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Ion conductivity improved polyethylene oxide/lithium perchlorate electrolyte membranes modified by graphene oxide

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Polyethylene oxide (PEO)-based solid electrolyte membrane modified via graphene oxide (GO) is prepared. A homogeneous dispersion of GO is achieved in PEO matrix. GO promotes the movement of ethylene oxide (EO) segment at EO/GO interface where the expansion of the free volume void occurs. GO sheets influence the confined helix of EO/lithium-ion (Li^+). Composites of GO/Li^+/GO, GO/Li^+/EO/Li^+/GO, and GO/EO/GO are suggested by the X-ray diffraction patterns, structures of which relate to the mechanisms of Li^+ dissolving into GO sheets of different concentrations. At 294 K, unexpected 70-fold increase in conductivity of electrolyte membrane is achieved at 0.6 wt% loading of GO. The superior conducting property is attributed to (a) a fine distribution of GO providing interconnected channel at EO/GO interface for fast ion transfer and (b) layered GO-intercalated composites.

1. Introduction

By incorporating alkali salts into the polar polymer matrix, solid electrolyte membrane emerged as one potential substitute of the conventional liquid electrolyte for advantages such as easy fabrication, thermal and mechanical stabilities, low cost and eco-friendliness [1]. The process of charged ion transfer of polymer electrolyte membrane was correlated with segment relaxation [1–5]. At room temperature, the crystallite of the pristine membrane restricts the segment movement thus the conductivity fails to meet the requirement of commercial application [5]. One commonly used modification is the addition of liquid plasticizer, such as low molecular weight polyethylene glycol or aprotic organic solvent, into the matrix to inhibit the crystallization of polymer. However, such method leads to the deterioration of the mechanical stability of membrane synthesized [6]. Incorporation of the nano-size filler into the polymer base has drawn considerable attention for the improvement of the electrical performance without sacrificing its mechanical strength. Choices of filler were prevailingly spherical for fine dispersions, *i.e.* zinc oxide [7], alumina [1], titania [8]. Progress has been made in developing these conventional composite membranes. Compared to fillers mentioned above, graphene oxide (GO) is a highly oxygenated, hydrophilic layered material that could result in significant changes in properties of composites at a very low content [9]. Meanwhile, GO could swell in organic solvent with strong polarity [10,11], realizing the intercalation of macromolecule into lamellar graphene sheets to achieve homogenous distribution of GO in polymeric matrix. The GO-modified membrane could be utilized as solid polymer electrolyte membrane in rechargeable lithium batteries which are widely applied as power source in devices such as cellular phone, laptop, electric vehicle, *etc.* [12,13].

Positron annihilation lifetime spectroscopy (PALS) could determine the mean radius and density of the free volume of polymeric matrix, since the processes of the formation and annihilation of positronium, *i.e.* the bound state of e^+ and e^-, are strongly influenced by property of the free volume void [14]. For polymer electrolyte membrane, the ion conducting is primarily associated with segment movement [5,6], which could be analyzed through the feature of the free volume void [7,15]. Coupled with the electrical measurement, PALS could be applied to explore the relationship between the microstructure and the electrical property of the polymer electrolyte membrane. Till now, the utilization of PALS in the polymer electrolyte/GO system has rarely been reported.

In this work, the solid polyethylene oxide (PEO)/lithium perchlorate electrolytes doped with different loadings of GO were prepared. *Via* techniques including scanning electron microscope (SEM), transmission electron microscope (TEM), differential scanning calorimetry (DSC), Raman spectroscopy, X-ray diffraction (XRD) spectroscopy and PALS, the mechanism of ion conducting in GO-modified membrane is investigated. In addition, the layered GO-intercalated composites in polymer matrix are presented.

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2. Experimental

2.1. Materials and preparation of GO-modified electrolyte membrane

GO-incorporated electrolyte membrane was prepared the following way. Graphite oxide was synthesized in the modified Hummers method [16,17]. PEO (300,000 M_w, Aldrich) and $LiClO_4 \cdot 3H_2O$ (Aldrich) was dried in a vacuum oven for 48 h at 333 K and 400 K respectively to acquire dry PEO and anhydrous lithium perchlorate. The molar ratio of ethylene oxide (EO)/lithium-ion (Li^+) was fixed at 8 for good ionic conductivity and preferable mechanical strength [18,19]. Therefore, calculated amounts of lithium perchlorate and PEO were dissolved in acetonitrile individually using magnetic stirring apparatus. Graphite oxide powder was ultrasonic dispersed in dimethylacetamide (DMAC) [10,11] for 2 h to obtain the swelled GO. Solutions of GO/DMAC and $LiClO_4$/acetonitrile were first mixed together to ensure Li^+ dissolving into GO sheets. In order to obtain different weight ratios of GO/PEO (x wt%, $x=0$, 0.2, 0.4, 0.6, 0.8), pre-calculated volume ratios of solutions were applied. Drop wise addition of PEO/acetonitrile into the Li/GO solution was performed for homogeneous dispersion of GO. The resulted solution was kept stirring for 12 h, then casted on Teflon plates and dried in a vacuum oven at 333 K for 24 h to evaporate the residual solvent. Samples labelled as (x wt% GO)/PEO/$LiClO_4$ were maintained in a glove box flowed with argon gas. The average thickness of the synthesized electrolyte membrane is about 1 mm.

2.2. Characterization of the prepared GO-modified electrolyte membrane

TEM was performed using the JEOL2011 facility. Dry graphite oxide powder was ultrasonic dispersed in purified water. The acquired solution was dipped in using a copper grid which was dried under ambient condition for observation. The fracture morphology of samples was examined using SEM (Supra55, Zeiss). The glass transition temperatures (T_g) of samples were determined using DSC (DSC-7, Perkin-Elmer). The heating rate was 10 K min^{-1} from 210 K to 270 K. Prior to measurement, the apparatus was flowed with argon gas for calibration and samples were maintained at 340 K to erase their thermal history then cooled down to 210 K and remained stable for 10 min. Empty aluminum pans were used as references. Raman spectra were recorded by a confocal Raman spectroscopy (RM-1000, Renishaw) setup with an excitation wavelength (514.5 nm) of an argon ion laser. Spectra of electrolytes were kept to a similar scale by setting the integrated intensity of the δCH_2 band to a constant value. XRD was carried out using a Cu-Kα radiation at a scanning rate of 5 °min^{-1} (D8 Advance, Bruker). The basal distance (d_{002}) of GO was calculated using the Bragg's equation:

$$\lambda = 2d \sin \theta \tag{1}$$

The crystallite size can be calculated from the X-ray line broadening using the Scherrer's equation:

$$L_c = \frac{0.9\lambda}{\beta_{hkl} cos\theta_{hkl}} \tag{2}$$

where λ, θ, β, and L_c is the wavelength of the X-ray radiation (1.5406 Å), the measured diffraction angle, the observed diffraction peak breadth at half-maximum intensity in radians, and the average thickness of the crystallite perpendicular to the diffraction plane (hkl), respectively. The mean number (N) of GO sheets stacked along the c-axis is calculated in terms of the crystallite size and the basal spacing using the following equation:

$$N = L_c / d_{002} \tag{3}$$

PALS was performed on a conventional fast–fast coincidence system at room temperature (294 K). A ^{22}Na radiation source was sandwiched between two pieces of identical electrolytes investigated. The recorded spectroscopy contained 10^6 counts for the PATFIT [20] program to obtain three discrete components of positron annihilation lifetimes. The long-lived lifetime (τ_3, 1.3–2.6 ns) and the intensity (I_3) of the ortho-positronium (o-Ps) annihilation in polymer cavities are of the most interest investigating the relaxation of the polymeric matrix. The average radius of small cavities is estimated using the following equation [14]:

$$\tau_3 = \left[2\left(1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi} \sin \frac{2\pi R}{R+\Delta R} \right) \right]^{-1} \tag{4}$$

where R is the mean radius of free volume cavities and ΔR is 1.656 Å [21]. To estimate the mobility of the polymeric matrix, the fractional free volume (f_r) is approximately deemed as equation

$$f_r = (4/3)\pi R^3 I_3 \tag{5}$$

Conductivity (290–390 K) was measured in the following way. Membrane was placed between stainless counter electrodes. Electric current was supplied using Keithley 2400 sourcemeter while corresponding voltage was measured using Keithley 2182 voltmeter. The conductivity σ of the prepared electrolyte membrane was obtained using the following equation:

$$\sigma = \frac{l}{RS} \tag{6}$$

Here, R is the measured resistance of the prepared membrane, l is the thickness of the prepared membrane between counter electrodes, and S is the contact area of the prepared membrane and the electrodes. Prior to measurement, sample was maintained at the set temperature for 10 min. Each data is an average value of 5 recordings taken every 3 min.

3. Results and discussion

3.1. Micrographs of graphene oxide and prepared electrolyte membrane

The morphology of the prepared GO is exhibited in Fig. 1(a) (TEM). After treatment of ultrasonic dispersion in distilled water, the exfoliated GO sheet exhibits silk-like appearance, planar width of which is about 500 nm. Fig. 1(b)–(d) shows SEM images of fracture surfaces of (x wt% GO)/PEO/$LiClO_4$ electrolytes. Fig. 1 (b) and (c) shows fine dispersions of GO sheets while $x=0.2$ and 0.6, indicating that GO is highly compatible with hydrophilic PEO matrix. An overview of the electrolyte fracture suggests the interconnected arrangement of GO sheets while $x=0.6$ in Fig. 1(d).

3.2. Raman spectra of prepared electrolyte membrane

Recorded Raman spectra of prepared electrolyte membranes are given in Fig. 2. PEO standard band assignments are CH_2 twisting mode (1282 cm^{-1}) and CH_2 bending modes (1444 cm^{-1} and 1479 cm^{-1}) [22]. Peaks of GO are G band (1580 cm^{-1}) and D band (1350 cm^{-1}) [23]. Peaks of all PEO/$LiClO_4$ based electrolytes at 458 cm^{-1}, 624 cm^{-1}, and 931 cm^{-1} are assigned to the normal active modes of free anion ClO_4^- [24] It should be noticed that no clear variances are observed in intensities and shapes of these ClO_4^- peaks, indicating the quantity and existence form of ClO_4^- are not significantly affected by GO, neither are the number of