can be due to the decomposition of the organic part and/or the reaction with air and the destroyed of the Keggin structure. Different to the pure PWA (curve d), the physical adsorbed water in the as-synthesized was little or nothing. The weight losses of the 200 °C annealed composite were similar to the as-synthesized. In the case of the 400 °C annealed composite, there were two clear weight losses, around 110 and 550 °C, corresponding to the loss of the adsorbed water and the decomposition of the Keggin structure, respectively. Weight loss at 200–500 °C was due to the decomposition of the remaining organic part and was fewer since most of the organic part of the BMIm/PWA had been removed during the calcination process, and this result was consisted with the element analysis. It was noted that the adsorbed water in the 400 °C annealed composite was easier to lose respecting to the two

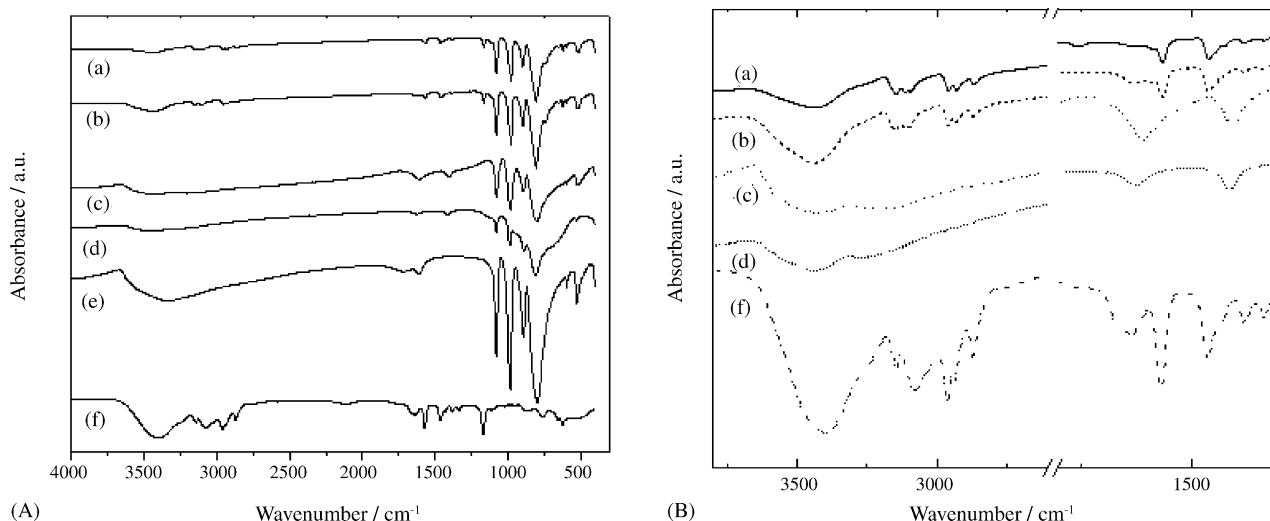


Fig. 1. (A) FT-IR spectra of (a) as-synthesized BMIm/PWA, (b) BMIm/PWA annealed at 200 °C, (c) BMIm/PWA annealed at 350 °C, (d) BMIm/PWA annealed at 400 °C, (e) pure PWA and (f) pure BMImCl. (B) The enlarge part of (A) in the range of 1300–3800 cm<sup>-1</sup>.

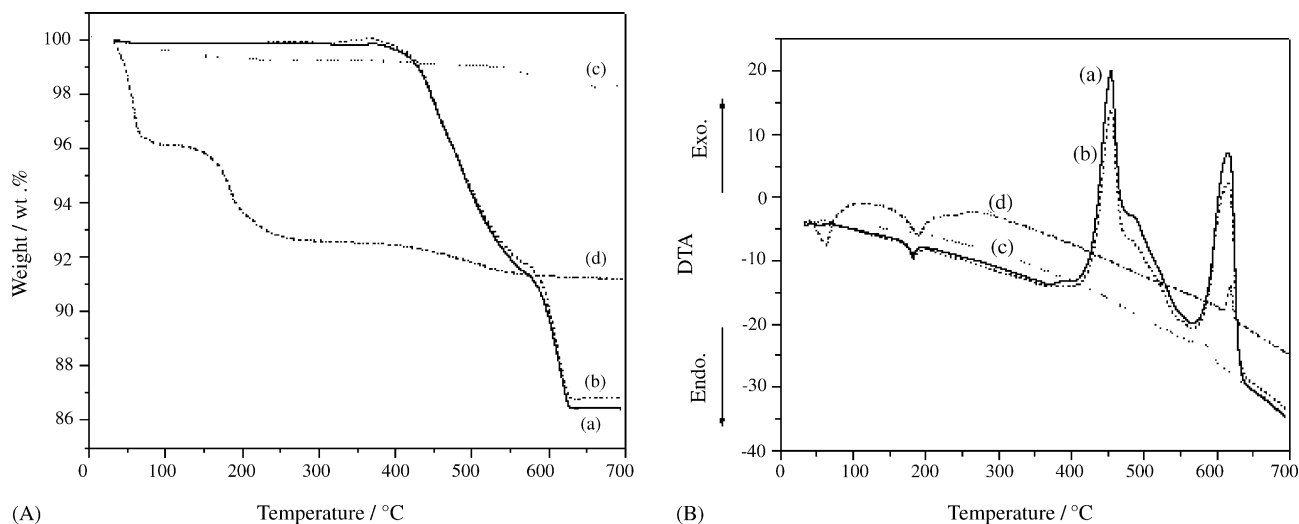


Fig. 2. (A) TGA and (B) DTA curves of (a) as-synthesized BMIm/PWA, (b) BMIm/PWA annealed at 200 °C, (c) BMIm/PWA annealed at 400 °C and (d) pure PWA.

former samples, indicating that it was more sensitive to humidity, as discussed below.

Fig. 3 shows the XRD patterns of (a) as-synthesized BMIm/PWA sample, (b–c) 200–400 °C annealing treatment and (d) pure PWA sample annealed at 400 °C. The diffraction lines for both the as-synthesized  $[(C_8H_{15}N_2)_3 \cdot (PW_{12}O_{40})]$  and that annealed at 200 °C were sharp at low angles, and showed broad lumps at angles greater than 20° ( $2\theta$ ). These features showed indicative of long-range ordering of BMIm/PWA molecules. Its crystal structure present was not clear. With increasing the annealing temperature, the diffractions in low angles due to BMIm/PWA ordering structure disappeared and those in high angles appeared (Fig. 3(c)). The sample annealed at 400 °C showed diffraction patterns similar to that of pure PWA annealed at 400 °C (Fig. 3(d)). The lower hydrates of the 12-heteropoly compounds generally have cubic ( $Pn3m$ ) crystal structures and the PWA composite was considered to remain cubic, irrespective

of the amount of water in the structure [43]. Therefore, it was suggested that the sample annealed at 400 °C had the structure of  $[[N(CH_3)_xH_{4-x}]_3 \cdot (PW_{12}O_{40})]$ .

The BMIm/PWA composites were applied as assistant catalyst associated with platinum for the electrochemical oxidation of methanol. The electrocatalytic activities of Pt–BMIm/PWA system were characterized by cyclic voltammetry in an electrolyte of 0.5 M  $H_2SO_4$  and 0.5 M  $CH_3OH$  at  $100\text{ mV s}^{-1}$ , and the resulting voltammograms are shown in Fig. 4. The current from methanol oxidation becomes apparent as the potential rose above 0.35 V. In the forward scan, methanol oxidation produced a prominent anodic peak around 0.66 V. In the reverse scan, an anodic peak appeared at around 0.51 V. This anodic peak in the reverse scan could be attributed to the removal of the incompletely oxidized carbonaceous species formed in the forward

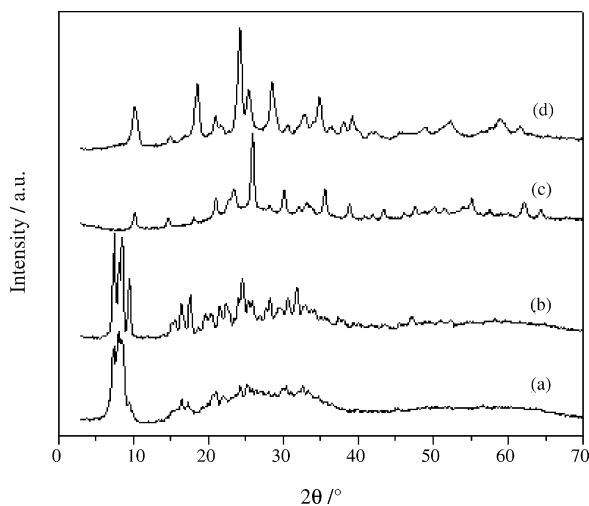


Fig. 3. XRD patterns of (a) as-synthesized BMIm/PWA, (b) BMIm/PWA annealed at 200 °C, (c) BMIm/PWA annealed at 400 °C and (d) pure PWA annealed at 400 °C.

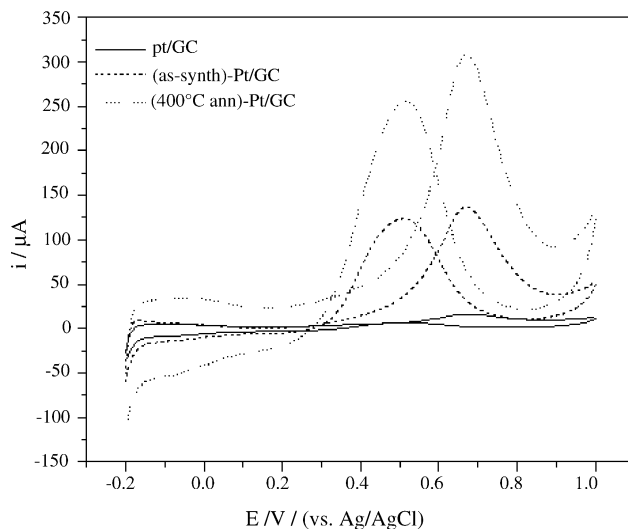


Fig. 4. Cyclic voltammograms of the different catalysts modified glass carbon electrode in  $0.5\text{ mol L}^{-1} H_2SO_4$  and  $0.5\text{ mol L}^{-1} CH_3OH$  solution with a scanning rate of  $100\text{ mV s}^{-1}$ . Solid line, Pt catalyst; dashed line, as-synthesized BMIm/PWA/Pt catalyst; dotted line, 400 °C-annealing BMIm/PWA/Pt catalyst.

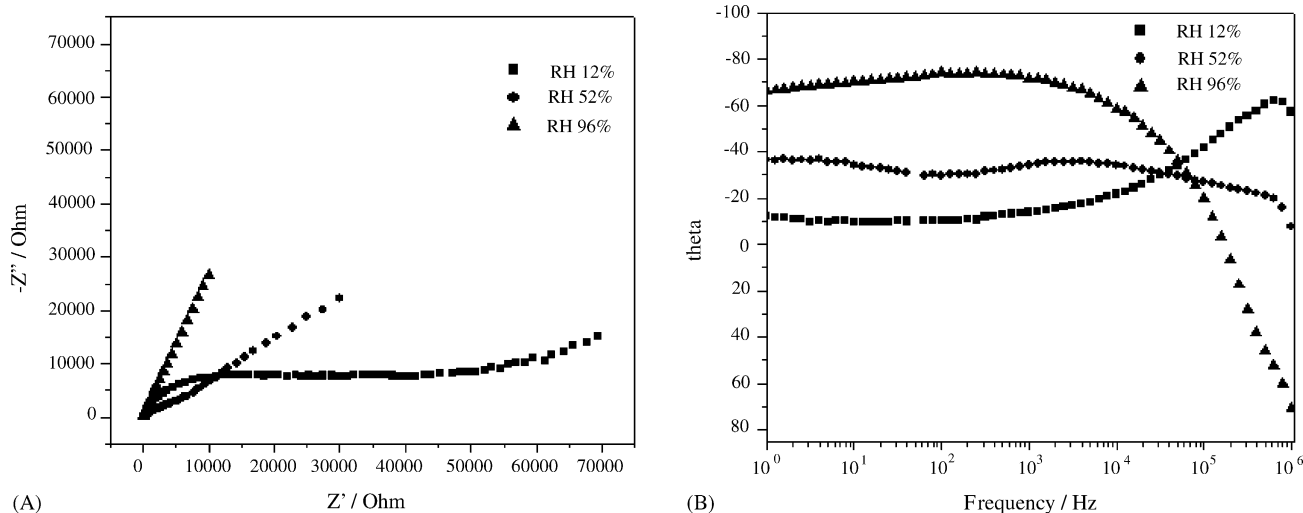


Fig. 5. Complex impedance spectra of the sample BMIIm/PWA annealed at 400 °C under different relative humidity at room temperature. (A) Nyquist plot; (B) Bode plot. Data were collected at open circuit with ac perturbation signal of 10 mV and the frequency range of 1 MHz–1 Hz.

scan [44]. The results of cyclic voltammetry proved that the additives had obvious promotion effect on the methanol oxidation reaction. Though the potentials had no obvious change, the peak current increased apparently with the addition of the BMIIm/PWA composites. The anodic current of the 400 °C-annealing BMIIm/PWA–Pt/GC electrode (dotted line) was two times higher than that of the as-prepared BMIIm/PWA–Pt/GC electrode (dashed line), which indicated that the catalyst prepared with the 400 °C-annealing salt had excellent catalytic activity on methanol electro-oxidation.

The typical complex impedance spectra (Nyquist and Bode plots) obtained at different relative humidity for the sample annealed at 400 °C are shown in Fig. 5. At high RH, the spectra showed only an inclined line caused by the diffusion process of protons. With the decrease of the RH, part of a semicircle through the real axis at the high frequency was present along with an inclined line at the low frequency. The semicircle at high frequency was explained with the capacitive behavior of the interface between electrodes and electrolyte, and the straight line was due to the migration of ions. The different shape of the impedance plots meant the different transport behavior of the ions at different relative humidity.

The variations of ionic conductivities with the relative humidity for the composite electrolytes annealing at 350 and 400 °C are shown in Fig. 6. The bulk electrolyte resistance  $R_b$  can be estimated from the high frequency end of the straight line, and the ionic conductivity ( $\sigma$ ) of the gel electrolyte is calculated by

$$\sigma = l / (AR_b) \quad (1)$$

where  $l$  is the thickness of the electrolyte and  $A$  is the area of the SS electrode. The proton conductivity of the annealing composite was found to be quite dependent on humidity. Ionic conductivities of both the electrolytes increased with increasing relative humidity. The value of conductivity at RH 96% was about two orders of magnitude higher than that at RH 12% at the same temperature. That is, relative humidity influenced the

amount of water adsorbed on the composites and influenced the protonic conductivities. The sample conductivity was proportional to the concentration of the mobile protons within the sample, and the variety of RH gave a possibility of forming different protonic species. The high conductivity at high RH might originate from that the adsorbed water provided the ionic conduction path with continuous channels, which greatly enhanced the rate of the proton movement.

Fig. 7 shows the proton conductivities of (a) as-synthesized and (b–e) 200–400 °C-annealing treatment BMIIm/PWA samples equilibrated under 96% relative humidity at each temperature, respectively. It was interesting to note that the samples being annealed at higher temperatures gave higher ionic conductivities after equilibrated under 96% relative humidity, except for the samples annealing at 400 and 350 °C almost had the equal value of conductivity. The conductivities of the as-synthesized sample and that annealed at 200 °C were lower than those of

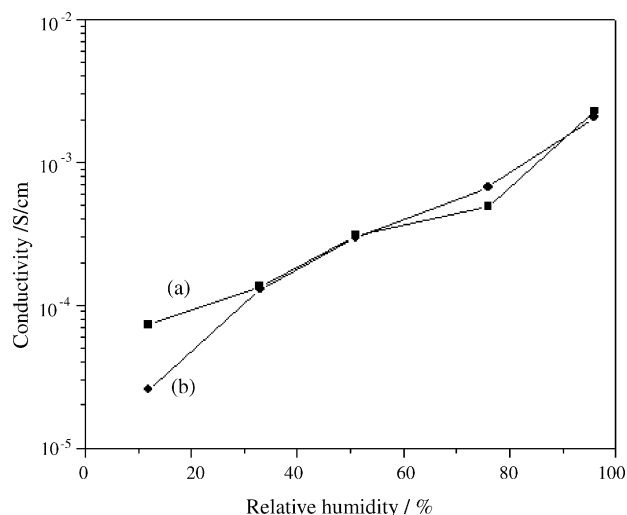


Fig. 6. Ionic conductivities at different relative humidity of the sample (a) BMIIm/PWA annealed at 350 °C and (b) BMIIm/PWA annealed at 400 °C.

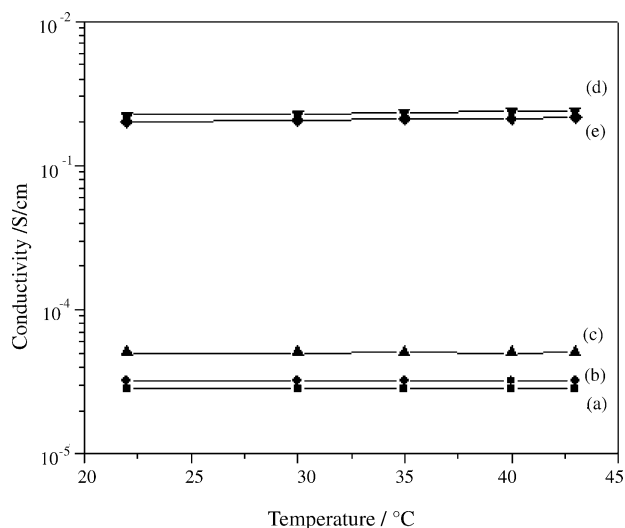


Fig. 7. Proton conductivities under 96% relative humidity of (a) as-synthesized BMIIm/PWA, (b) BMIIm/PWA annealed at 200 °C, (c) BMIIm/PWA annealed at 300 °C, (d) BMIIm/PWA annealed at 350 °C and (e) BMIIm/PWA annealed at 400 °C.

others. It was speculated that the imidazolium cation and the hydrophobicity of the alkyl chains in the as-synthesized sample and that annealed at 200 °C, whose formulas were estimated to be  $[(C_8H_{15}N_2)_3 \cdot (PW_{12}O_{40})]$ , reduced the adsorbed water in the composite materials. As for the salt annealed at 400 °C, which was estimated to be  $[[N(CH_3)_xH_{4-x}]_3 \cdot (PW_{12}O_{40})]$ , showed a high proton conductivity of  $2 \text{ mS cm}^{-1}$  at 30 °C. From the IR, TG and XRD results, the organic part of the BMIIm/PWA composite annealed above 350 °C was decomposed, and the increase of the hydrophilicity provided easier uptake of the adsorbed and crystal waters into the composite. In the hydrophilic sample under the high humidity condition, water-equilibrated composites had proton carriers such as  $H_3O^+$  and  $H_5O_2^+$  to be mobile, as in acidic solutions. This might contribute to the increasing of conductivities.

#### 4. Conclusions

New high proton-conducting composite material was synthesized from 12-phosphotungstic acid and 1-butyl-3-methyl-imidazolium chloride. The structures of BMIIm/PWA composites for as-synthesized, 200 and 400 °C annealed samples were estimated to be  $[(C_8H_{15}N_2)_3 \cdot (PW_{12}O_{40})]$ ,  $[(C_8H_{15}N_2)_3 \cdot (PW_{12}O_{40})]$  and  $[[N(CH_3)_xH_{4-x}]_3 \cdot (PW_{12}O_{40})]$ , respectively. The BMIIm/PWA composites kept Keggin structure and had excellent assistant catalytic activity on methanol electro-oxidation associated with Pt catalyst especially when the BMIIm/PWA composite had been treated at 400 °C. The BMIIm/PWA salt formed by annealing at 400 °C displayed a high proton conductivity of  $2 \text{ mS cm}^{-1}$  at 30 °C under 96% relative humidity conditions. From the IR, TG and XRD results, the high proton conductivity was due to the decomposition of the organic part, the crystallization of BMIIm/PWA salt and the increase of adsorbed and/or structural waters on PWA. The composite material with large proton conductivity and thermal and

chemical stability can offer the opportunities of developing functional materials in the fields of catalyst, electrochemical devices, fuel cells, etc.

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