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A lithium poly(pyromellitic acid borate) gel electrolyte membrane for lithium-ion batteries

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Abstract Lithium poly(pyromellitic acid borate) (PPAB) was synthesized via polymerization of lithium tetramethanolatoborate and silylated pyromellitic acid. The synthesized material was characterized by Fourier transformation infrared spectroscopy, ^{11}B nuclear magnetic resonance, scanning electron microscopy, and thermogravimetric analysis. And electrochemical characterizations were carried out on the blended PPAB/PVDF-HFP membrane. The PPAB-based composite membrane exhibits high lithium ionic conductivity, a broad electrochemical window and a high lithium-ion transference number. The battery cells assembled with the PPAB/PVDF-HFP/EC:PC composite membrane as the electrolyte perform reasonably well not only at elevated temperature but also at room temperature with good cyclability and discharge capacity, making the material suitable for applications in lithium-ion batteries.

Introduction

Rechargeable lithium-ion batteries have been widely used to power a wide range of electronic devices and deemed to be one of the major power sources for electric vehicles [1]. To continue enhancing the battery performance to meet increasing energy demand, design and development of novel electrode and electrolyte materials with better thermal and electrochemical properties is of fundamental importance. In recent years, numerous novel electrode materials with higher capacity and improved stability have been discovered [2–4]. In comparison, efforts to develop stable electrolytes capable of sustaining high voltage electrochemical processes have remained relatively modest.

Commercial liquid electrolyte $LiPF_6$ has been known to suffer from moisture sensitivity and thermo instability, and thus may lead to safety-related consequences [5]. To overcome this shortcoming, polymer electrolytes have been developed by using small inorganic lithium salts as the ion carriers in polymer matrices [6, 7]. Nevertheless, problems associated with concentration polarization and small Li^+-ion transference numbers still persist. The concept of single-ion polymer electrolytes (SIPEs), in which only lithium ions are mobile and the counter ions are anchored in the polymer backbones [8–14], was recently proposed with the aim to achieve higher ionic conductivity and better electrochemical and thermal stability. Unfortunately, the majority of SIPE-based batteries reported to date have been found to display relatively low ionic conductivity and to be operative only at elevated temperatures [8, 14–24]. SIPE-based batteries with room temperature performance have only been recently reported [25].

In this paper, we report room temperature performance of a Li-ion battery with a SIPE membrane as the electrolyte. The SIPE material is made of sp^3-boron atoms residing in a polymeric framework; each boron atom is linked by four covalently bonded oxygen atoms associated with aromatic groups in the polymer backbones to facilitate charge delocalization through π-conjugation. To maintain charge neutrality, Li-ions are introduced in the polymer matrix with a weak association with the anionic centers. The charge separation in the compound gives rise to high ionic conductivity and thus enables room temperature

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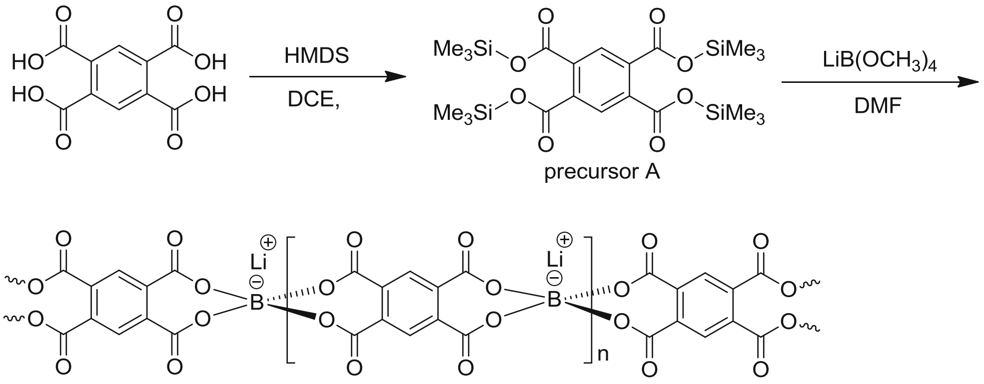


Scheme 1 Procedure of PPAB synthesis

battery performance. The poly(pyromellitic acid borate), PPAB electrolyte, reported in a previous communication [24], was successfully synthesized and the material displays a reasonably high ionic conductivity. However, batteries assembled with the PPB/PVDF blended membrane could not perform because of the high interfacial resistance between electrodes and the electrolyte membrane. This is chiefly attributed to the high crystalline nature of PVDF, which limits the swelling capability of the membrane required to accommodate the organic solvents inside the battery cells [26, 27]. To overcome the problem, PVDF-HFP, a copolymer with much lower crystallinity than PVDF [28], was used for casting the PPAB/PVDF-HFP solution to form membranes. The resultant membranes are with tunable thickness and flexibility and thus reduce the interfacial resistance significantly. As a consequence, significant room temperature battery performance was observed. The results demonstrate that the SIPE-based membranes are well suited for applications in Li-ion batteries in a wide temperature range.

Experimental

The synthesis protocol of the sp^3 boron-based polymer electrolyte with the polyanions in the backbone was done through polymerization of the two monomers shown in Scheme 1.

Materials

Pyromellitic acid (Alfa-Aesar), hexamethyldisilazane (HMDS; Alfa-Aesar), trimethyl borate (Alfa-Aesar), lithium metal (Chemmetall), trimethylsilyl chloride (Alfa-Aesar), 1,2-dichloroethane (DCE; Merck), methanol (Fisher), *N*,*N*-dimethylformamide (DMF; Tedia), acetonitrile (Tedia).

Synthesis of poly(pyromellitic acid borate)

Synthesis of lithium tetramethanolatoborate ($LiB(OCH_3)_4$)

Lithium tetramethanolatoborate was synthesized and purified according to the procedure proposed by Wuhr [29]. Nuclear magnetic resonance (NMR) spectra in DMSO-d_6: ^{1}H, δ 3.16 ppm (s); ^{13}C, δ 48.50 ppm; ^{11}B (relative to $BF_3{\cdot}Et_2O$), δ 3.62 ppm.

Synthesis of silylation derivative of pyromellitic acid (precursor A)

The silylation was carried out under argon atmosphere through a pyromellitic acid reaction with anhydrous HMDS in dehydrated DCE at 100 °C. The organic solvent (DCE) and an excess of hexamethyldisilazane (HMDS) were then removed using Rota vapor. The silylated pyromellitic acid was characterized by ^{1}H NMR ($CDCl_3$): δ ppm 7.96 (2H, s), 0.39 (18H, s).

Synthesis of PPAB

The polymerization was done by stirring silylated pyromellitic acid with lithium tetramethanolatoborate in DMF at 50 °C for 3 days under argon atmosphere. The resultant product was collected through filtration followed by purification by a soxhlet extraction with acetonitrile. The product was then dried at 120 °C for 24 h. Fourier transformation infrared spectroscopy (FT-IR) data (KBr, cm^{-1}): 1356, 1300, 1263 and 1117. NMR spectra in DMSO-d_6: ^{11}B (referenced to $BF_3{\cdot}Et_2O$) δ ppm 2.37, 20.11.

Gel polymer electrolyte membrane preparation

150 mg PPAB, 150 mg PVDF-HFP, and 8 mL DMF were added into a small vessel and kept stirring at 80 °C to obtain a transparent solution, which was then casted onto a

petri dish and dried in an oven at 80 °C. The membrane was further dried in a vacuum oven at 80 °C for 12 h. Finally, the membrane was transferred into a glove box filled with argon and placed in an EC/PC (1:1) solution.

Methods

The IR spectroscopy of PPAB was obtained using Shimadzu 8400 FT-IR spectrophotometer with a frequency range of 600–4000 cm^{-1}. The boron NMR of the synthesized material was performed using a Bruker Avance 500 MHz. Thermal stability of the compound was investigated by thermogravimetric analysis (TGA) using SDT TA Instruments 2960 Simultaneous DTA–TGA from room temperature to 900 °C with 10.0 °C min^{-1} ramp under nitrogen atmosphere. The microstructure of the polymer and its membrane was imaged using EOL JSM-6701F field emission scanning electron microscopy (FE-SEM). Samples were platinum-sputtered (40 s, 20 mA) before imaging.

Ionic conductivity of the prepared PPAB/PVDF-HFP/EC:PC composite membrane was measured in a sandwich SS/membrane/SS cell using electrochemical impedance spectroscopy (EIS) with a potentiostat–galvanostat Autolab model PGSTAT12/30/302 over the frequency range of 1 Hz–4 MHz with the oscillating voltage of 5 mV. The electrochemical stability measurement was conducted using a CHI workstation in the range from 2.5 to 6 V at the rate of 1 mV s^{-1}. A lithium foil was employed as a counter and reference electrode. Lithium-ion transference number was measured by sandwiching the membrane with two lithium foil electrodes. After initial resistance was measured by EIS, a potential of 100 mV was applied until a steady state was reached. Subsequently, the final resistance was measured again.

To analyse the battery performance, a multichannel battery testing instrument Arbin BT-2000 was used for the discharge capacity measurement of the coin cells assembled with the synthesized polymeric electrolyte membrane. The composite cathode was prepared by casting a well stirred solution of $LiFePO_4$ (75 %), PVDF (10 %), acetylene black (10 %), and lithium sulphonamide monomer ionic conductor (5 %) as a supporting electrolyte in the NMP solvent onto an aluminum foil. The resulting electrode was dried in a vacuum oven at 80 °C for 12 h and subsequently cut in a circular shape used in coin cells. The assembling of the standard coin cells (CR2025) was done inside a glove box.

Results and discussion

Synthesis and characterization of PPAB

As depicted in Scheme 1, PPAB was synthesized via polymerization of a silylated pyromellitic acid with lithium tetramethanolatoborate. GPC analysis of the polymer in the aqueous phase gives the number average molecular weight (M_n) of 7400, weight average molecular weight (M_w) of 8900, and a poly dispersity index of 1.21 based on the polystyrene standard. The IR spectra of PPAB (shown in Fig. 1) exhibit the characteristic absorption bands associated with the B–O stretching modes in the range of 1000–1400 cm^{-1}. Specifically, pronounced features are observed at 1356, 1300, 1263, and 1117 cm^{-1} as expected. The broad peak at ~3000 cm^{-1} is attributed to the absorbed moisture and the strong peak at 1700 cm^{-1} corresponds to $\nu_{c=o}$. The ^{11}B NMR spectra of PPAB (Fig. 2) clearly indicate that the majority of the boron atoms in the compound adopt a sp^3-configuration [30]. Nevertheless, a sp^2 boron component is still visible due to the strong tendency of boron to form a planar configuration.

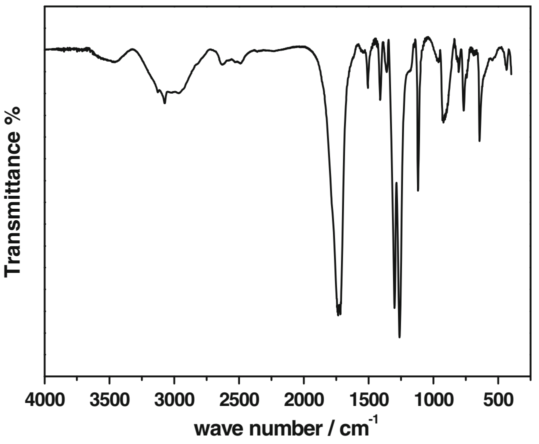


Fig. 1 The FT-IR spectrum of poly(pyromellitic borate) (PPAB)

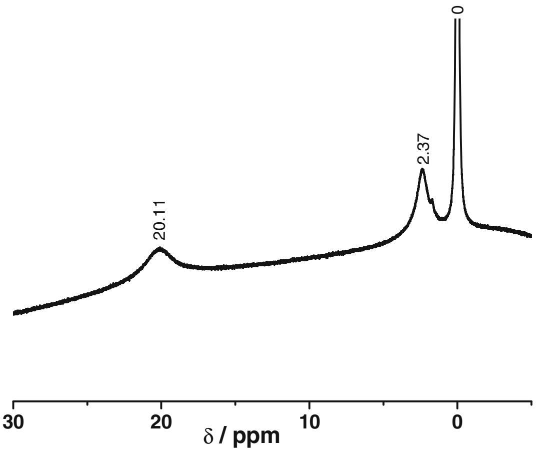


Fig. 2 The ^{11}B NMR in DMSO-d_6 referred to $BF_3{\cdot}Et_2O$

The TGA curve of PPAB under nitrogen is shown in Fig. 3. The first 5 % weight loss before 100 °C is attributed to the evaporation of residual solvent or moisture. No

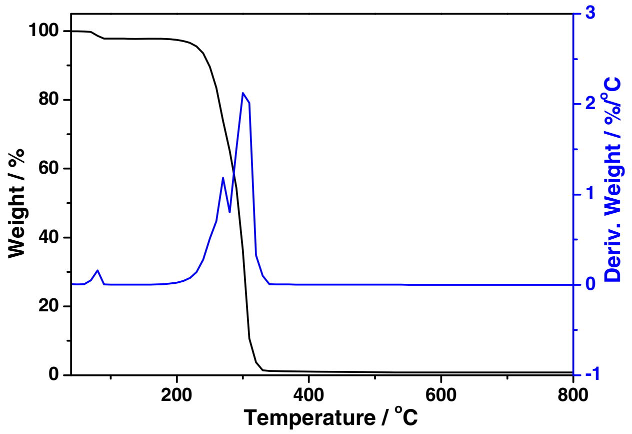


Fig. 3 The TGA thermograph of PPAB (N_2, 10 °C min^{-1}, RT–800 °C)

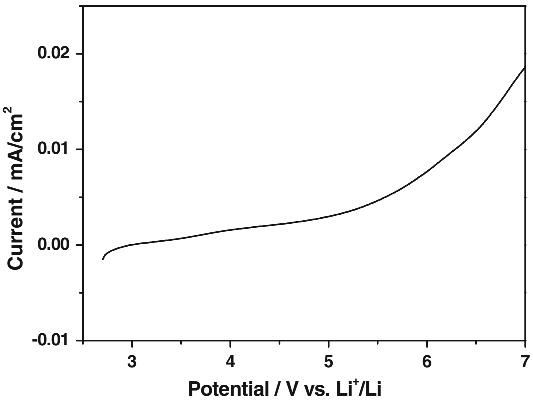


Fig. 5 The linear sweep voltammetry of PPAB/PVDF-HFP/EC:PC composite membrane (1 mV s^{-1})

weight loss is observed till 220 °C, after which the compound decomposes completely. Thermal degradation is probably due to the cleavage of B–O bonds since the pyromellitic acid part is very stable. This one step degradation is probably due to the homogeneity of the four B–O bonds in the polymer. The result suggests that PPAB exhibits sufficient thermal stability up to 220 °C, suitable for battery operation at elevated temperatures.

The FE-SEM images of the PPAB powder (left) and the PPAB/PVDF-HFP polymer electrolyte membrane (right) are shown in Fig. 4. Here, the PPAB particles display a cube-like morphology with a length of approximately 1 µm. The PPAB/PVDF-HFP membrane exhibits pores and channels, which facilitate migration of lithium ions between the electrodes. This porous membrane structure is attributed to the phase separation caused by the rigid PPAB morphology and the flexible PVDF-HFP structure.

Electrochemical stability

The electrochemical stability of the PPAB/PVDF-HFP/EC:PC composite membrane was measured using linear sweep voltammetry shown in Fig. 5. Electrochemically, substantial oxidative degradation of the prepared membrane occurs around 5 V versus Li$^+$/Li, indicating a wide electrochemical window. The result suggests that the PPAB membrane should be stable for battery operation with most commonly used cathode materials [3], such as $LiFePO_4$ (3.8 V), Mn_xO_y (4.2 V) and perhaps even multicomponent metal oxides (4.4–4.8 V) [3].

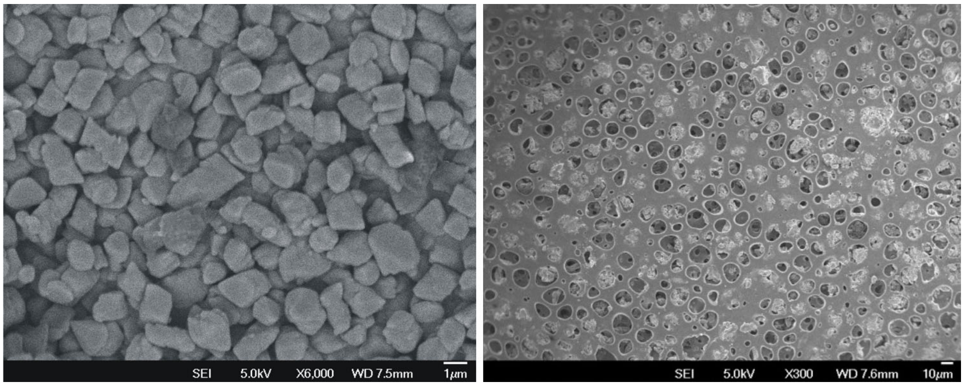
Ionic conductivity

The ionic conductivity was calculated using the equation defined by:

$$\sigma = \frac{l}{Ra},$$

where σ is the ionic conductivity, l is the thickness of the electrolyte membrane, R is the bulk resistance, and a is the surface area. The ionic conductivity derived from the EIS graph shown in Fig. 6 at 298 K is 2.13×10^{-4} S cm^{-1}, which is typical for single ion gel electrolytes [20–22, 31, 32]. The relatively high ionic conductivity is attributed to

Fig. 4 The FE-SEM images of the PPAB powder (*left*) and the PPAB/PVDF-HFP membrane (*right*)



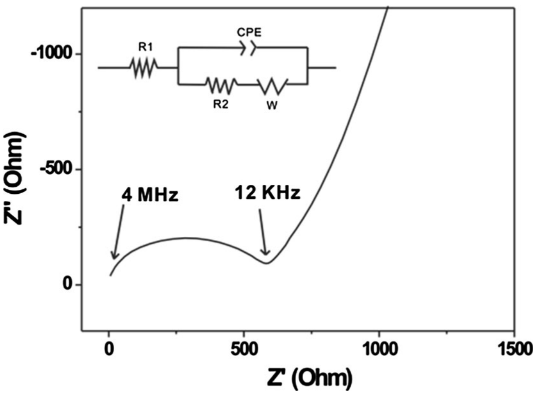


Fig. 6 The EIS graph of the PPAB/PVDF-HFP composite membrane at room temperature

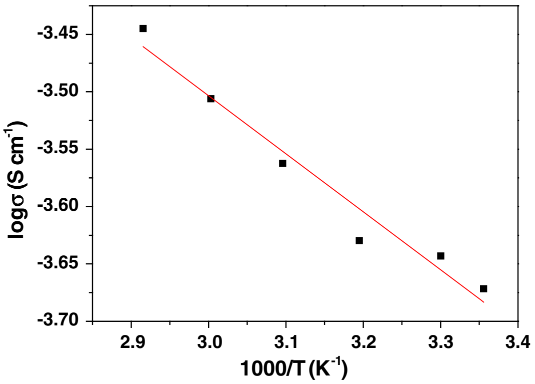


Fig. 7 The temperature dependence of ionic conductivity of the PPAB/PVDF-HFP/EC:PC composite membrane

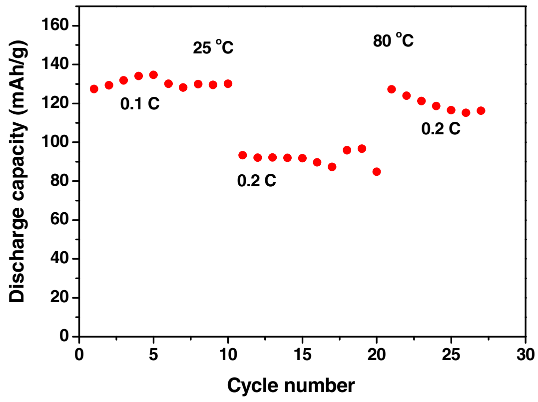


Fig. 8 The cycle performance of the $LiFePO_4$|PPAB/PVDF-HFP|/Li metal cell

the strong electron delocalization effect arising from the sp^3 boron environment in the polymer, which enhances the mobility of Li ions in the polymer matrix.

The temperature dependence of ionic conductivity between 70 and 25 °C downwards is shown in Fig. 7, which displays the typical Arrhenius behavior. The activation energy was calculated to be 9.86 kJ mol^{-1}, on the same order of magnitude of other single-ion electrolytes [20, 22]. The relatively low activation energy arises from the mechanical coupling between the ion transport and the mobility of the polymer host at a given temperature according to the free volume law [17, 19]. The highest ionic conductivity at 70 °C is 3.59×10^{-4} S cm^{-1}.

Lithium-ion transference number

The lithium-ion transference number, t_{Li}^{+}, was measured by sandwiching the prepared membrane between two electrodes [16, 33]. Subsequently, the value was derived using the equation proposed by Evans et al. [34]:

$$t_{\mathrm{Li}}^{+} = \frac{I_{\mathrm{s}}(\Delta V - I_{\mathrm{o}}R_{\mathrm{o}})}{I_{\mathrm{o}}(\Delta V - I_{\mathrm{s}}R_{\mathrm{s}})},$$

where ΔV is the potential applied across the cell, R_{o} and R_{s} are the initial and the steady-state resistances of the passivation layer on the electrodes, and I_{o} and I_{s} are the initial and the steady-state currents. For the PPAB membrane, the calculated value of t_{Li}^{+} is 0.74 at room temperature, which is substantially higher than the values of conventional liquid electrolytes and gel polymer electrolytes [35] but still significantly far from unity. There are two possible reasons. One is due to the relatively small molecular weight, as shown in the GPC data, which promotes concentration polarization. Therefore, increasing molecular weight through optimization of experimental conditions may significantly increase the ion transference number. The second reason may be attributed to some small lithium salt trapped inside the polymer matrix after soxhlet extraction with acetonitrile. Again, optimization of polymerization conditions may help eliminate the problem.

Battery performance

To evaluate battery performance of the PPAB/PVDF-HFP/EC:PC composite membrane, we assembled several coin cells with $LiFePO_4$ as the cathode and a Li foil as the anode.

The discharge cycle performance of the device is displayed in Fig. 8. Remarkably, the battery exhibits performance even at room temperature, which is rare for Li-ion batteries with a SIPE. The results suggest that the electrolyte membrane is indeed battery active, reversible discharge capacities at room temperature was found to be 125 and 90 mAh g^{-1} at 0.1 and 0.2 °C, respectively, still considerably lower than the theoretical value of 170 mAh g^{-1}. There is no significant capacity decline after 10 cycles at 0.1 and 0.2 °C due to the high stability of the prepared membrane. At an elevated temperature (80 °C), the discharge capacity increases to 115 mAh g^{-1} at 0.2 °C as a result of a lower resistance.

The assembled battery failed to work at higher charge/discharge rates likely due to the higher resistance caused by concentration polarization. Once again, it is envisaged that the battery performance can be significantly improved by increasing the molecular weights.

Conclusions

We have synthesized a PPAB complex and used it as a SIPE for Li-ion batteries. The sp^3 boron configuration facilitates delocalization of anionic charges in the polymer framework, leading to enhanced mobility of lithium ions in the polymer matrix. As a consequence, the composite membrane displays a high ionic conductivity on the order of 10^{-4} S cm^{-1} at room temperature and the measured lithium transference number of the SIPE membrane becomes substantially higher than the value of conventional liquid electrolytes and gel polymer electrolytes. The membrane also exhibits good thermostability and electrochemical stability. The battery performance with the composite membrane was evaluated using an assembled coin cell of $LiFePO_4$/SIPE/Li. The cathode delivers a moderately high reversible discharge capacity both at room temperature and at an elevated temperature, remarkable for a SIPE. The battery was demonstrated to be operative in a broad working temperature range. Further enhancement in battery performance is envisaged through improvement of electrode–electrolyte interfacial resistance and reduction of concentration polarization by increasing the molecular weight of the polymer.

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