



# A new single-ion polymer electrolyte based on polyvinyl alcohol for lithium ion batteries

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## ABSTRACT

In this study, a novel single-ion conducting polymer electrolyte, lithium polyvinyl alcohol oxalate borate (LiPVAOB), from the reaction of poly(vinyl alcohol) (PVA) with different molar ratio of boric acid, oxalic acid and lithium carbonate was prepared. The prepared materials were characterized by Fourier transformation infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetry (TG), differential thermal analysis (DTA), electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry. Ionic conductivity of these polymer electrolytes from adding an assistant (about 20 wt.% propylene carbonate) is dependent on molar ratio of the reactants and can up to  $6.11 \times 10^{-6} \text{ S cm}^{-1}$  at ambient temperature. Their electrochemical window can be stable up to 7 V (vs.  $\text{Li}^+/\text{Li}$ ), which is of great attraction for high voltage lithium ion batteries with high energy density.

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## 1. Introduction

Lithium ion batteries have gained an unprecedented importance in the last several decades as the energy storage of portable devices such as cell phones and laptop computers [1,2]. Furthermore, lithium ion batteries are also considered as the optimal power sources for hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs) [3,4]. However, most lithium ion batteries comprising of liquid electrolytes have potential safety problems due to the existence of large amount of organic solvents. In order to solve the safety problems, polymer electrolytes (PEs) have received great attention. In the case of application of solid PEs, there is still quite some space because of the low ionic conductivity [5]. Gel PEs, which have the characteristics of the solid and liquid electrolytes, have got increasing attention for its good ionic conductivity, wide electrochemical window, good compatibility with the electrodes, good thermal stability and so on [6–8]. Poly(vinylidene fluoride) (PVDF) [9–11] and its copolymer poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-co-HFP)) [12–15], poly(ethyleneoxide) (PEO) [16,17], polyacrylonitrile (PAN) [18], poly(methyl methacrylate) (PMMA) [19] have been widely studied as polymer matrices for the preparation of gel PEs in order to make them feasible for commercial applications.

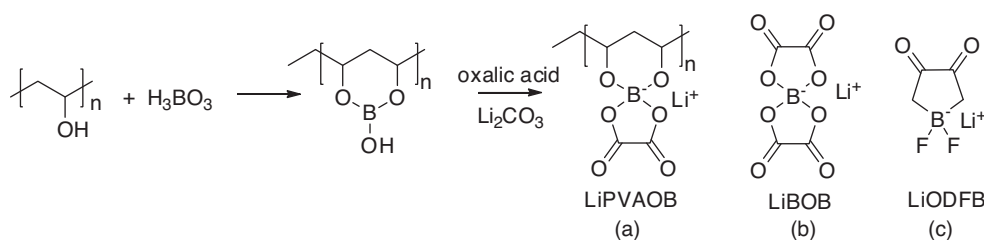
The mechanism of ion conduction in solid PEs was explained based on dissolving alkali metal salts in polyether matrix [20,21]. Ion conduction takes place in the amorphous phase of polymers such as polyethylene oxide and ether oxygen atoms act as ion-coordinating sites. The ether oxygen atoms interact with the cations (Lewis acid–base interactions) and cause salt solvation. The cation transport is assisted by segmental motion of the polymer chains. The counter anions in the polymer electrolytes have weak interactions with the polyethers, hence transport more easily compared to cations. Thus a major drawback of dual ion conducting in PEs is the low lithium ion transference number (0.3–0.5) [21]. In the same time, the mobility of anions results in polarization and reduces the lithium ion transference number. Therefore it is necessary to design single-ion conducting polymer electrolytes to guarantee the stability of anions to gain good performance for lithium ion batteries.

To date, two approaches have been reported to reduce the mobility of anions. The first one deals with introduction of interacting sites that preferentially interact with the anions [22,23]. The other is to anchor anions to the polymer backbone [24,25], which is a common method to achieve single-ion conducting PEs. However, it should be noted that the ionic conductivity of single-ion PEs is generally lower than that of dual ions conducting system because of the lost conductivity contribution from anion transference. In order to improve their ionic conductivity, various methods have been tried [22,26,27]. However, the subject still remains as a big challenge and there have been very few publications on single-ion polyester-based electrolytes.

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**Scheme 1.** (a) The preparation process of LiPVAOB and the structures of (b) LiBOB and (c) LiODFB.

Polyvinyl alcohol (PVA) is a water-soluble polyhydroxyl polymer whose physical properties are dependent on the degrees of polymerization and alcoholysis. PVA has an excellent chemical resistance, thus it can be used in many practical applications such as adhesives, textiles, and pharmaceutical and biomedical industries due to nontoxic and biodegradable properties [28,29]. It can also be modified by chemical reactions, which is a highly versatile method to improve the chemical, thermal, and mechanical properties [30]. One of the most common methods is the reaction of hydroxyl groups of PVA with aldehydes to form acetal or hemiacetal [31]. PVA can also physically cross-link with boric acid through hydrogen bonding and ionic interactions in the hydrated state [29,32].

Lithium chelatoborates as electrolyte salts have been widely studied and its aim is to substitute  $LiPF_6$  [33–36]. The latter is unstable at elevated temperature and sensitive with trace amount water [37]. Among the borates, lithium bis(oxalate)borate (LiBOB) and lithium oxalyl difluoroborate (LiODFB) (Scheme 1) are the promising candidates used as electrolyte salts in lithium ion batteries [36,38]. The merits of these lithium salts are not only the low production cost, wide potential window, good thermal stability but also they can form effective solid electrolyte interface (SEI) to stabilize the graphitic anode structure. LiBOB and LiODFB have the similar structure based on an oxalate-chelated borate and present good electrochemical performance. However, little attention has been paid on lithium chelatoborates polymer electrolytes, let alone on the single-ion conductor. From this point of view, lithium chelatoborate-based polymer electrolytes may be an alternative system to promote the applications of lithium rechargeable battery.

In this work, we reported the synthesis and electrochemical properties of a novel single-ion conducting polymer electrolyte, lithium polyvinyl alcohol oxalate borate (LiPVAOB, Scheme 1a), whose monomer is structurally similar to LiBOB (Scheme 1b), based on PVA, boric acid ( $H_3BO_3$ ), lithium hydroxide (LiOH) and oxalic acid ( $H_2C_2O_4$ ). The structure, thermal property, morphology and electrochemical property of the as-prepared single-ion conducting PEs have been investigated and the primary results show that the prepared PEs have good electrochemical performance.

## 2. Experimental

The polymer membrane was synthesized by the reaction of PVA (degree of alcoholysis  $\geq 98\%$ , Mw: 105,000), lithium carbonate, boric acid, oxalic acid according to the chemical equation (Scheme 1a). All chemicals were provided from Sinopharm Chemical Reagent Co., Ltd. Boric acid and PVA were dissolved into DMSO and heated to  $80^\circ C$  for 5 h to give a homogeneous and transparent solution. Then lithium carbonate and oxalic acid were added. The mixture was stirred at  $100^\circ C$  for 24 h. Cooled to room temperature, the solution was later cast on a flat glass plate at  $70^\circ C$  to remove the solvent to get membranes with a thickness of 50–70  $\mu m$ . The membranes were punched into circular pieces ( $d = 19$  mm) and further dried under vacuum at  $70^\circ C$  for 48 h to remove the trace amount of solvent. Later, the pieces were soaked in propylene carbonate

(PC) over 12 h in a glove box (water content  $< 1$  ppm) to get the PEs for further measurement. LiPVAOB based on different molar ratios of reactants ( $n_{-OH}/n_{H_3BO_3}/n_{Li_2CO_3}/n_{H_2C_2O_4} = 2/0.9/0.45/0.9, 2/0.95/0.475/0.95, 2/1/0.5/1, 2/1.05/0.525/1.05, 2/1.1/0.55/1.1$ ) were marked as LiPVAOB<sub>0.9</sub>, LiPVAOB<sub>0.95</sub>, LiPVAOB<sub>1.0</sub>, LiPVAOB<sub>1.05</sub> and LiPVAOB<sub>1.1</sub>.

The conventional KBr disk method was employed to measure the Fourier transformation infrared spectroscopy (FT-IR) of the membranes. Before FT-IR spectra measurements, the samples were dried at  $70^\circ C$  under vacuum for 12 h and then stored in the dry box for 2 h. The IR spectra were recorded with a BRUKER VECTOR-22 spectrometer. X-ray diffraction (XRD) was performed on a Bruker D8 X-ray diffractometer (50 kV, 50 mA) with a copper target ( $\lambda = 1.5405 \text{ \AA}$ ) and Ni filter at a scan rate of  $5^\circ \text{ min}^{-1}$  from  $10^\circ$  to  $90^\circ$ . Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the polymers were carried out by utilizing a Perkin-Elmer TGA7/DTA7. The samples were heated from room temperature to  $400^\circ C$  at a heating rate of  $10^\circ C \text{ min}^{-1}$  under nitrogen atmosphere. The surface morphology of the prepared membranes was investigated by Philips XL30 scanning electron microscopy (SEM). The membranes were dipped into liquid nitrogen and broken into two parts, and then the SEM micrographs of the cross-sections were taken. All of the samples were sputtered with gold prior to the SEM measurement. The thickness of the membranes was measured with a micrometer (SM & CTW, Shanghai).

The ionic conductivities of the PEs were measured by the electrochemical impedance spectroscopy (EIS) method. The samples were prepared in the glove box under argon atmosphere with a humidity  $< 1$  ppm. They were measured in blocking-type cells which were fabricated by sandwiching the membranes between two stainless steel electrodes. The experiments were performed in a cylindrical cell of an electrode diameter of 1.80 cm. Impedance data were obtained with a computer interfaced with an electrochemical working station CHI660C (Chenhua) in the frequency range from 10 Hz to 100 kHz. The cells were placed in a temperature-controlled oven and the impedance responses were recorded in the range of  $25\text{--}85^\circ C$ . The linear sweep voltammetry for the as-prepared PEs was carried out on a two-electrode cell. Stainless steel was used as the working electrodes and lithium foil was used as the counter and reference electrode, respectively. The measurement was done between 0 and 7 V (vs.  $Li^+/Li$ ) at a scan rate of  $2 \text{ mV s}^{-1}$  at  $25^\circ C$  with an electrochemical working station CHI660C (Chenhua).

## 3. Results and discussion

The reaction of PVA with  $H_3BO_3$ ,  $Li_2CO_3$  and  $H_2C_2O_4$  is expected to take place well under a mild condition as shown in Scheme 1. It is necessary to control the reaction conditions to ensure the obtaining of the product LiPVAOB and the addition serial of the reactants is very important. PVA is a water-soluble polymer and cannot dissolve well in some organic solvents. However, the amount of water is strictly controlled in lithium batteries. To get the target material, the polymer must react with organic materials, inorganic compounds and salts. As a result, DMSO, an aprotic polar solvent which

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