



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

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### ARTICLE INFO

#### Article history:

Received 8 November 2012

Received in revised form

21 December 2012

Accepted 5 January 2013

Available online 15 January 2013

#### Keywords:

Polymer electrolytes

Lithium salts

High temperature

Lithium ion batteries

### 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 upsizing 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

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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 °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 °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-DYNTherm-HP) under the atmosphere at heating rate of 10 °C/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 °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 1–10<sup>6</sup> 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<sup>6</sup>–1 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 C = 140.0 mAh  $\text{g}^{-1}$ ).

## 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 –CH in PLTB shifted from 4.31 ppm to 4.05–4.28 ppm. In addition, the proton signals of –OH and –COOH disappeared after reaction. These facts verified that –OH and –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 °C, when compared with that of LiBOB (302 °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.

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