To immobilize polyethylene glycol-borate ester/lithium fluoride in graphene oxide/poly(vinyl alcohol) for synthesizing new polymer electrolyte membrane of lithium-ion batteries

Y. F. Huang^{1,2}, M. Q. Zhang², M. Z. Rong², W. H. Ruan^{1*}

¹Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education of China, GD HPPC Lab, School of Chemistry and Chemical Engineering, Sun Yat-sen University, 510275 Guangzhou, China

²Materials Science Institute, Sun Yat-sen University, 510275 Guangzhou, China

Received 15 June 2016; accepted in revised form 22 August 2016

Abstract. Polymer electrolyte membranes (PEMs) are potentially applicable in lithium-ion batteries with high safety, low cost and good performance. Here, to take advantages of ionic conductivity and selectivity of borate ester-functionalized small molecules as well as structural properties of polymer nanocomposite, a strategy of immobilizing as-synthesized polyethylene glycol-borate ester/lithium fluoride (B-PEG/LiF) in graphene oxide/poly(vinyl alcohol) (GO/PVA) to prepare a PEM is put forward. Chemical structure of the PEM is firstly characterized by ¹H-, ¹¹B- and ¹⁹F-nuclear magnetic resonance spectra, and Fourier transform infrared spectroscopy spectra, respectively, and then is further investigated under consideration of the interactions among PVA, B-PEG and LiF components. The immobilization of B-PEG/LiF in PVA-based structure is confirmed. As the interactions within electrolyte components can be further tuned by GO, ionic conductivity ($\sim 10^{-3} \text{ S} \cdot \text{cm}^{-1}$), lithium-ion transfer number (~ 0.49), and thermal ($\sim 273 \text{ }^{\circ}\text{C}$)/electrochemical ($>4 \text{ V}$) stabilities of the PEM can be obtained, and the feasibility of PEMs applied in a lithium-ion battery is also confirmed. It is believed that such PEM is a promising candidate as a new battery separator.

Keywords: nanocomposites, polymer electrolyte membrane, borate ester, graphene oxide, lithium-ion batteries

1. Introduction

Polymer electrolyte membranes (PEMs) are permeable membranes for the electrolyte ions flowing between a battery's anode and cathode [1–4]. They can serve both as ionic conductors of lithium-ions (Li^+) and separators with high safety, low cost and good performance when assembled into lithium-ion batteries. In contrast to traditional polyolefin separators which often own 30–50% open porosity [5], PEMs can be non-porous [6], so fabrication of PEMs can be simplified, and be cheaper, without using pore forming technologies that often require expensive processing machines and cumbersome processing route. As the ions which transport through the membranes

can have a strong interaction with the polymer matrix, PEMs can have the ion-selective feature, *e.g.* single-ion transportation of Li^+ , which is beneficial to improve the performance of lithium-ion batteries [7–9]. Polymer matrix for PEMs is often chosen among PEO, PMMA, PAN, PVC, PVA, PVDF or their derivatives, since the polar groups of these polymer chains can benefit for dissolution of electrolyte salts and endow the membranes with ionic conductivity [10, 11], which can be further enhanced by the incorporation of inorganic nanoparticles (*e.g.* nano- SiO_2 [12], nano- Al_2O_3 [13], nano- TiO_2 [14] or graphene oxide [15]) owing to rich polar groups on their surface [16]. However, one drawback of most

*Corresponding author, e-mail: cesrwh@mail.sysu.edu.cn
© BME-PT

PEMs without pore forming is the relatively low ionic conductivity in solid state, which frustrates their real applications for lithium-ion batteries [17–19]. Today, there are several ways to improve the conductivity of PEMs [4]. By incorporation of a certain amount of liquid electrolyte into PEMs, the gelled PEMs with a sufficient conductivity can be prepared [1]. To lower the molecular weight of the polymer chains incorporated into PEMs or using viscous polymer electrolyte [20, 21], is another strategy. However, these ways would sacrifice some properties of PEMs, *e.g.* ionic selectivity or mechanical properties due to absorption of much liquid electrolyte or poor shape retain ability.

It has been reported that borate ester-functionalized polymer electrolyte can be a candidate for preparing PEMs with single-ion transporting property [22, 23]. This type of electrolyte is also regarded as a kind of macromolecular salt based on the embedded borate structure. It may be feasible to immobilize borate ester-functionalized small molecules in a polymer component through the interactions (*e.g.* hydrogen/chemical bonding) between the borate center and the polymer chain to prepare a new PEM. In this case, the PEM can possibly maintain a high ionic conductivity and selectivity from borate ester-functionalized component, while good film forming ability from the polymer component. However, relevant issues on this strategy to obtain a PEM are still less involved. To confirm above idea, a new PEM was prepared by incorporating polyethylene glycol-borate ester/lithium fluoride (B-PEG/LiF) into graphene oxide/poly(vinyl alcohol) (GO/PVA). Firstly, the small molecules of B-PEG/LiF as a type of liquid polymer electrolyte were synthesized. The combination of polymer borate ester with LiF has some advantage for preparing ion-selective electrolyte due to the strong affinity of fluorine ion (F⁻) into boronic structure [24, 25]. In order to immobilize B-PEG anions, the B-PEG/LiF was further incorporated into PVA or GO/PVA [26, 27]. Owing to the excellent ionic conductivity and mechanical properties of GO/PVA [28], such composite structure is proposed to be a suitable ion-conductive framework for anchoring B-PEG/LiF molecules through the interaction between borate center and oxygen atoms in the polymer or GO. As a result, relevant structure properties, ionic transportation properties, electrochemical and thermal

properties of the PEM were characterized and analysed.

2. Experimental section

2.1. Synthesis of polyethylene glycol-borate ester/lithium fluoride/poly(vinyl alcohol) (B-PEG/LiF/PVA) incorporated without or with graphene oxide (GO)

Solution A

Polyethylene glycol (PEG400, AR, Aladdin agent, Shanghai, China), boric acid (AR, Aladdin agent, Shanghai, China), benzene (AR, Aladdin agent, Shanghai, China) and lithium fluoride (LiF, AR, Aladdin agent, Shanghai, China) were mixed together and stirred at 90 °C to achieve a homogeneous solution. The boric acid was used as chemical cross-linker for hydroxyl groups of PEG400. The mole proportion of PEG400 and boric acid was set to 3:1, 2:1 or 1:0. The mole proportion of PEG400 and LiF was set to 1:2, 1:1 or 3:1 while that of PEG400 and boric acid maintained at 3:1. The benzene was used as azeotrope for the synthesis of borate ester [29]. The reaction of the mixture was kept for 45 min. Then the temperature was raised to 120 °C and maintained for 45 min. The resulting solution of B_{1/3}-PEG/LiF was marked as solution A.

Solution B

Graphite oxide was prepared from natural graphite flakes (100 mesh, XF026, Nanjing XF Nanomaterials Technology Co., LTD, China) by Hummer method [30]. The GO solution (~1 mg/mL) was prepared by dispersing a certain amount of graphite oxide in dimethyl sulfoxide (DMSO, AR, Aladdin agent, Shanghai, China) by ultrasonic dispersion. After that, the homogenous GO solution was blended into some polyvinyl alcohol (PVA, alcoholysis degree >99%, AR, Aladdin agent, Shanghai, China) solution (10 wt%, solvent: DMSO), and stirred for 30 min. The resulting solution was marked as solution B.

Preparation of polymer electrolyte membranes (PEMs)

A certain mass proportion of solution A, and solution B with or without GO, were mixed and vigorously stirred. The mass ratio of PEG400 and PVA was set to 1:1. After then, a gel product of B_{1/3}-PEG/LiF

blended with PVA or GO/PVA could be obtained. Then the product was hot-pressed between two stainless steel plates at 160 °C. The gel film was further dried to remove residual solvent in a vacuum oven at 70 °C and kept balanced for 24 h. So the PEM was prepared. Before using PEM, the dried samples should be stored at least for 1 week under the circumstance of the glovebox (<0.1 ppm H₂O, <0.1 ppm O₂). The thickness of PEMs for the following characterizations is <100 µm, which further facilitates the exchange of possible absorbed solvent in the PEMs with the dried inert gas in the glovebox.

2.2. Structural characterizations

A nuclear magnetic resonance spectrometer (¹H, ¹¹B and ¹⁹F-NMR, Varian, INOVA500NB, USA; d-DMSO as solvent) was used to characterize the structure of samples. Infrared absorption spectroscopy of B_{1/3}-PEG/LiF/PVA was characterized with a Fourier transform infrared spectrometer (FTIR, Tensor 27, Bruker, USA) in attenuated total reflection (ATR) mode. Glass transition temperature of PEM was determined by a differential scanning calorimeter (DSC, TA, Q10, USA) with a heating/cooling rate of 10 °C·min⁻¹. A wide angle X-ray diffractometer (WXR, Rigaku/D-MAX 2200 VPC, Japan) was used to characterize the crystallization properties of samples. Thermal stability of the PEMs without and with GO was evaluated by a thermogravimetric analyzer (TGA, TA, Q50, USA) with a heating rate of 10 °C/min from 50 to 600 °C. A scanning electron microscope (SEM, FEI/OXFORD/HKL, Quanta 400F, USA) was used to characterize the morphologies of samples. Tensile tests were carried out on a Heating stage (Linkam, TST350, England) to measure the mechanical properties of PEMs at different temperature under a drawing speed of 10 mm/min.

2.3. Electrochemical characterizations

The PEMs with a thickness ranging from 100 to 200 µm were cut into small discs (ø18 mm) to investigate their electrochemical properties. The ionic conductivity (σ) of the B_{1/3}-PEG/LiF/PVA with or without GO was measured by a dielectric/impedance thermal analyzer (DETA, Triton, DS6000, England). The PEM was sandwiched between two stainless steel-plated parallel electrodes. The electrodes consisted a top electrode (ø10 mm) and a bottom elec-

trode (ø15 mm), and both were fixed by electrode clamping block in a chamber. The temperature could be controlled with an accuracy ± 0.1 °C under liquid nitrogen. All tests were carried out at an amplitude of 1.0 V under a dry inert atmosphere. The ionic conductivity (σ) was calculated by using the Equation (1) at high frequencies [31]:

$$\sigma = 2\pi f \epsilon_0 \epsilon'' \quad (1)$$

where f was scanning frequency, $f \sim 100$ kHz, ϵ_0 was permittivity of free space, $\epsilon_0 \sim 8.854 \cdot 10^{-12}$ F/m, ϵ'' was dielectric loss constant.

The PEM was saturated in a lithium-ion liquid electrolyte (1 mol/LiPF₆, PC/EC = 1/1 (v/v)), and cyclic voltammetry was used to investigate the electrochemical stability by using two stainless steel plates as block electrodes between 0 and 5 V at a scanning rate of 5 mV/s. To assemble a lithium-ion battery with a PEM, a LiFePO₄ electrode, a PEM saturated with liquid electrolyte and a graphite electrode were sandwiched and sealed in into a 2032 button battery. Transference number (t^+) of a PEM in the lithium-ion liquid electrolyte was measured in a simulated battery by the assembly of metal lithium/PEM/metal lithium together. The measurements of electrochemical stability, cell test and t^+ were done on the electrochemical workstation (IME6e, Zahner Zennium, Germany).

3. Results and discussion

3.1. Polymer electrolyte membrane (PEM) consisting of polyethylene glycol-borate ester/lithium fluoride (B-PEG/LiF) and poly(vinyl alcohol) (PVA)

3.1.1. Chemical structure of B-PEG/LiF/PVA

Figure 1 illustrated a synthetic route of B_{1/3}-PEG/LiF with PVA for a PEM. To confirm the chemical structure of B_{1/3}-PEG/LiF/PVA PEM, Nuclear magnetic resonance (NMR) and attenuated total reflection Fourier transform Infrared (ATR-FTIR) spectra of the resulting product were investigated, respectively. Figure 2a–2c showed the ¹H-, ¹¹B- and ¹⁹F-NMR spectra. In Figure 2a, the triplet (3.3, 3.4 and 3.6 ppm) belonged to ethylene oxide protons of –CH₂CH₂O– not linked to borate ester. The protons of –CH₂CH₂O– linked to the boronic structure appeared at higher chemical shifts of 4.2 and 4.5 ppm.

Figure 1. The synthetic route of polyethylene glycol-borate ester/lithium fluoride/poly (vinyl alcohol) (B_{1/3}-PEG/LiF/PVA)

Figure 2. The nuclear magnetic resonance (NMR) spectra of B_{1/3}-PEG/LiF/PVA: (a) ¹H-NMR; (b) ¹¹B-NMR (internal standard, BF₃(OCH₂CH₃)₂); (c) ¹⁹F-NMR (internal standard, CFCl₃); solvent: d-DMSO. (d) Attenuation infrared absorption spectra of the B₀-PEG/LiF/PVA (B₀), B_{1/3}-PEG/LiF/PVA (B_{1/3}) and B_{1/2}-PEG/LiF/PVA (B_{1/2}), respectively.

Methylene backbone protons of PVA were assigned to the multiplet (1~2 ppm). Hydroxyl protons of the composite structure appeared at ~3.8 ppm. Protons of DMSO solvent was assigned to 2.5 ppm. In Figure 2b–2c, the doublets of ¹¹B- and ¹⁹F-NMR spectra showed that in the structure of B_{1/3}-PEG/LiF/PVA

blends, two types of boron atoms (5.1 and 17.4 ppm) and two types of fluorine atoms (167 and 182 ppm) coexisted. As illustrated in Figure 1, B_{1/3}-PEG/LiF in a liquid state can exist in two forms of (I) and (II) within a dynamic equilibrium. The fluorine atoms in the electrolyte could exist as F- or in B-F bonds. Ac-

cordingly, three- or four-coordinated boron sites could appear.

The ATR-FTIR spectra (Figure 2d) were used to ensure the functional groups of the $B_{1/3}$ -PEG/LiF/PVA ($B_{1/3}$), compared with those without boric acid (B_0) or with more boric acid ($B_{1/2}$). The peak at 665 cm^{-1} was assigned to O–B–O vibration [26], and such peak was not found in B_0 . The intensity of the peak increased with the content of boric acid. Except this, all the FTIR curves were so similar. For $B_{1/3}$, 1140, 1092, 1092 cm^{-1} were attributed to the coupled stretching vibration modes of polyether (–OCH₂CH₂OCH₂CH₂O–) [22, 23]. The wide band around $\sim 3300\text{ cm}^{-1}$ corresponded to the absorption of hydroxyl groups of PEG and PVA structures. The strong bands (2935 , 2904 and 2864 cm^{-1}) were due to C–H stretching modes.

3.1.2. Interactions among poly(vinyl alcohol), polyethylene glycol-borate ester and lithium fluoride

To further characterize the structure of $B_{1/3}$ -PEG/LiF/PVA, the component interactions between PVA, $B_{1/3}$ -PEG and LiF were investigated by differential scanning calorimetry (DSC) [32] and X-ray diffraction (XRD). In the DSC curves (Figure 3a), 67 and 80°C in different curves were the glass transition temperatures (T_g s) of pure PVA, and the PVA incorporated with $B_{1/3}$ -PEG/LiF, respectively. The difference between the T_g s showed the strong interaction between PVA chains and borate ester structure, confirming immobilization of $B_{1/3}$ -PEG into PVA structure. On the other hand, according to the XRD patterns, a broad characteristic peak of PVA crystals

($2\theta \sim 20^\circ$) existed. Characteristic peaks of LiF crystals (~ 39 and $\sim 45^\circ$) corresponded to the diffraction directions of crystal surfaces of (1 1 1) and (2 0 0), respectively [33]. So the solubility of LiF crystals in the $B_{1/3}$ -PEG/PVA with various LiF moles could be concerned from the result of XRD. It was shown that when the mole ratio of boron atoms and LiF equalled to 1 ($x = 1/3$), LiF could be totally dissolved into the blends, for the relevant diffraction signals were not observed. The excess LiF could not be ionized due to poor solubility of PVA. As a result, the LiF mole was set to the same as the mole of boron atoms for later studies.

3.2. PEMs consisting of B-PEG/LiF and graphene oxide/poly(vinyl alcohol) (GO/PVA)

3.2.1. Interactions of GO in PVA with B-PEG/LiF

Figure 4a exhibited the ATR-FTIR spectrum of the $B_{1/3}$ -PEG/LiF/PVA with GO, with the characteristic peaks almost the same as the case without GO (Figure 2d). In order to characterize the interaction of GO with PEG component of $B_{1/3}$ -PEG/LiF/PVA, T_g of PEG within the electrolyte with different GO content was measured (Figure 4b). It was found that when GO content was near 0.1 wt%, the T_g was almost constant, but as GO content further increased, it dropped significantly, and then balanced. This plasticization effect of GO on the PEG chains probably was ascribed to the reaction between the polar groups of GO, and three-coordinated boron sites of borate ester. When $B_{1/3}$ -PEG/LiF interacted with PVA without GO, the movements of PEG chains would be

Figure 3. (a) The differential scanning calorimetry (DSC) patterns of PVA and $B_{1/3}$ -PEG/LiF/PVA. (b) The X-ray diffraction patterns of the $B_{1/3}$ -PEG/(LiF)_x/PVA with x mole of LiF (x : 1/3, 1, 2) and pure LiF.

Figure 4. (a) Attenuated total reflection infrared absorption spectrum of the B_{1/3}-PEG/(LiF)_x/PVA with GO. (b) A plot of glass transition temperature (T_g) of polyester segments ($-\text{O}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{O}-$) within B_{1/3}-PEG/LiF against GO content. (c) Plots of antisymmetric stretching vibration wavenumbers of polyester segments ($-\text{O}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{O}-$) ($\nu_{\text{O-C-C-O-}}$) and boric ester structure ($\nu_{\text{O-B-O-}}$) within B_{1/3}-PEG/LiF/PVA PEMs against GO content. (d) X-ray diffraction patterns of the B_{1/3}-PEG/LiF/PVA PEMs under various GO content.

Figure 5. Schematic drawing of the proposed interaction mode between GO sheet and B_{1/3}-PEG/LiF

frustrated by the spatial entanglements of PVA chains (Figure 1). While B_{1/3}-PEG/LiF interacted with GO, the PEG chains on the GO would be more flexible owing to more free space (Figure 5), so the wavenum-

bers of stretching vibration of segments of $-\text{O}-\text{C}-\text{C}-\text{O}-$ and $\text{O}-\text{B}-\text{O}$ reduced (Figure 4c). Under various GO content, the behaviors of the wavenumbers were consistent with the trend of the T_g .

In addition, the borate ester center of B_{1/3}-PEG/LiF could interact with the functional groups of GO, leading to the conversion from B-F bonds to B-O bonds (see Figure 5). So the GO addition could cause the decrease of solubility of LiF within the electrolyte film. As a result, the XRD characteristic peaks (~39 and ~45°) of LiF crystals emerged (Figure 4d), when GO was added into B_{1/3}-PEG/LiF/PVA composite. However, the GO without reacting with borate ester might benefit for the solubility of LiF, as the intensity of XRD characteristic peaks of LiF crystals was reduced with further increasing GO content.

3.2.2. Ionic conductivity of B-PEG/LiF/PVA incorporated with GO

Ionic conductivity (σ) of B_{1/3}-PEG/LiF/PVA PEM increased with frequency, but became constant near 100 kHz (see Figure 6b). Therefore, to compare the σ_s of different samples under various temperature (T) conveniently, all the measure condition of frequency was set at 100 kHz. At GO content <0.5 wt%, it was exhibited that σ was higher than that without GO at

the same T , and the relationship between σ and T satisfied Arrhenius empirical equation, as the logarithm conductivity plotted as a function of $1000/T$ showed a good linear relationship in the temperature range (Figure 4a). The Arrhenius equation was shown as Equation (2) [34]:

$$\sigma = \sigma_0 \exp^{-E_a/RT} \quad (2)$$

where σ_0 was the pre-exponential factor, T was the absolute temperature, E_a was the activation energy, R was the gas constant, $R \sim 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

However, at GO content >0.5 wt%, the σ was lower than that without GO. The σ increased with T at first, and then decreased. The transition position of T was around 70 °C, where corresponded to the T_g range of PVA component (Figure 3a) and also the gradual thermal reduction of GO [35]. So the fitting T range of Arrhenius equation for GO content >0.5 wt% was chosen below the T_g .

To further investigate ionic conduction behavior of B_{1/3}-PEG/LiF/PVA PEM with GO, the T_g (DSC) of

Figure 6. (a) A plot of the AC ionic conductivity of B_{1/3}-PEG/LiF/PVA against the frequency. (b) Temperature dependence of ionic conductivity (100 kHz) of B_{1/3}-PEG/LiF/PVA PEMs on GO content. (c) Plots of activation energy (E_a) of B_{1/3}-PEG/LiF/PVA PEMs, and glass transition temperature (T_g) of PVA segment within PEMs against GO content.

PVA chains with the E_a was plotted against the GO content (Figure 6c). T_g of PVA chains decreased at the low GO content (~ 0.1 wt%). The improved flexibility of PVA chains was because the interaction of PVA with borate ester structure was weakened by GO (Figure 5). So the ion transportation of electrolyte membrane was enhanced. However, with the increase of GO, the GO could further interact with PVA chains, so the T_g was increased instead as the movement of the polymer chains became slow. As a result, the ionic conductivity was reduced. The suggested mechanism to account for the mirror image of the trends of E_a and T_g was probably relevant with the solubility of LiF within the electrolyte film (Figure 4c), as E_a could decrease with increasing LiF solubility. The low GO addition could cause the decrease of solubility of LiF within the electrolyte film. So E_a increased firstly, and then dropped due to the interaction of GO and LiF. In all, the ionic conduction property of GO incorporated electrolyte depended on GO content. The results showed the best σ was

$7.83 \cdot 10^{-5}$ S/cm (30°C) and $1.48 \cdot 10^{-2}$ S/cm (100°C) at GO wt% = 0.125.

3.2.3. Thermal and electrochemical stabilities, mechanical properties and lithium-ion transfer number

Figure 7a, 7b showed the influence of GO on the thermal and electrochemical stabilities. From the thermogravimetric (TG) curves in Figure 7a, it was found that GO could significantly increase the initial decomposition temperature of PEM, with the increasing from 200°C without GO to 273°C with GO. In another aspect, GO could improve the electrochemical stability (Figure 7b). The electrochemical window of electrolyte without GO was ~ 3 V, but that with GO could increase to 5 V.

The electrochemical instability at ~ 3 V was ascribed to the decomposition of hydroxyl groups within the electrolyte. The reason why GO could benefit for improving the stability was found under investigation of morphological structure of surfaces of $\text{B}_{1/3}\text{-PEG/}$

Figure 7. (a) Thermal stability and (b) cyclic voltammograms (CVs) of $\text{B}_{1/3}\text{-PEG/LiF/PVA}$ PEMs with and without the incorporation of GO. (c) Cell performance of the LiFePO_4/C batteries assembled with PEM containing GO or with Cergard PP separator. (d) Discharge curve of the LiFePO_4/C battery assembled with PEM containing GO.

Figure 8. Scanning electronic microscopy (SEM) images of B_{1/3}-PEG/LiF/PVA morphological structure with different GO content: (a) 0 wt%; (b) 0.5 wt%; (c) 2 wt%. (d) Mechanical curves of the B_{1/3}-PEG/LiF/PVA PEM containing GO, including the tensile properties of PEMs at 30 and 100 °C, respectively.

LiF/PVA with and without GO. As shown in Figure 8a–8c, no microscale phase separation or structure of open holes in the electrolyte membranes were observed. This was very different from commercial PP micro-porous membrane. The surface of PVA/B-PEG/LiF without GO (Figure 6a) was homogenous but became shrink-wrapped with the increasing of GO content (Figure 8b–8c). The surface roughness of electrolyte membrane with GO was improved so that interfacial reaction of electrolyte decomposition would be suppressed due to less electrode-separator

contact. Therefore, the electrochemical stability of the interface could be improved. But actually, slight decomposition of PEM containing GO near 3 V still existed as the CV curve was further enlarged (see the inset of Figure 7b).

Moreover, lithium-ion transference number (t^+) and ionic conductivity (σ) of the moistened PEM (GO wt% = 0.125) and commercial PP separator by being immersed in a lithium-ion liquid electrolyte was measured. The values of t^+ and σ were calculated according to the Equations (3) and (4):

Figure 9. (a) The chronoamperometry curve of B_{1/3}-PEG/LiF/PVA assembled in a metal lithium/polymer electrolyte membrane/metal lithium cell; (b) the electrochemical impedance spectra of metal lithium/polymer electrolyte membrane/metal lithium cell at different potentials (0 and 50 mV). Frequency range: 100 mHz~500 kHz.

$$t^+ = \frac{I_S(\Delta V - I_0 R_i^0)}{I_0(\Delta V - I_S R_i^S)} \quad (3)$$

$$\sigma = \frac{L}{AR_0} \quad (4)$$

where I_0 was the initial current; ΔV was the applied potential; I_S was the steady-state current; R_i^0 and R_i^S were the electrode resistance before and after the potentiostatic polarization, respectively. The parameters of I_0 , I_S , R_i^0 and R_i^S were determined by chronoamperometry and impedance measurements (see Figure 9). L was the thickness of the separator; A was the electrode/separator contact area; R_0 was the bulk resistance of moistened separator. It was found that the t^+ of the PEM assembled with lithium-ion liquid electrolyte can be ~ 0.49 , while that of porous PP separator was only ~ 0.28 , almost like the pure liquid electrolyte used. The improved t^+ of the PEM resulted from some immobilized anions in the boronic structure of composite structure which endowed the ion-selective property. Additionally, the σ of the PEM immersed in liquid electrolyte had obtained a high ionic conductivity of $1.1 \cdot 10^{-3} \text{ S} \cdot \text{cm}^{-1}$.

As a result, a LiFePO_4/C cell system with PEM containing GO was further adopted to confirm the working of PEM, compared with that assembled with PP separator. During the working potential between 2.2–2 V, the intercalation/deintercalation redox peak near 3.6 V shown in Figure 7c when being charged were assigned to reduction of the anode when lithium-ions were normally inserted into the layered intercalation compound. A discharge capacity of 145 mAh/g was obtained according to the discharge curve of the lithium-ion battery with PEM containing GO.

In addition, the PEM owned good mechanical properties, with tensile strength of $\sim 6.5 \text{ MPa}$, elongation at break of $\sim 40\%$ at 30°C and $\sim 5.9 \text{ MPa}$, $\sim 35\%$ at 100°C , respectively. It was shown that the PEM can still have a good bendable property as shown in Figure 8d. In all, the above studies have confirmed the feasibility of such PEM to be used in lithium-ion batteries.

4. Conclusions

In general, this work reported a new type of PEMs of polyethylene glycol-borate ester/lithium fluoride (B-PEG/LiF) blended with graphene oxide/poly(vinyl

alcohol) (GO/PVA) for lithium-ion batteries. Different from commercial PP separator, this type of PEMs as a battery separator owned an intrinsic high ionic conductivity without needs for pore forming technologies. The chemical structure of the PEM was confirmed by ^1H -, ^{11}B - and ^{19}F -NMR spectra and ATR-FTIR spectrum. According to DSC and XRD results, it was shown that both PVA chains and LiF had strong interactions with boronic structure of B-PEG. Moreover, the GO in the PEMs could participate in the interactions with borate ester. The ionic conductivity behaviors of PEMs were investigated under various GO content. The ionic conduction of PEM with GO had the best obtained conductivities of $7.83 \cdot 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ (30°C) and $1.48 \cdot 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ (100°C) when GO wt% is 0.125. It was also shown that thermal and electrochemical stabilities of the PEM could be enhanced by GO. The PEM within a simulated lithium-ion battery had a better lithium-ion transference number than PP separator, with $\sigma \sim 10^{-3} \text{ S} \cdot \text{cm}^{-1}$. It was confirmed that the PEM could work normally in a lithium-ion battery of LiFePO_4/C . Therefore, this type of borate ester-functionalized composite PEMs is promising as a good candidate for the battery separator material.

Acknowledgements

The authors are grateful for the support of the National Natural Science Foundation of China (Grant: 51473186, U1201243), the Natural Science Foundation of Guangdong, China (Grants: 2012B0901000065, 2013B010135001 and 2015B090925002) and the Science and Technology Program of Guangzhou, China (Grant: 201508010052, 201604010105), and the Fundamental Research Funds for the Central Universities (Grant: 161gpy17).

References

- [1] Zhang J., Sun B., Huang X., Chen S., Wang G.: Honeycomb-like porous gel polymer electrolyte membrane for lithium ion batteries with enhanced safety. *Scientific Reports*, **4**, 6007–6013 (2014).
<https://doi.org/10.1038/srep06007>
- [2] Wang Y., Chen K. S., Mishler J., Cho S. C., Adroher X. C.: A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research. *Applied Energy*, **88**, 981–1007 (2011).
<https://doi.org/10.1016/j.apenergy.2010.09.030>
- [3] Zhang H., Shen P. K.: Recent development of polymer electrolyte membranes for fuel cells. *Chemical Reviews*, **112**, 2780–2832 (2012).
<https://doi.org/10.1021/cr200035s>

- [4] Arora P., Zhang Z.: Battery separators. *Chemical Reviews*, **104**, 4419–4462 (2004).
<https://doi.org/10.1021/cr020738u>
- [5] Zhang S. S.: A review on the separators of liquid electrolyte Li-ion batteries. *Journal of Power Sources*, **164**, 351–364 (2007).
<https://doi.org/10.1016/j.jpowsour.2006.10.065>
- [6] Zhou G., Li F., Cheng H.-M.: Progress in flexible lithium batteries and future prospects. *Energy and Environmental Science*, **7**, 1307–1338 (2014).
<https://doi.org/10.1039/C3EE43182G>
- [7] Balaish M., Kraysberg A., Ein-Eli Y.: A critical review on lithium–air battery electrolytes. *Physical Chemistry Chemical Physics*, **16**, 2801–2822 (2014).
<https://doi.org/10.1039/C3CP54165G>
- [8] Scheers J., Fantini S., Johansson P.: A review of electrolytes for lithium–sulphur batteries. *Journal of Power Sources*, **255**, 204–218 (2014).
<https://doi.org/10.1016/j.jpowsour.2014.01.023>
- [9] Scrosati B., Vincent C. A.: Polymer electrolytes: The key to lithium polymer batteries. *MRS Bulletin*, **25**, 28–30 (2000).
<https://doi.org/10.1557/mrs2000.15>
- [10] Dias F. B., Plomp L., Veldhuis J. B. J.: Trends in polymer electrolytes for secondary lithium batteries. *Journal of Power Sources*, **88**, 169–191 (2000).
[https://doi.org/10.1016/S0378-7753\(99\)00529-7](https://doi.org/10.1016/S0378-7753(99)00529-7)
- [11] Song J. Y., Wang Y. Y., Wan C. C.: Review of gel-type polymer electrolytes for lithium-ion batteries. *Journal of Power Sources*, **77**, 183–197 (1999).
[https://doi.org/10.1016/S0378-7753\(98\)00193-1](https://doi.org/10.1016/S0378-7753(98)00193-1)
- [12] Nan C.-W., Fan L., Lin Y., Cai Q.: Enhanced ionic conductivity of polymer electrolytes containing nanocomposite SiO₂ particles. *Physical Review Letters*, **91**, 266104/1–266104/4 (2003).
<https://doi.org/10.1103/PhysRevLett.91.266104>
- [13] Marcinek M., Bac A., Lipka P., Zalewska A., Zukowska G., Borkowska R., Wiczeorek W.: Effect of filler surface group on ionic interactions in PEG–LiClO₄–Al₂O₃ composite polyether electrolytes. *Journal of Physical Chemistry B*, **104**, 11088–11093 (2000).
<https://doi.org/10.1021/jp0021493>
- [14] Croce F., Appetecchi G. B., Persi L., Scrosati B.: Nanocomposite polymer electrolytes for lithium batteries. *Nature*, **394**, 456–458 (1998).
<https://doi.org/10.1038/28818>
- [15] Yang X., Zhang F., Zhang L., Zhang T., Huang Y., Chen Y.: A high-performance graphene oxide-doped ion gel as gel polymer electrolyte for all-solid-state supercapacitor applications. *Advanced Functional Materials*, **23**, 3353–3360 (2013).
<https://doi.org/10.1002/adfm.201203556>
- [16] Stephan A. M., Nahm K. S.: Review on composite polymer electrolytes for lithium batteries. *Polymer*, **47**, 5952–5964 (2006).
<https://doi.org/10.1016/j.polymer.2006.05.069>
- [17] Agrawal R. C., Pandey G. P.: Solid polymer electrolytes: Materials designing and all-solid-state battery applications: An overview. *Journal of Physics D: Applied Physics*, **41**, 223001/1–223001/18 (2008).
<https://doi.org/10.1088/0022-3727/41/22/223001>
- [18] Mazor H., Golodnitsky D., Peled E., Wiczeorek W., Scrosati B.: A search for a single-ion-conducting polymer electrolyte: Combined effect of anion trap and inorganic filler. *Journal of Power Sources*, **178**, 736–743 (2008).
<https://doi.org/10.1016/j.jpowsour.2007.09.056>
- [19] Kurian M., Galvin M. E., Trapa P. E., Sadoway D. R., Mayes A. M.: Single-ion conducting polymer–silicate nanocomposite electrolytes for lithium battery applications. *Electrochimica Acta*, **50**, 2125–2134 (2005).
<https://doi.org/10.1016/j.electacta.2004.09.020>
- [20] Cameron G. G., Ingram M. D., Sarmouk K.: Conductivity and viscosity of liquid polymer electrolytes plasticized by propylene carbonate and tetrahydrofuran. *European Polymer Journal*, **26**, 1097–1101 (1999).
[https://doi.org/10.1016/0014-3057\(90\)90009-S](https://doi.org/10.1016/0014-3057(90)90009-S)
- [21] MacCallum J. R., Vincent C. A.: Polymer electrolyte reviews, Vol 2. Springer, London (1989).
- [22] Zhu Y. S., Wang X. J., Hou Y. Y., Gao X. W., Liu L. L., Wu Y. P., Shimizu M.: A new single-ion polymer electrolyte based on polyvinyl alcohol for lithium ion batteries. *Electrochimica Acta*, **87**, 113–118 (2013).
<https://doi.org/10.1016/j.electacta.2012.08.114>
- [23] Çelik S. Ü., Bozkurt A.: Polymer electrolytes based on the doped comb-branched copolymers for Li-ion batteries. *Solid State Ionics*, **181**, 987–993 (2010).
<https://doi.org/10.1016/j.ssi.2010.05.039>
- [24] Lee H. S., Ma Z. F., Yang X. Q., Sun X., McBreen J.: Synthesis of a series of fluorinated boronate compounds and their use as additives in lithium battery electrolytes. *Journal of Electrochemical Society*, **151**, A1429–A1435 (2004).
<https://doi.org/10.1149/1.1779407>
- [25] Li L. F., Lee H. S., Li H., Yang X. Q., Nam K. W., Yoon W. S., McBreen J., Huang X.: New electrolytes for lithium ion batteries using LiF salt and boron based anion receptors. *Journal of Power Sources*, **184**, 517–521 (2008).
<https://doi.org/10.1016/j.jpowsour.2008.03.016>
- [26] Huang Y., Zhang M., Ruan W.: High-water-content graphene oxide/polyvinyl alcohol hydrogel with excellent mechanical properties. *Journal of Materials Chemistry A*, **2**, 10508–10515 (2014).
<https://doi.org/10.1039/C4TA01464B>
- [27] Aydın H., Şenel M., Erdemi H., Baykal A., Tülü M., Ata A., Bozkurt A.: Inorganic–organic polymer electrolytes based on poly(vinyl alcohol) and borane/poly(ethylene glycol) monomethyl ether for Li-ion batteries. *Journal of Power Sources*, **196**, 1425–1432 (2011).
<https://doi.org/10.1016/j.jpowsour.2010.08.020>

- [28] Huang Y-F., Wu P-F., Zhang M-Q., Ruan W-H., Gian-nelis E. P.: Boron cross-linked graphene oxide/polyvinyl alcohol nanocomposite gel electrolyte for flexible solid-state electric double layer capacitor with high performance. *Electrochimica Acta*, **132**, 103–111 (2014).
<https://doi.org/10.1016/j.electacta.2014.03.151>
- [29] Kato Y., Suwa K., Yokoyama S., Yabe T., Ikuta H., Uchi-moto Y., Wakihara M.: Thermally stable solid polymer electrolyte containing borate ester groups for lithium secondary battery. *Solid State Ionics*, **152–153**, 155–159 (2002).
[https://doi.org/10.1016/S0167-2738\(02\)00370-3](https://doi.org/10.1016/S0167-2738(02)00370-3)
- [30] Hummers W. S., Offeman R. E.: Preparation of graphitic oxide. *Journal of the American Chemical Society*, **80**, 1339 (1958).
<https://doi.org/10.1021/ja01539a017>
- [31] Dyre J. C.: The random free-energy barrier model for AC conduction in disordered solids. *Journal of Applied Physics*, **64**, 2456–2468 (1988).
<https://doi.org/10.1063/1.341681>
- [32] Sepe M. P.: Thermal analysis of polymers. iSmithers Rapra Publishing, Singapore (1997).
- [33] Singh M., Sahare P. D.: Redox reactions in Cu-activated nanocrystalline LiF TLD phosphor. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, **289**, 59–67 (2012).
<https://doi.org/10.1016/j.nimb.2012.08.003>
- [34] Xu K.: Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. *ChemInform*, **104**, 4303–4418 (2004).
<https://doi.org/10.1002/chin.200450271>
- [35] Chen W., Yan L.: Preparation of graphene by a low-temperature thermal reduction at atmosphere pressure. *Nano-scale*, **2**, 559–563 (2010).
<https://doi.org/10.1039/B9NR00191C>