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A novel SPEEK/$PW_{11}V$/rGO hybrid film for proton conduction

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ABSTRACT

A SPEEK/$PW_{11}V$/rGO hybrid film was prepared by a simple method through sulfonated polyether ether ketone (SPEEK), tungstovanadophosphoric acid ($H_4PW_{11}VO_{40}$, abbreviated as $PW_{11}V$) and reduced graphene oxide (rGO) in this work. The results indicate that the Keggin framework of $PW_{11}VO_{40}^{4-}$ anion still remain in the hybrid film and confirm the homogeneous dispersion of $PW_{11}V$ on the surface of graphene sheet, which results in a better stability of $PW_{11}V$. The electrochemical impedance spectroscopy shows that this film exhibits high proton conductivity of 2.22×10^{-2} S cm^{-1} at 17 °C and 6.43×10^{-2} S cm^{-1} at 65 °C (65% relative humidity). Its activation energy value for proton conduction is 18.9 kJ mol^{-1}, suggesting that the conduction mechanism for this film is a mix of Vehicle mechanism and Grotthuss mechanism. It is an alternative film material which may be applied in the field of fuel cells.

1. Introduction

Heteropoly acids (HPAs) and their polyoxometalates (POMs), a class of discrete and negative charge transition metal oxide clusters, have attracted considerable attention in the fields of catalysis, biology, medicine and materials science during the last decades [1–3]. In particular, HPAs have received much special interest as attractive conductive materials due to their high solid-state proton conductivity [4]. They exhibit extremely high proton conductivity owing to its strong acidity, which makes them one of the best proton carriers among the inorganic solid electrolytes [5].

Organic/inorganic hybrids have drawn great attention because of the potential of combining distinct properties of organic and inorganic components [6]. The construction of organic/inorganic hybrids is useful for obtaining multifunctional materials [7]. Sulfonated polyether ether ketone (SPEEK), an inexpensive polymer, has been widely used as film material matrix in the field of fuel cell due to its good mechanical strength and high chemical stability [8,9]. An approach to improve the proton conductivity of SPEEK-based film is to form composite with inorganic components. The addition of HPAs into SPEEK matrix could enhance the proton conductivity of SPEEK-based film. However, embedded HPAs will leach out due to its high solubility in water [10], which will result in the decrease of properties of HPAs-based hybrid materials. To address this problem, a pathway is to use graphene to support HPAs [11].

Graphene has inspired great enthusiasm due to its excellent physical and chemical properties [12]. For the large scale production of graphene-based materials, a widely adopted strategy is to use graphene oxide (GO) as a precursor and convert it to reduced GO (rGO) [13]. Owing to its exceptionally high specific surface area, rGO could immobilize HPAs even at very high loading by the electron transfer and electrostatic interaction between HPAs and the residual oxygen-containing groups of rGO [14]. Besides, the residual hydrophilic sites of rGO, such as —O—,—OH and —COOH, could further improve the proton conductivity of matrix by forming hydrogen-bonds [15–18]. So it is practicable to introduce HPAs/rGO hybrid material into SPEEK to increase the properties of SPEEK-based film.

Hence, in this paper, we chose tungstovanadophosphoric ($H_4PW_{11}VO_{40}$, abbreviated as $PW_{11}V$), which has more negative charge of the heteropolyanions and larger number of protons in their structure to afford the conductivity when compared with its parent acids ($H_3PW_{12}O_{40}$), and GO to synthesized $PW_{11}V$/rGO composite firstly, and added it to SPEEK to prepare the SPEEK/$PW_{11}V$/rGO hybrid film.

2. Experimental section

2.1. Characterization techniques and reagents

IR spectrum was recorded on a NICOLET NEXUS470 FT/IR spectrometer. XRD was carried out on a BRUKER D8 ADVANCE X-ray diffractometer in the range of $2\theta = 3$–40° at the rate of 0.02° s^{-1}. Morphology was observed by a Hitachi S–4800 (Japan) scanning electron microscope (SEM) and HF-3300 (Hitachi) transmission electron microscopy (TEM). Conductivity measurement was taken by a four-point-probe method using AC impedance spectroscopy over a frequency range of 100 mHz–100 kHz, 10 mV AC perturbation. A sheet of membrane (5 cm × 1.8 cm) was placed on the test cell.

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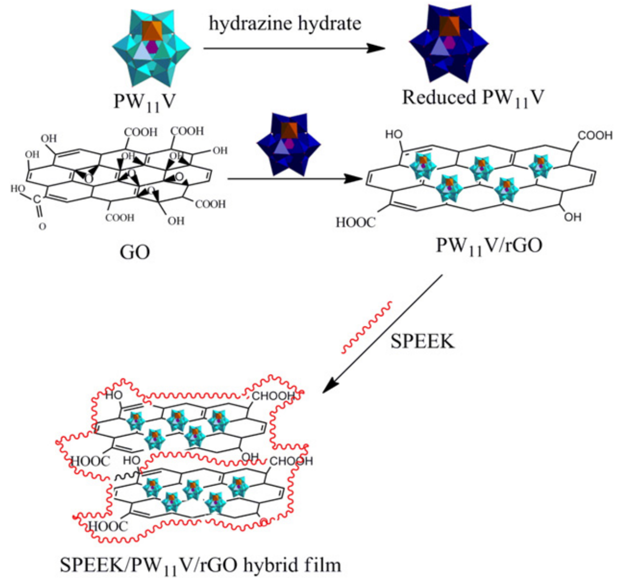
GO was sponsored by the group of Professor Chao Gao. They synthesize GO by a new scalable and effective method [19]. $PW_{11}V$ and SPEEK were synthesized according to our literature procedures [20,21]. The procedure from polyether ether ketone (PEEK) to SPEEK is shown in Fig.1. All reagents are analysis grade.

2.2. Preparation

$PW_{11}V$ powder was reduced by hydrazine hydrate to obtain the reduced $PW_{11}V$, which is often called 'heteropoly blue' (HB). GO (10 mg) and heteropoly blue (0.35 g) were dissolved in 30 mL water, and the solution was stirred for 2 h. The solution turned black because the consecutive electron has transferred from HB to GO and rGO formed. Afterwards, the solution was dried at 60 °C to get the $PW_{11}V$/rGO composite. SPEEK (0.14 g) was firstly dissolved in dimethylformamide (DMF) and the above obtained $PW_{11}V$/rGO was added into the solution of SPEEK. The resulting mixture was stirred for 4 h to form a suspension. After evaporation of most of the solvent, the mixture was cast onto a glass plate using a casting knife. Then the cast material was dried at room temperature for 48 h. The thickness of the SPEEK/$PW_{11}V$/rGO film is 134 μm, and the film is flexible, black and homogeneous. The weight ratio of the film material is about 28% (SPEEK), 70% ($PW_{11}W$) and 2% (graphene). The procedure is depicted as Scheme 1.



Scheme 1. Preparation procedure of SPEEK/$PW_{11}V$/rGO hybrid film.

3. Results and discussion

3.1. IR spectra

Infrared spectrum is fairly useful for studies on properties of materials. Fig. 2 shows the IR spectra of GO, $PW_{11}V$, $PW_{11}V$/rGO and SPEEK/$PW_{11}V$/rGO. The spectrum of GO indicates the presence of O—H (ν_{O-H} at 3425 cm^{-1}), C=O ($\nu_{C=O}$ at 1730 cm^{-1} from carboxyl group) and C—O (ν_{C-O} at 1060 cm^{-1} in alkoxy groups, at 1230 cm^{-1} in epoxy groups). While in $PW_{11}V$/rGO composite, the peak intensities of these oxygen-containing groups have decreased as the consequence of the deoxygenation process [22], indicating that GO, to some extent, has been reduced by heteropoly blue. The characteristic peaks of pure $PW_{11}V$ are 1080 cm^{-1}, $\nu_{as}(P—O_a)$; 984 cm^{-1}, $\nu_{as}(M—O_d)$; 883 cm^{-1}, $\nu_{as}(M—O_b—M)$ and 797 cm^{-1}, $\nu_{as}(M—O_c—M)$ (M=W,V). The spectrum of SPEEK/$PW_{11}V$/rGO also exhibits several similar peaks, which appear at 1074 cm^{-1}, 968 cm^{-1}, 880 cm^{-1} and 803 cm^{-1}. It confirms the Keggin framework of $PW_{11}V$ still remain in this hybrid film. But there are some frequency shifts when compared with pure $PW_{11}V$, which is believed to be due to the interaction between the terminal oxygen of the HPA and matrix [23]. What is worth explaining is that the M—O_d stretching is a proportional function of the anion-anion interaction, the introduction of other material into $PW_{11}V$ would undoubtedly weaken the anion-anion interactions. So it results in the $\nu_{as}(M—O_d)$ band has a red-shift of about 16 cm^{-1}, from 984 cm^{-1} to 968 cm^{-1}. Besides, the peaks at 1230 cm^{-1}, 1021 cm^{-1} and 702 cm^{-1} are assigned to the stretching vibration of sulfonic acid groups (—SO_3H) of SPEEK [8,24].

3.2. Morphology characterization

TEM image was used to characterize the morphology of the as-obtained $PW_{11}V$/rGO composite material. Fig.3a illustrated the wrinkled and flake-like shape, which is the feature structure of graphene nanosheets [25]. In Fig.3b, the presence of the $PW_{11}V$ clusters on the surface of graphene is clearly detected as small dots. The homogeneous dispersion of $PW_{11}V$ confirms that the strong interaction between graphene with HPAs, which will increase the stability of HPAs. Fig.3c and Fig.3d are the SEM images of SPEEK/$PW_{11}V$/rGO film. It shows the black SPEEK/$PW_{11}V$/rGO film has a rough surface, and graphene still show some wrinkles at high magnification [9].

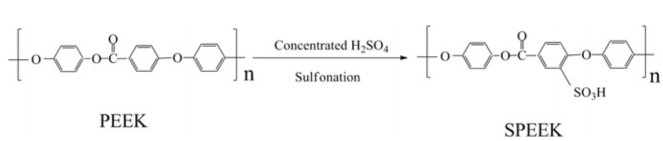


Fig. 1. Structures of PEEK and SPEEK.

3.3. X-ray powder diffraction

Fig. 4 presents the X-ray powder diffraction patterns of $PW_{11}V$ and SPEEK/$PW_{11}V$/rGO. Compared with pure $PW_{11}V$, only the most intense characteristic peak at the range of $2\theta = 7°–11°$ is still identified in the pattern of SPEEK/$PW_{11}V$/rGO composite. It is the evidence that the Keggin anion $PW_{11}VO_{40}^{4-}$ retains in this hybrid material [26]. This is consistent with the result of IR. The broad diffraction peaks at 15°–38° is observed for SPEEK/$PW_{11}V$/rGO, suggesting that the hybrid material is considered amorphous without long-range order [27].

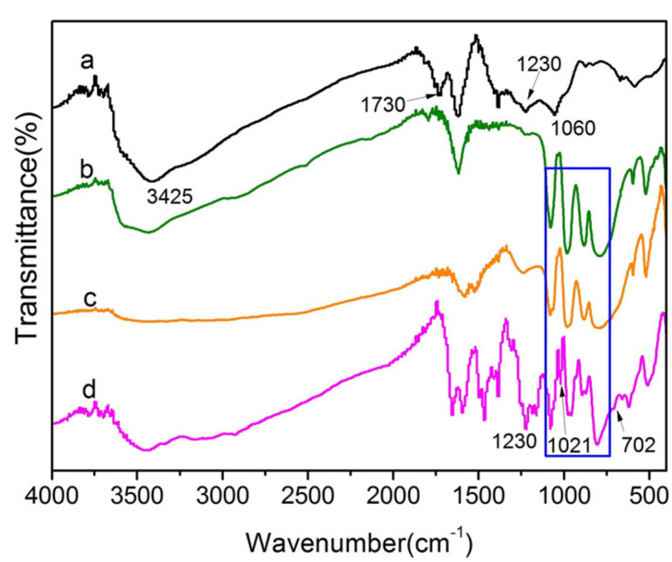


Fig. 2. FT-IR spectra of (a) GO, (b) $PW_{11}V$, (c) $PW_{11}V$/rGO and (d) SPEEK/$PW_{11}V$/rGO.