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A single-ion polymer electrolyte based on boronate for lithium ion batteries

Y.S. Zhu, X.W. Gao, X.J. Wang, Y.Y. Hou, L.L. Liu, Y.P. Wu *

New Energy and Materials Laboratory (NEML), Department of Chemistry & Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, China

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ABSTRACT

A novel single-ion polymer electrolyte, LiPAAOB (lithium oxalate polyacrylic acid borate), was prepared with different ratio of polyacrylic acid, boric acid, lithium hydroxide and oxalic acid. The obtained membranes were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, thermogravimetry and differential thermal analysis. After absorbing 3% solvent (propylene carbonate), the as-prepared LiOPAAB presents a single ion conductive behavior. Its ionic conductivity at ambient temperature can be up to 2.3×10^{-6} S cm^{-1} and electrochemical window can be stable up to 7.0 V (vs. Li$^+$/Li), which is of great attraction for 5 V lithium ion batteries with high energy density.

1. Introduction

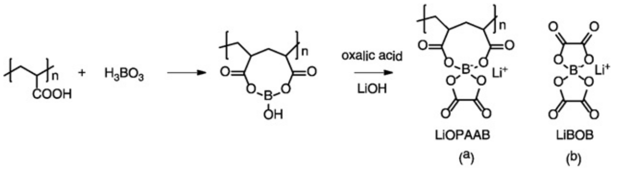
Lithium ion batteries using polymer electrolytes (PEs) have received great attention as the power sources for electric vehicle (EVs) and other electronic equipments [1–5]. Gel PEs have been used in the commercial lithium ion batteries [6,7]. In contrast, there is still some space for the application of solid PEs because of their low ionic conductivity [8].

In traditional solid PEs, ion conduction takes place in the amorphous phase [9]. The cation transport is assisted by segmental motion of the polymer chains. The counter anions in the PEs have weaker interactions with the main chains and transport more easily compared to cations [10]. Thus a major drawback of dual ion conduction in PEs is the low Li$^+$ transference number (0.3–0.5) [11]. In the same time, the mobility of both cation and anion results in electrode polarizations leading to poor electrochemical performance [12]. Therefore it is desirable to design single-ion conducting polymer electrolytes with fixed anions to gain good performance for batteries. To date, two approaches have been reported to reduce the mobility of anions. The first one is to introduce interacting sites that preferentially interact with the anions [13,14]. The other one is to anchor anions to the polymer backbone [15,16], which is well-used 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 ion conducting system. In order to improve their ionic conductivity, various methods have been tried [4,10,17]. However, the subject still remains as a big challenge and new ways and polymers are needed to explore.

So far little attention has been paid on lithium chelatoborates polymer electrolytes though lithium bis(oxalate) borate (LiBOB) presents promise to replace $LiPF_6$ in lithium ion batteries [18–20]. Here we report the synthesis and electrochemical properties of a novel single-ion conducting polymer electrolyte, LiOPAAB (lithium oxalate polyacrylic acid borate) (Scheme 1a), based on polyacrylic acid (PAA), boric acid (H_3BO_3), lithium hydroxide (LiOH) and oxalic acid ($H_2C_2O_4$), and a small amount (3 wt.%) of propylene carbonate (PC) as the plasticizers. The as-prepared LiOPAABs are structurally similar to that of LiBOB (Scheme 1b).

2. Experimental

Polymer membranes were prepared based on Scheme 1. Boric acid (Sinopharm) and PAA (Aladdin, Mw: 450000) were dissolved into deionized water and heated at 80 °C for 5 h to give a homogeneous and transparent solution. Then LiOH (Sinopharm) and $H_2C_2O_4$ (Sinopharm) were added and refluxed for 24 h. After being cooled to room temperature, the solution was later cast on a flat glass plate at 60 °C to remove the solvent to get membranes with thickness of 50–70 μm. The membranes were punched into circular pieces (d = 19 mm) and further dried under vacuum at 70 °C for 48 h to remove the trace amount of solvent. Then the pieces were soaked in propylene carbonate (PC) for 12 h in a glove box (water content < 1 ppm) to give the PEs for further measurement. LiOPAAB based on different molar ratios of PAA, H_3BO_3,



Scheme 1. The preparation process of LiOPAAB and the structure of LiBOB.

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* Corresponding author. Tel./fax: +86 21 55664223.
E-mail addresses: wuyp@fudan.edu.cn, wuyuping99@yahoo.com (YP. Wu).

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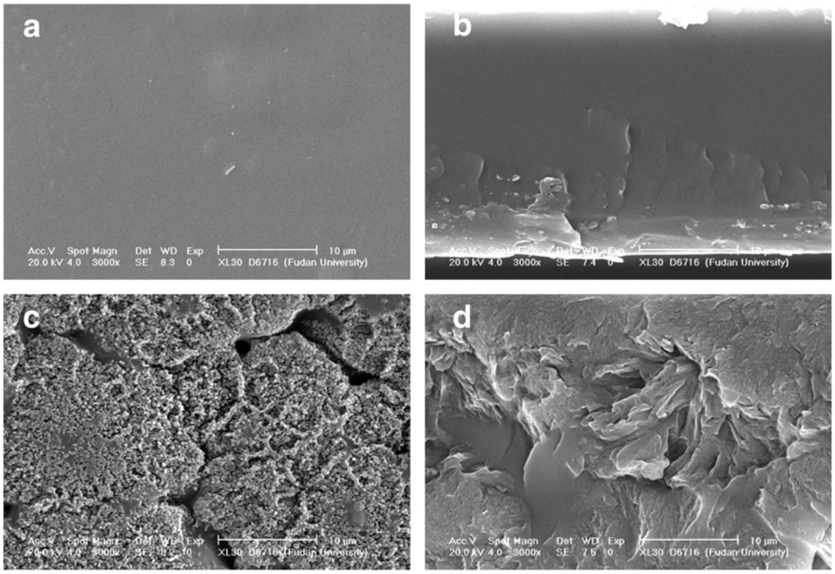

Fig. 1. SEM images of (a), (b) surface and cross-section of PAA; (c), (d) surface and cross-section of $LiOPAAB_{1.0}$.

LiOH and $H_2C_2O_4$ ($n_{-COOH}/n_{H_3BO3}/n_{LiOH}/n_{H_2C2O4} = 2/0.9/0.9/0.9$, 2/0.95/0.95/0.95, 2/1/1/1, 2/1.05/1.05/1.05, 2/1.1/1.1/1.1) was marked as $LiOPAAB_{0.9}$, $LiOPAAB_{0.95}$, $LiOPAAB_{1.0}$, $LiOPAAB_{1.05}$ and $LiOPAAB_{1.1}$.

The morphology of the membranes was examined by scanning electron microscope (SEM, Philip XL30). The thickness of the membranes was measured with a micrometer (SM & CTW). X-ray diffraction

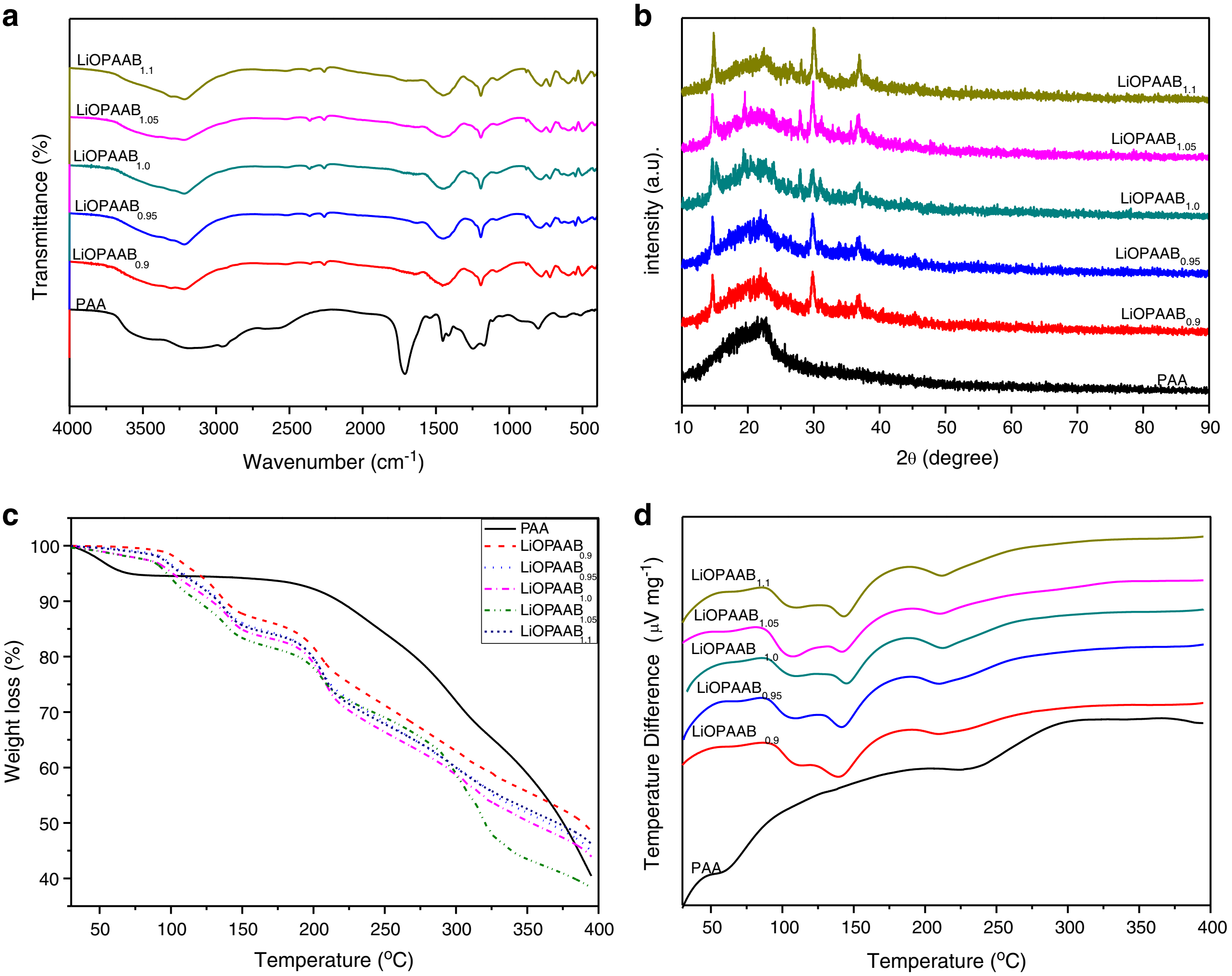

Fig. 2. (a) FT-IR spectra of PAA and LiOPAAB, (b) X-ray diffraction pattern of PAA and LiOPAAB, (c)and(d) thermogravimetry (TG) and differential thermal analysis (DTA) curves of PAA and LiOPAAB. Scan rate 10 °C min^{-1}.