Remarkable heat-resistant halloysite nanotube/polyetherimide composite nanofiber membranes for high performance gel polymer electrolyte in lithium ion batteries

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ARTICLE INFO

ABSTRACT

The high performance gel polymer electrolytes (GPEs) based on remarkable heat-resistant composite nanofiber membrane composed of polyetherimide (PEI) and halloysite nanotubes (HNTs) were obtained through the activation of stacked membranes immersed into liquid electrolyte. The crystallization behavior, microstructure and thermal stability of nanofiber membranes were analyzed. The HNT/PEI composite nanofiber membranes showed the sufficient porosity and good affinity between the nanofibers and the electrolyte as well as the electrode, which led to a superb saturated electrolyte uptake and conservation rate. Thus, the GPEs involving the HNT/PEI composite nanofiber membranes displayed excellent electrochemical performances, such as high ionic conductivity, adequate lithium-ion transference number, good interfacial stability and cycle performance. In particular, the GPEs based on 1 wt% HNT/PEI nanofiber membranes demonstrated high ionic conductivity of $5.30 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$ and low interfacial resistance of 180 Ω. In addition, in contrast with the Li/GPE/LiCoO$_2$ cells containing the commercial Celgard 2500, the assembled cells with the 1 wt% HNT/PEI nanofiber membranes possessed outstanding initial discharge capacity, cycle performance and C-rate capability. Consequently, the GPEs involving HNT/PEI heat-resistant skeleton materials can satisfy the high-performance requirements of energy storage devices.

1. Introduction

With the rapid development of the electronics industry, lithium ion batteries (LIBs) have attracted considerable attentions in various applications of power source, including consumer electronic products, electric vehicles and energy storage equipment over the past few decades [1–5]. To enhance the performance and security of LIBs, the researchers have put forward higher requirements for electrolyte which is an important constituent part in LIBs. Based on higher ionic conductivity, good electrochemical stability, proper mechanical strength and thermal stability, as well as reduced electrolyte leakage, polymer electrolytes could be considered to be optimal choice for alternative liquid electrolyte [6]. Generally, polymer electrolytes are composed of solid polymer electrolytes (SPEs) and gel polymer electrolytes (GPEs) [7]. In comparison with SPEs, the GPEs based on skeleton materials with polyporous structure show the comprehensive performance advantage in ionic conductivity and contact/interfacial properties. Hence, the GPEs have been applied in the commercial polymer LIBs [8,9]. To date, polymer hosts used in GPE include poly(ethylene oxide) (PEO)

[10,11], poly-(acrylonitrile) (PAN) [12], poly(methyl methacrylate) (PMMA) [13], poly(vinylidene fluoride) (PVDF) [14], polyimide (PI) [15], and poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VDF-HFP)) [16,17], etc. However, for the LIBs in the application of power source, when the batteries were charged or discharged at high C-rate and recurrently used, a large amount of heat produced and released will bring about a significant rise of battery temperature. This ultimately will result in insufficient capacity, short circuit, overheating and even explosion [18–20]. Thus, the polymer skeletons must possess good thermal stability to reduce and avoid these risks caused by polymer meltdown at high temperature.

Polyetherimide (PEI) is a sort of engineering plastics with superior high temperature stability and outstanding electrical insulation property as well as native flame retardancy [21,22]. Moreover, the good affinity between the skeleton materials and the polar liquid electrolyte can be expected to obtain due to the existence of ether bonds and amide bonds in PEI molecular chains. It can be anticipated that selecting PEI as polymer skeleton can endow the GPEs with predominant thermostability for high performance LIBs. Recently, Shi et al. [23] prepared

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the porous PEI membrane with high thermal stability as separator of LIBs, while no ideal electrochemical properties were obtained because of the limited uptake ability of the solution casting membranes. In recent years, with the development of electrospinning technology, it has been suggested as an effective and promising method to prepare polyporous polymer skeleton materials for GPEs [24]. The polyporous structure of the polymer nanofiber membranes with porosity beyond 30% can provide a lot of transport channels for lithium ion and improve the electrode/electrolyte interface compatibility and stability [25]. Here, a polyporous PEI nanofiber membrane was prepared via electrospinning and immersed into the GPEs for LIBs through the activation in liquid electrolytes.

To further develop the electrochemical performance of the GPEs, the halloysite nanotubes (HNTs) as a novel kind of functional nanofillers were incorporated. This natural clay with abundant hydroxyl groups and hollow tubular structure was expected to improve the electrochemical properties of the GPEs [26]. Consequently, the GPEs based on HNT/PEI composite nanofiber membranes with good thermal stability were obtained, which showed relatively high ionic conductivity, low interfacial resistance as well as superior electrochemical performance, and can fulfill the necessary requirements for the application and development of high-performance batteries.

2. Experimental

2.1. Preparation of polyporous polymer nanofiber membranes

In this study, the electrospinning technology was applied to prepare the porous PEI polymer nanofiber membranes, which was conducted at room temperature with the relative humidity of 30%. A certain content of PEI (Ultem 1000, average molecular weight of 25,000 g mol^{-1}, General Electric Co., USA) was dissolved in *N*-methyl-pyrrolidone (NMP) with magnetic stirring for 24 h at ambient temperature, then the electrospun precursor solution of PEI (25 wt%) was obtained. When conducting electrospinning, the PEI solution was transferred into a plastic syringe and injected via the spinneret at a flow rate of 0.6 mL h^{-1}. The high voltage of the electrostatic field was 16 kV, and the distance between the needle and the received roller was 18 cm. The obtained nanofiber membranes were vacuum-dried for 24 h at 60 °C to remove remaining solvent. To prepare the HNT/PEI composite nanofiber membranes with different content of HNTs (0.5 wt%, 1 wt%, 2 wt%), the accurately weighed HNTs (Hebei Mineral Instrument Institute Co., China) was added into NMP with ultrasonic dispersion for 30 min, followed by adding PEI under properly stirring to form a stable spinning solution. Then the HNT/PEI composite nanofiber membranes were prepared through the same electrospinning process.

2.2. Preparation of GPEs

Firstly, the polyporous polymer nanofiber membranes were stacked together with an appropriate thickness. Then, the stacked nanofiber membranes were punched into single small rounds as the skeleton materials of GPEs, and the diameter of the round was 22 mm. Before put into a glove box with filled argon (moisture level < 10 ppm), the skeleton materials need to be dried in a vacuum oven for 12 h at 60 °C. Next, the nanofiber membranes were immersed in 1 M lithium hexafluorophosphate (LiPF$_6$)/ethylene carbonate (EC):dimethyl carbonate (DMC) (1:1, v/v) (Battery grade, MERCK) until the forming GPEs were saturated, and the excessive liquid electrolyte was removed with filter papers, which were for the characterization and measurement of electrochemical and relevant properties. The commercial Celgard 2500 separator were also applied in this study as a comparison.

2.3. Characterization

The chemical structure of HNTs and nanofiber membranes was

characterized using Fourier transform infrared spectroscopy (FTIR, Nicoiet 8700, USA). The crystal structure of nanofiber membranes was tested through X-ray diffraction (XRD, Rigaku D-Max/2550VB +, Japan), and differential scanning calorimetry (DSC, TA Q200, USA) analysis was also studied as assistance. The thermogravimetric analysis (TGA, TA Q50, USA) was operated at a heating rate of 10 °C min^{-1} from 25 °C to 750 °C in N$_2$ atmosphere. The surface morphology of polymer nanofiber membranes was observed by scanning electron microscope (SEM, Hitachi S4700, Japan). The diameter of the prepared nanofibers was surveyed through image visualization software ImageJ 1.34s (National Institutes of Health, USA). The microstructure of HNTs and HNT/PEI nanofibers were investigated using transmission electron microscope (TEM, Tecnai T20, USA). The porosity of the nanofiber membranes was calculated through the N-butanol uptake method [27]. The saturated electrolyte uptake of prepared nanofiber membranes was tested and obtained in accordance with the following equation:

$$\text{Uptake (\%)} = (W_1 - W_0)/W_0 \times 100 \tag{1}$$

where W_1 is the mass of membranes after immersing liquid electrolyte, W_0 is the mass of dry nanofiber membranes [28]. All electrochemical performances were examined at ambient temperature using Autolab PGSTAT 302N (Metrohm). The cells involving the GPEs were assembled with two stainless steel (SS) blocking electrodes to test the ionic conductivity via AC impedance spectroscopy over the frequency range of 0.1 Hz to 100 kHz [29]. The linear sweep voltammetry obtained using Li/GPE/SS cells was applied to evaluate the electrochemical window that the scan rate was 1 mV s^{-1} and the potential voltage ranged from 2 V to 6 V. The Li/GPE/Li cells were prepared to measure the lithium ion transference number through the chronoamperometry (CA) with a polarization voltage of 5 mV [30]. The impedance spectra were also obtained on above cells and the scanning frequency range was from 0.1 Hz to 200 kHz. The charge/discharge performance and C-rate capabilities of the Li/GPE/LiCoO$_2$ cells were examined on a LAND CT2001A battery tester that the potential range was 2.7–4.2 V and the current density was 0.1 C.

3. Results and discussion

3.1. Structure and morphology of the nanofiber membranes

Fig. 1 exhibits FT-IR spectra of the HNTs, PEI and HNT/PEI composite nanofiber membranes, respectively. The characteristic absorption peaks of PEI were observed at 1783, 1720 cm^{-1} (−C═O stretching), 1276, 1102 cm^{-1} (C−O−C stretching), and 1355 cm^{-1} (C−N stretching) [23]. These polar groups would facilitate the adsorption of liquid electrolytes and contribute to a better electrochemical performance. For the HNT samples, the absorption peaks around
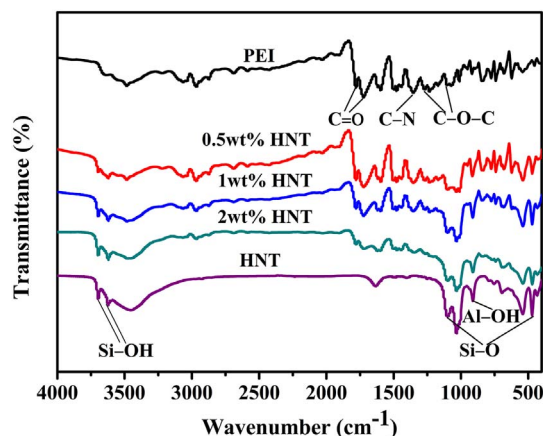

Fig. 1. FTIR spectra of HNT, pure PEI and HNT/PEI nanofiber membranes.