



## Exploring polymeric lithium tartaric acid borate for thermally resistant polymer electrolyte of lithium batteries

Xuejiang Wang, Zhihong Liu\*, Chuanjian Zhang, Qingshan Kong, Jianhua Yao, Pengxian Han, Wen Jiang, Hongxia Xu, Guanglei Cui\*

Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

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### ABSTRACT

A novel polymeric lithium tartaric acid borate (PLTB) was synthesized via an one-step reaction in aqueous solution. The polymer electrolyte of PLTB@PVDF-HFP (poly(vinylidene fluoride-co-hexafluoropropene)) was developed by a doctor-blading followed by a soaking process in propylene carbonate (PC). It was manifested that the PC swollen PLTB@PVDF-HFP exhibited excellent electrochemical stability and compatibility with lithium metal electrode, high ionic conductivity and high lithium ion transference number at an operating temperature of 80 °C. The cells using the PC swollen PLTB@PVDF-HFP as electrolyte showed stable charge/discharge profiles, preferable rate capability and satisfactory cycling performance at high temperature. These superior performances of PC swollen PLTB@PVDF-HFP could endow this class of polymer electrolyte a very promising application in lithium batteries operating at relatively high temperature.

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### 1. Introduction

Recently, lithium ion batteries are emerging as main power sources for electric vehicles (EVs), hybrid electric vehicles (HEVs), power tools and robots [1,2]. In order to widespread the application, the batteries require to be able to deliver high energy density and high power density as well [3–8]. However, the up-sizing claims more safety concerns, because fire or explosions at abnormal conditions may lead to serious hazards owing to the hidden peril of commercial electrolyte system [8–13]. LiPF<sub>6</sub> is predominant lithium salt in state-of-the-art technology [14,15]. Nevertheless, LiPF<sub>6</sub> is known to thermally degrade at about 60 °C in inert atmosphere, and its decomposition components consist of high toxic HF, PF<sub>5</sub> and POF<sub>3</sub>, where HF can dissolve cathode active materials, PF<sub>5</sub> can react with organic solvents and consequently bring about thermal runaway [16–18]. Besides, expensive costs and intricate processing of LiPF<sub>6</sub> limits its future application in EVs and HEVs. So it is obligatory to explore high safe, low cost and superior thermal resistance electrolyte system for meeting the demand of batteries in EVs and HEVs. Very recently, researchers are making great efforts to develop alternative lithium salts. Some new lithium salts were synthesized in the last few years, such as lithium bis(oxalato)borate (LiBOB), lithium oxalyldifluoroborate (LiODFB), lithium bis[1,2-benzenediolato(2-)-O,O']borate

(LBBB) and lithium bis[salicylato(2-)]borate (LBSB) [19–25]. They present superior thermal stability, considerable lithium ion transference number and fair dissociation constant. This type of lithium salts is possessed of boron as central atom, surrounded by four oxygen ligands to form a big  $\pi$ -conjugated system. The molecular configuration is helpful to delocalize the negative charge of the central ion, and the anion becomes more thermodynamically stable.

Compared with liquid electrolyte, polymer electrolyte was explored owing to the characteristics of light quality, good film performance and excellent viscoelasticity, etc. [26–28]. Angell et al., who initially invented the LiBOB, has developed polymer electrolytes based on hybrid composition of LiBOB and poly(ethylene glycol)s (PEGs) in the last few years [29–31]. The poly[oligo(ethylene glycol)-oxalate] P(EG<sub>n</sub>O) solid electrolytes reported by physical mixture and polyanionic solid electrolytes (P(LiOEG<sub>n</sub>B), P(LiOPG<sub>n</sub>B), P(LiMEG<sub>n</sub>B)) reported by chemical reaction were attained. However, the ionic conductivities only reached 10<sup>-5</sup> S/cm at room temperature and the transference number of Li<sup>+</sup> was far away from the theoretical value even for the polyanionic solid electrolytes, owing to the presence of some anion impurity produced unavoidably during synthesis [30]. It is generally accepted that the strategy to achieve high transference number of lithium ion is to synthesize a polyanion structure [32–34]. Herein, we synthesize a novel polymeric lithium tartaric acid borate salt (PLTB) with polyanion as a main chain, which possesses a higher lithium ion concentration per unit than LiBOB. In addition, the PLTB in our case is low cost owing to abundant tartaric acid from

\* Corresponding authors. Tel.: +86 532 80662746; fax: +86 532 80662744.

E-mail addresses: [liuzh@qibebt.ac.cn](mailto:liuzh@qibebt.ac.cn) (Z. Liu), [cuigl@qibebt.ac.cn](mailto:cuigl@qibebt.ac.cn) (G. Cui).

biomass and facile synthesis with one-step reaction in an aqueous solution. It is expected that high lithium ion transference number and resultant enhanced ionic conductivity can be acquired. At the same time, PVDF-HFP was reported to be a good scaffold for polymer electrolyte owing to its intrinsic characteristics, such as chemical corrosion resistance, heat resistance, good mechanical property, high dielectric constant and excellent electrochemical performance [35]. In this paper, we report a new class of polymer electrolyte based on PLTB@PVDF-HFP swollen in PC. The thermal behavior, ionic conductivity, lithium ion transference number, electrochemical stability and performance of lithium battery will also be discussed in details.

## 2. Experimental

### 2.1. Materials

Boric acid (99.99%, Alfa Aesar), lithium hydroxide mono-hydrate (GR, Aladdin), Tartaric acid (Sinopharm Chemical Reagent Co., Ltd.), PVDF-HFP (Aldrich,  $M_w = 400,000$ ), *N,N*-Dimethylformamide (99.8%, superdry, J&K), cyclohexane (AR, Fu Yu Co., Ltd.), PC (Capchem Technology Co., Ltd.),  $\text{LiFePO}_4$  (Tianjin Strain Energy Science and Technology Ltd., particle size:  $3 \pm 1.0 \mu\text{m}$ , carbon content: 1.5–2.0%).

### 2.2. Synthesis and characterization of PLTB

The procedure for the synthesis of PLTB is shown in Scheme 1. Equimolar amounts of boric acid (1.546 g, 0.025 mol), lithium hydroxide monohydrate (1.049 g, 0.025 mol) and 50 mL deionized water were added into a 250 mL three-necked flask equipped with a Dean-Stark adaptor and stirred for 1 h. The tartaric acid (3.752 g, 0.025 mol) aqueous solution (50 mL water) was added dropwise to the homogeneous solution and reacted for 6 h at  $95^\circ\text{C}$ . Then 60 mL cyclohexane was added into the flask for azeotropic water removal. After water removal, some white precipitate was obtained in cyclohexane. The precipitate was filtered, collected and dried at  $120^\circ\text{C}$  under vacuum to afford 3.930 g PLTB (yield 96.0%).  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra of this polymer in  $\text{DMSO}-d_6$  were conducted on a nuclear magnetic resonance spectrometer (Bruker AVANCE-III). The thermal behavior of PLTB was measured on thermo gravimetric analyzer (TGA, Rubotherm-DYNTERM-HP) under the atmosphere at heating rate of  $10^\circ\text{C}/\text{min}$ .

### 2.3. Preparation of PC swollen PLTB@PVDF-HFP membrane

4.000 g PLTB and 4.000 g PVDF-HFP were added into 15 mL anhydrous DMF and mixed to be a transparent and homogeneous solution. Then the PLTB@PVDF-HFP membranes were prepared by a doctor-blading process followed by a vacuum drying at high temperature to remove DMF. The PC swollen PLTB@PVDF-HFP membrane was prepared after being soaked in PC for just one minute and removed extra solvent on the surface. The thickness of dry PLTB@PVDF-HFP membrane was  $50 \mu\text{m}$  and the mass ratio of PLTB/PVDF-HFP/PC was 0.25/0.25/0.5 (w/w/w).

### 2.4. Electrochemical characterization of PLTB@PVDF-HFP membranes

The electrochemical performance of the PC swollen PLTB@PVDF-HFP membrane was characterized at high temperature of  $80^\circ\text{C}$  because PC has a high boiling point. The electrochemical stability of PC swollen PLTB@PVDF-HFP membrane was evaluated by a cyclic voltammetry experiment performed on a working electrode of stainless-steel and a counter electrode of lithium metal at a scan rate of  $1 \text{ mV s}^{-1}$ . The ionic conductivity of PC

swollen PLTB@PVDF-HFP membrane between two stainless-steel plate electrodes was obtained by an AC impedance analysis using a Zahner Zennium electrochemical working station over a frequency range of  $1\text{--}10^6 \text{ Hz}$ . Lithium ion transference number was measured according to the method described by Evans et al. [36]. The method involved sandwiching the sample membrane in both lithium electrodes. After having measured the total initial resistance by AC impedance, a DC potential of 10 mV was applied until a steady state was reached. Finally, the resistance was again measured by AC impedance.

$$t^+ = \frac{I_S(\Delta V - I_0 R_0^{\text{el}})}{I_0(\Delta V - I_S R_S^{\text{el}})}$$

where  $t^+$  is the cationic transference number,  $\Delta V$  is the potential applied across the cell,  $R_0^{\text{el}}$  and  $R_S^{\text{el}}$  are the initial and steady-state resistances of the passivating layers on the Li electrode,  $I_0$  and  $I_S$  are the initial and steady-state currents.

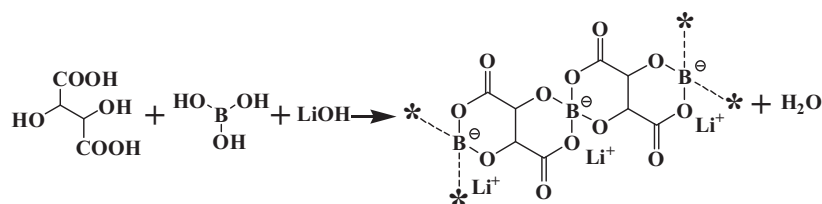
The interfacial resistances between PC swollen PLTB@PVDF-HFP membrane and lithium metal electrodes were measured by monitoring the impedance of symmetrical lithium cells under open-circuit conditions. The experiments were conducted on the same instrument for the ionic conductivity measurement over a frequency range of  $10^6\text{--}1 \text{ Hz}$  using two lithium electrodes instead of the stainless-steel plate electrodes. The Al passivation measurement was valued by controlled potential coulometry performed on a working electrode of Al foil and a counter electrode of lithium foil.

A half coin cell (2032-type) was assembled by sandwiching the PC swollen PLTB@PVDF-HFP membrane between a lithium metal foil and  $\text{LiFePO}_4$  electrode. The  $\text{LiFePO}_4$  electrode was prepared by a doctor-blading and the mass ratio of  $\text{LiFePO}_4$ /carbon black/PVDF was 0.8/0.1/0.1 (w/w/w). All assembly of cells was carried out in an argon-filled glove box. The charge/discharge C-rate capability and cycling ability of cells were examined using a LAND battery test system under high temperature. The C rate was often used to describe battery loads or battery charging. 1 C was the capacity rating (Amp-hour) of the battery ( $1 \text{ C} = 140.0 \text{ mAh g}^{-1}$ ).

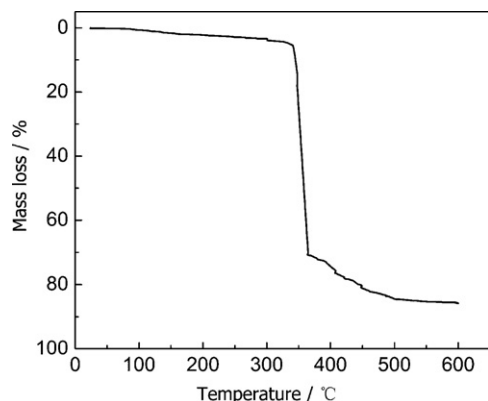
## 3. Results and discussion

### 3.1. Characterization of PLTB and PC swollen PLTB@PVDF-HFP membrane

The PLTB was characterized by  $^1\text{H}$  and  $^{11}\text{B}$  NMR measurement to confirm its chemical structure. The  $^1\text{H}$  NMR spectra of tartaric acid and PLTB in  $\text{DMSO}-d_6$  were shown in Fig. S1(a) and (b), respectively. It could be seen that the proton signal of  $-\text{CH}$  in PLTB shifted from 4.31 ppm to 4.05–4.28 ppm. In addition, the proton signals of  $-\text{OH}$  and  $-\text{COOH}$  disappeared after reaction. These facts verified that  $-\text{OH}$  and  $-\text{COOH}$  had reacted with boron acid to form polymeric borate. The  $^{11}\text{B}$  NMR spectrum of PLTB in  $\text{DMSO}-d_6$  was presented in Fig. S2. It further verified the formation of polymeric borate. Besides, three possible chemical structures (seen in Fig. S3) were identified by  $^{11}\text{B}$  NMR spectra. The thermo gravimetric analysis (TGA) curve of PLTB was shown in Fig. 1. It could be seen that PLTB exhibited a slightly higher thermal decomposition temperature at  $330^\circ\text{C}$ , when compared with that of LiBOB ( $302^\circ\text{C}$ ) [19]. The PC swollen PLTB@PVDF-HFP membrane was homogeneous which was vital to prevent the generation of Li dendrite (See Fig. 2 and Fig. S4) and this will be further discussed below. The stress-strain curve of PLTB@PVDF-HFP membranes was depicted in Fig. S6. It was observed that the electrolyte membranes possessed tensile strength of 20 MPa with 60% strain. So our polymer electrolyte membranes possess a good mechanical strength.



**Scheme 1.** Procedure for the one-step synthesis of PLTB in an aqueous solution.



**Fig. 1.** Thermal gravimetric analysis of PLTB under the atmosphere at heating rate of 10 °C/min.

### 3.2. Electrochemical stability of the PC swollen PLTB@PVDF-HFP membrane

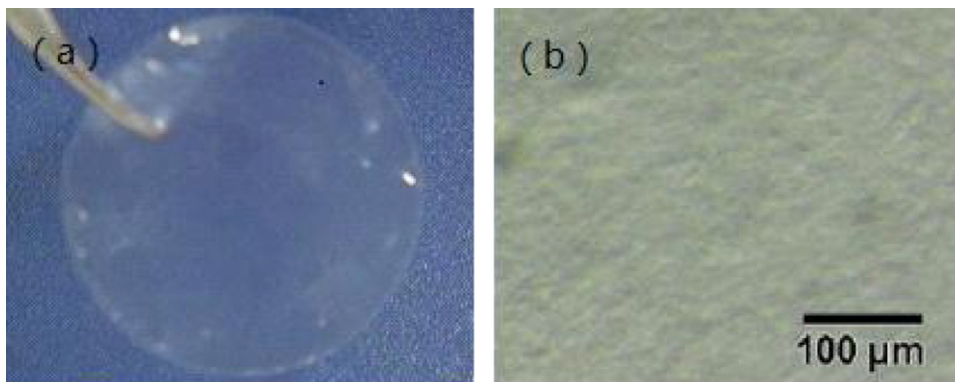
The electrochemical stability of the PC swollen PLTB@PVDF-HFP membrane was measured by the cyclic voltammetry. The anodic current onset may be associated with the electro-chemically oxidized decomposition of polymer electrolyte. From Fig. 3, it was observed that the PC swollen PLTB@PVDF-HFP membrane started to oxidatively degrade above 5.0 V vs  $\text{Li}^+/\text{Li}$  at 25 °C and 4.7 V vs  $\text{Li}^+/\text{Li}$  at 80 °C, respectively. This was slightly better than that of LiBOB electrolyte (4.5 V vs  $\text{Li}^+/\text{Li}$ ) at ambient temperature [19], indicating high electrochemical stability of the polymer electrolyte even at elevated temperature, which might be due to the more stable structure of our polyanion. The electrochemical stability of the PC swollen PLTB@PVDF-HFP could endow this polymer electrolyte for a high voltage battery application even at elevated temperature of 80 °C. The cathodic current onset observed about −0.3 V vs  $\text{Li}^+/\text{Li}$  corresponded to the electrochemical deposition of lithium and a hump at around 0 V vs  $\text{Li}^+/\text{Li}$  was related to the stripping

of lithium. So, the PC swollen PLTB@PVDF-HFP membrane showed very excellent lithium deposition-stripping performance.

### 3.3. Interfacial compatibility and Al passivation of the PC swollen PLTB@PVDF-HFP membrane

The interfacial compatibility of lithium metal with polymer electrolytes plays an important role in lithium batteries. The reactivity of the anode electrode with polymer electrolytes can lead to an uncontrolled passivation process, and then result in the formation of a thick and non-uniform surface layer, which will cause an uneven lithium deposition during the charging process and eventually lead to a dendritic growth and subsequent short circuit of the battery. The compatibility of the PC swollen PLTB@PVDF-HFP membranes with a lithium metal anode was demonstrated by the measurement of the related interfacial impedance. In Fig. 4, it was manifested that the bulk resistance ( $R_b$ ) of the battery varied from 41  $\Omega$  to 49  $\Omega$  and the passivation film resistance ( $R_f$ ) varied from 114  $\Omega$  to 130  $\Omega$  at 80 °C with one month. Both the  $R_b$  and  $R_f$  slightly varied with the storage time. This confirmed that the PC swollen PLTB@PVDF-HFP membranes possessed a good compatibility with the lithium foil.

The Al passivation in PC swollen PLTB@PVDF-HFP membrane was also studied using the method described by Angell et al. at 80 °C [20]. From Fig. 5, it could be seen that the initial rapid decrease of the anodic current on fresh Al surface indicated an instant formation of passivation film, and this film showed no sign of breakdown as the potential was stepped up to 4.75 V, as proven by the absence of increase in current with time at all potentials. Since a semisteady state was reached in the time scale studied, i.e., 10<sup>3</sup> s, a polarization plot was made from the corrosion current collected at  $t = 10^3$  s vs the applied potential, which is shown as an inset of Fig. 5. We can draw preliminary conclusion that this polyanion protects the Al substrate and its presence in lithium batteries will not cause cathode substrate corrosion, which was better than Al cathode corrosion caused by the sulfonic salts for the nafion lithium membrane.



**Fig. 2.** (a) Photograph of the PC swollen PLTB@PVDF-HFP membrane (PLTB/PVDF-HFP/PC = 0.25/0.25/0.5 (w/w/w)) and (b) its surface morphology observed by optical microscope.

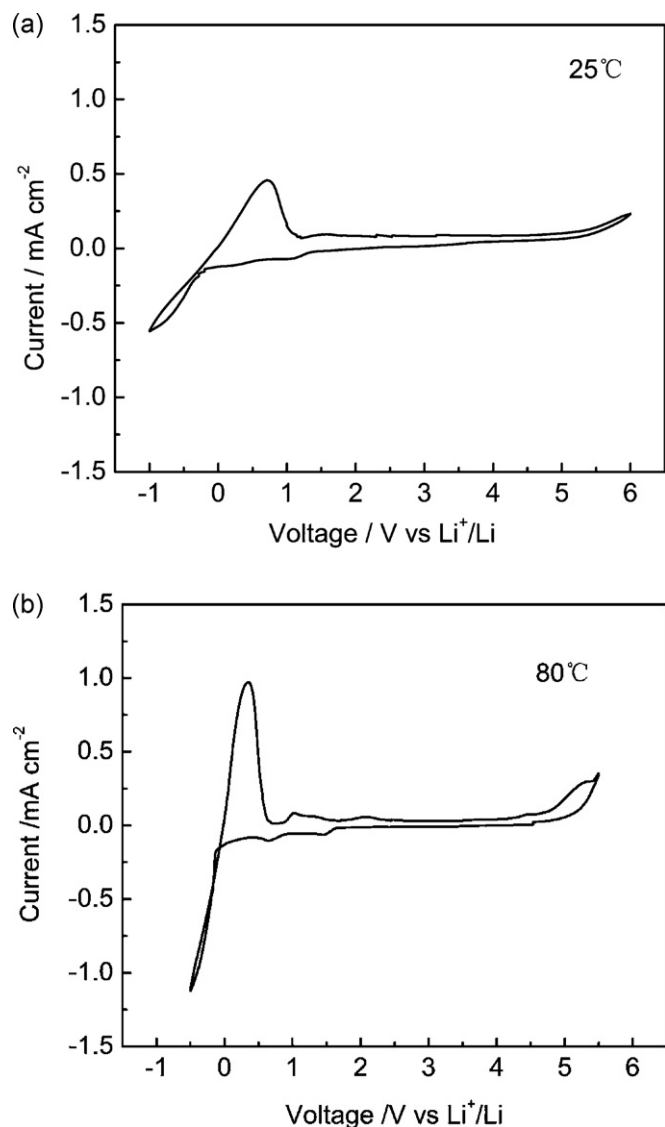


Fig. 3. Electrochemical stability of PC swollen PLTB@PVDF-HFP membrane (a) at 25 °C and (b) at 80 °C, respectively (scan rate = 1 mV s<sup>-1</sup>).

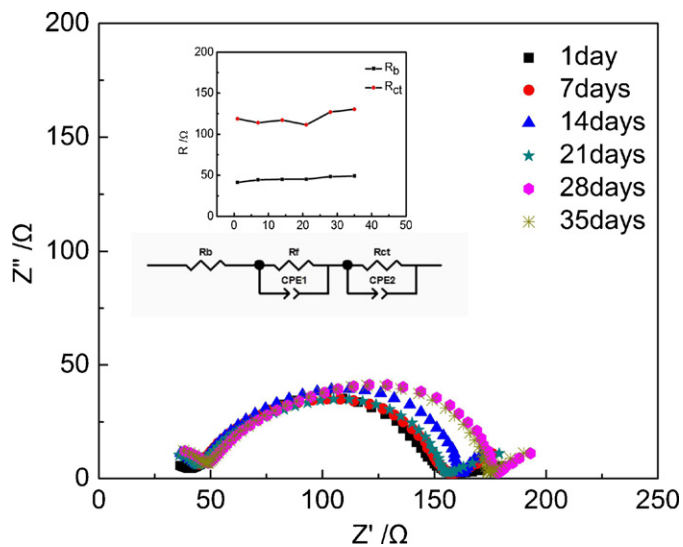


Fig. 4. Impedance spectra of Li/PC swollen PLTB@PVDF-HFP/Li at 80 °C with the storage time. Inset: variations of the passivation film resistance ( $R_f$ ) and the bulk resistance ( $R_b$ ) as a function of the storage time.

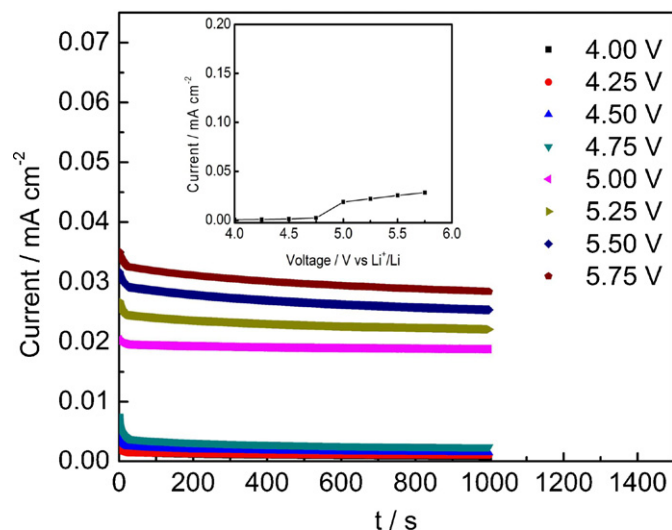


Fig. 5. Time-decaying current density obtained on an Al electrode at various potentials vs Li<sup>+</sup>/Li in the PC swollen PLTB@PVDF-HFP membrane. Inset: the dependence of steady state current density (at  $t = 10^3$  s on applied potential as obtained on an Al electrode in polymer electrolyte). Temperature: 80 °C.

### 3.4. Ionic conductivity and Li<sup>+</sup> transference number of the PC swollen PLTB@PVDF-HFP membrane

Fig. 6 showed the temperature dependence of ionic conductivity of PC swollen PLTB@PVDF-HFP membrane. It could be observed that the temperature dependence of the ionic conductivity agreed with the Arrhenius equation over the temperature range of 20–90 °C. The ionic conductivity was  $1.408 \times 10^{-4}$  S/cm at 20 °C and  $7.836 \times 10^{-4}$  S/cm at 80 °C, respectively. The activation energy was calculated to be 12.043 kJ mol<sup>-1</sup>, which was close to that of other polymer electrolytes described by others [10,32,37]. The transference number of Li<sup>+</sup> measured using the steady-state current method (Fig. S9) was to be 0.93, which is much higher than that of LiBOB based electrolytes (<0.6) [38]. This might because the polymeric lithium salt prepared in our work had a polyanion structure that possessed bulky volume and could hinder the migration of anion, when compared to the dimer structure of BOB<sup>-</sup> in LiBOB.

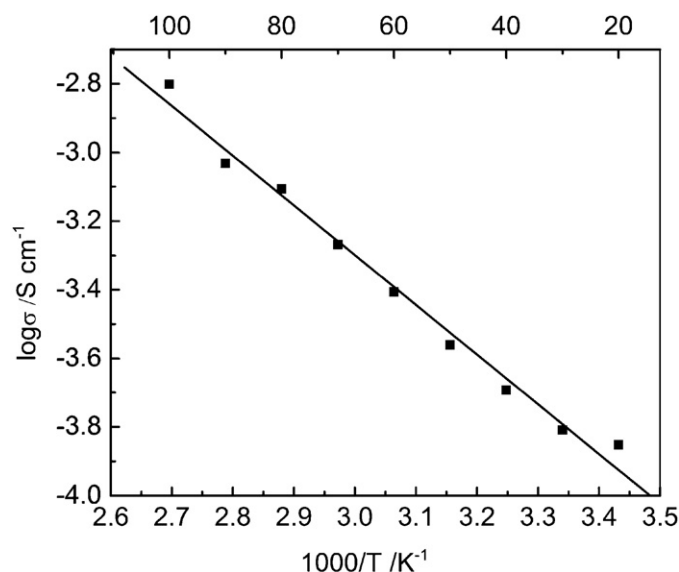
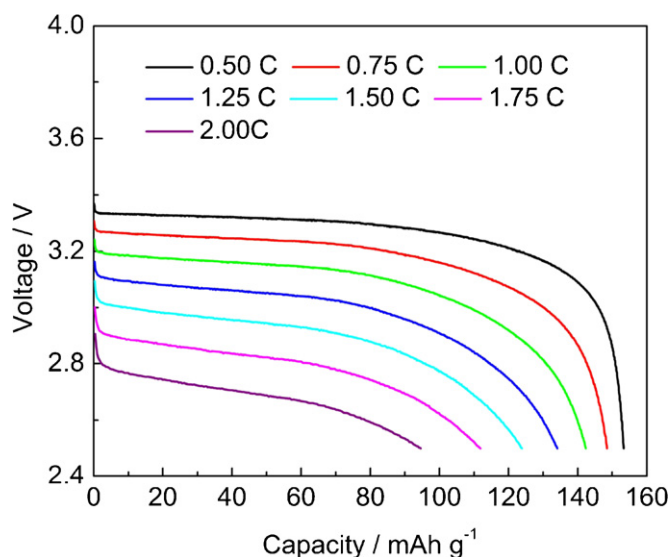


Fig. 6. Temperature dependence of ionic conductivity of PC swollen PLTB@PVDF-HFP membrane.

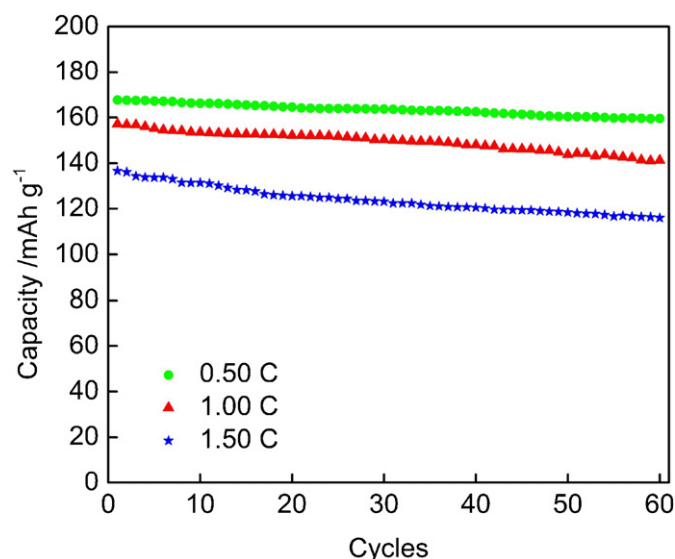




**Fig. 7.** Discharge voltage profiles of the Li/PC swollen PLTB@PVDF-HFP/LiFePO<sub>4</sub> battery at different discharge rates. Temperature: 80 °C, charge rate: 0.5 C.

### 3.5. Battery performance of the PC swollen PLTB@PVDF-HFP membrane

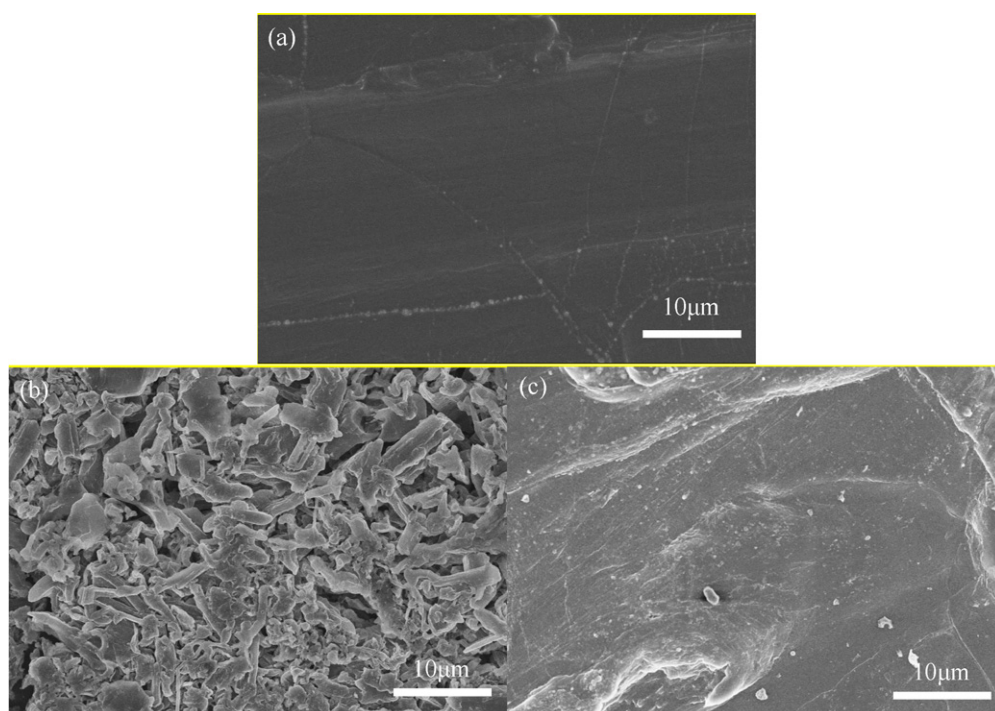
To evaluate the electrochemical performance of the Li/PC swollen PLTB@PVDF-HFP/LiFePO<sub>4</sub> batteries, the discharge rate at 80 °C was varied from 0.5 C to 2 C, whereas the charge rate was fixed at 0.5 C. From Fig. S10, it could be seen that the first charge/discharge voltage profiles was quite stable at 0.5 C even at high temperature of 80 °C. The initial charge and discharge capacities were 155.1 mAh g<sup>-1</sup> and 153.3 mAh g<sup>-1</sup>, respectively, which indicated the initial coulombic efficiency of 98.9%. The rate capability of the batteries was demonstrated in Fig. 7. As is well known that the theoretical capacity of the LiFePO<sub>4</sub> cathode is



**Fig. 8.** Cycling performance of the Li/PC swollen PLTB@PVDF-HFP/LiFePO<sub>4</sub> batteries at different charge/discharge rates. Temperature: 80 °C.

170 mAh g<sup>-1</sup>. It could be seen that the capacities of the batteries were 153.3 mAh g<sup>-1</sup> (0.5 C), 142.4 mAh g<sup>-1</sup> (1 C), 123.9 mAh g<sup>-1</sup> (1.5 C) and 94.6 mAh g<sup>-1</sup> (2 C), i.e. 90.2%, 83.8%, 72.9%, and 55.6% of the theoretical value, respectively. These results demonstrated that the battery had an excellent rate performance at 80 °C even at a lower content of PC (50%, w/w), when compared to that battery using a PC swollen lithiated perfluorinated sulfonic ion-exchange membrane with a higher content of PC (70%, w/w) [10]. This might be attributed to high lithium ion transference number, high lithium ion concentration and considerable ionic conductivity of the PC swollen PLTB@PVDF-HFP membrane.

The cycling performance of the Li/PC swollen PLTB@PVDF-HFP/LiFePO<sub>4</sub> batteries at 80 °C with different charge/discharge



**Fig. 9.** Surface morphologies of (a) pristine lithium metal foil, (b) the lithium metal foil in the Li/LiFePO<sub>4</sub> batteries using LiPF<sub>6</sub>/EC/DMC as electrolyte and Celgard 2500 as separator after 50 cycles at 50 °C and (c) the lithium metal foil in the Li/PC swollen PLTB@PVDF-HFP/LiFePO<sub>4</sub> batteries after 100 cycles at 50 °C.

rates was shown in Fig. 8. After 60 cycles, the capacity can retain  $159.6 \text{ mAh g}^{-1}$  at 0.5 C,  $141.2 \text{ mAh g}^{-1}$  at 1.0 C and  $115.9 \text{ mAh g}^{-1}$  at 1.5 C, respectively. The capacity retention,  $R_{60/1}$ , defined as ratio of capacity at 60th cycle over that at first cycle, is 95.2% (0.5 C), 89.8% (1.0 C) and 84.8% (1.5 C). For comparison, we tested the cycling stability of Li/LiFePO<sub>4</sub> battery using the electrolyte LiPF<sub>6</sub>/EC/DMC (1 mol L<sup>-1</sup> LiPF<sub>6</sub> in EC: DMC = 1:1 (v:v)). The capacity after 60 cycles at 0.5 C can retain  $135.0 \text{ mAh g}^{-1}$  at room temperature (see Fig. S11). Unfortunately, at elevated temperature of 80 °C, Li/LiFePO<sub>4</sub> battery using the electrolyte LiPF<sub>6</sub>/EC/DMC failed to be charged to 3.5 V at first charge (seen in Fig. S12), probably owing to the poor thermal stability of LiPF<sub>6</sub>. It was verified that the Li/PC swollen PLTB@PVDF-HFP/LiFePO<sub>4</sub> batteries presented excellent cycling performance at high temperature.

To give insight into the positive effect of PC swollen PLTB@PVDF-HFP in preventing the generation of Li dendrite, the surface morphologies of lithium metal foils were studied by SEM after battery cycles, which were depicted in Fig. 9. It was shown in Fig. 9(a) that the surface of pristine lithium foils was rather smooth. In the Li/LiPF<sub>6</sub>/EC/DMC/LiFePO<sub>4</sub> battery using Celgard 2500 as separator, the surface of lithium metal foil became rather rough and was composed of a large amount of Li dendrites after 50 cycles at 50 °C. For the Li/PC swollen PLTB@PVDF-HFP/LiFePO<sub>4</sub> battery, the surface of lithium metal foil even after 100 cycles was relatively smooth indicating no obvious sign of Li dendrite when compared to that of Fig. 9(b). This may be due to the homogeneity of the PC swollen PLTB@PVDF-HFP membrane.

#### 4. Conclusions

In summary, we explored a high performance polymer electrolyte of PC swollen PLTB@PVDF-HFP for a high temperature application via an environmentally benign and low cost synthesis of PLTB. It is observed that PLTB possesses a high decomposition temperature at 330 °C, which is potential for improving the battery safety characteristic. The PC swollen PLTB@PVDF-HFP membrane exhibits not only considerable ionic conductivity and high lithium ion transference number, but also good interfacial compatibility with lithium metal anode as well as Al substrate and high anodic electrochemical stability (4.7 V vs Li<sup>+</sup>/Li) at 80 °C. The lithium batteries using PC swollen PLTB@PVDF-HFP membrane exhibit stable charge/discharge behavior, preferable rate capability and satisfactory cycling performance at 80 °C. The superior high temperature performance of PC swollen PLTB@PVDF-HFP could endow this kind of polymer electrolyte a very promising application for power battery of electric vehicle normally operating at relatively high temperature.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2013.01.026>.

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