

# Borate ester plasticizer for PEO-based solid polymer electrolytes

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**Abstract** Lithium rechargeable batteries featuring solvent-free highly conductive solid polymer electrolytes (SPEs) will make a dramatic impact on the electric and hybrid-electric vehicles (EV/HEV) industry by eliminating hazards related to the use of liquid electrolytes. In this paper, we report the synthesis and characterization of a star-shaped borate ester plasticizer, which was then incorporated into the poly(ethylene oxide) polymer matrix in different proportions. Significant improvement was observed in conductivity, with the best value of  $9.1 \times 10^{-5}$  S/cm at 30 °C. These borate ester plasticized SPEs also exhibited excellent thermal and electrochemical stabilities.

**Keywords** Solid Polymer Electrolytes · Ionic conductivity · Borate ester plasticizer

## Introduction

Solid polymer electrolytes (SPEs) exhibit many advantages over liquid electrolytes. With the absence of solvent, the SPEs sharply reduce the hazards of fire and environmental pollution. Problems associated with leakage of harmful liquids or gassing can also be avoided. New Li-ion batteries containing SPEs will increase the efficacy of manufacturing large flat types [1–3]. Among several polymer electrolyte systems, poly(ethylene oxide) (PEO) has shown great potential as the best solvating medium for a variety of

lithium salts. PEO easily solvates cations by interaction with the polar ether oxygen in the main chain and can coordinate effectively with cations to form homogenous solutions. Other advantages of PEO are good chemical, mechanical, and electrochemical stabilities, high flexibility, and the repeat unit  $-\text{CH}_2\text{CH}_2\text{O}-$  provides ideal spacing for maximum solvation of lithium ions. However, PEO-based SPEs exhibit very low ionic conductivity at room temperature because of the low mobility of the ionic charges in the polymer matrix. Various organic solvents, such as ethylene carbonate, have been used to improve ionic conductivity [4–5] but fail to eliminate the hazards related to solvent leakage.

Polyethylene glycol (PEG)-borate ester has been established as a low molecular weight plasticizer to improve the ionic conductivity of PEO-based SPE films. We have now synthesized the PEO-based star-shaped plasticizer,  $\text{BR}_3$  (molecular weight=896), wherein R has 6 PEO units, and incorporated it into the polymer matrix by the method of solvation. Similar work has been reported [6, 7], but our work clearly differs in the processing of SPE film, as it does not involve any polymerization. We used a much simpler method of solvation, with the films obtained by convenient evaporation of the solvent. Four different formulations of these PEO films have been studied, including ionic conductivity measured at different temperatures and electrochemical and thermal properties.

## Materials and methods

### Synthesis of borate ester plasticizer ( $\text{BR}_3$ )

In a Dean-Stark apparatus, 60.330 g (0.172 mol) of methoxy polyethyleneglycol [ $\text{CH}_3(\text{OCH}_2\text{CH}_2)_6\text{OH}$ ] and

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**Table 1** Formulation of the polymer electrolyte films

Sample	SPEC	SPE01	SPE02	SPE03
PEO (g)	1.0011	1.0023	1.0021	1.0009
BR <sub>3</sub> (g)	–	0.2001	0.3004	0.4008
LiTFSI (g)	0.5438	0.5439	0.5441	0.5432

2.004 g (0.02872 mol) of boric acid anhydride (B<sub>2</sub>O<sub>3</sub>) were dissolved in 220 ml of toluene and heated under reflux for 11 h under an argon atmosphere. All volatiles in the resulting liquid were removed in a rotary evaporator and finally, any traces of toluene under high vacuum. The yield was 97%. FTIR(neat): 2,898, 2,868, and 1,126 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 3.85–3.65 (d, 72H, J=12Hz), 3.38 (s, 9H); EA: calc. C 52.23% H 9.10%, found C 51.87% H 9.21%.

#### Preparation of polymer electrolyte films

Four different formulations were prepared to obtain polymer electrolyte films. The polymer chosen for the solid electrolyte system was PEO ( $M_v \sim 5,000,000$ ). The electrolyte salt was 3M's lithium bis(trifluoromethylsulfonyl) imide (LiTFSI), which possesses a very favorable low lattice energy and excellent electrochemical and thermal stability [8]. A 1:12 ratio of Li/O was used. The weight percentage of the plasticizer in the polymer matrix was varied from 1:0.2 to 1:0.4 to procure four different polymer films (Table 1). The amount of plasticizer incorporated into the polymer matrix has been optimized by observing the free-standing nature of the film. To get a free-standing film, it was noted that no more than 0.4 g of plasticizer can be incorporated in a polymer film containing 1 g of PEO.

The traditional solvent casting method was employed to cast the films. The components for each specimen were dissolved in 80 ml of acetonitrile taken in a round bottom flask and kept overnight. The solution was then poured into a beaker and kept at 60 °C under vacuum to remove the

solvent. The resulting film was placed between two Teflon-coated sheets and hot-pressed in a Carver press (150 °C, 15,000 psi, 1 min). The film thickness was controlled by placing two thin steel plates as spacers.

#### Measurement of ionic conductivity at different temperatures

The conductivities of PEO-based electrolyte films were measured by means of electrochemical impedance spectroscopy (EIS). The polymer films were cut circularly and sandwiched between two steel electrodes and subjected to the impedance analyzer. Ionic conductivity was measured for the four films at a temperature range of from 25 to 70 °C. A Solartron model SI 1287 electrochemical interface coupled to a Solartron model 1260 frequency response analyzer was used to obtain all EIS measurements. A 10 mV ac amplitude was applied over a frequency range of 10 and 10<sup>6</sup> Hz. The bulk resistance was obtained from the high frequency intercept of the real axis from the complex impedance plot. The conductivity was calculated using the equation  $\sigma = l/R_b A$ , where  $l$  is the thickness and  $A$  is the area of the respective films.  $R_b$  is the measured bulk resistance.

#### Thermal and electrochemical stability measurements

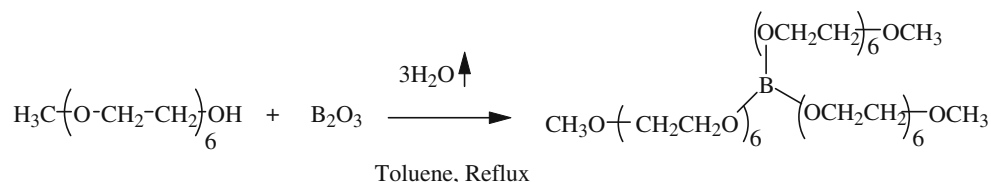
The thermal stability of the polymer electrolyte films were measured by thermogravimetric analysis (TGA). A film composed of SPE03 was subjected to the thermogravimetric analyzer from 25 to 550 °C at a heating rate of 10 °C per minute.

The electrochemical stability of the same film was determined using cyclic voltammetric experiments. A three-electrode electrochemical cell, comprising a working, a counter and a lithium reference electrode was employed. Stainless steel was used as the working electrode.

#### Glass transition temperature ( $T_g$ ) measurement

Differential scanning calorimetry (DSC) measurements were conducted with two of the polymer electrolyte films.

**Fig. 1** Synthesis of polyethylene glycol (PEG)-borate ester plasticizer



**Table 2** Ionic conductivities of solid polymer electrolyte films at various temperatures

Sample	Conductivity (S/cm)					
	25 °C	30 °C	40 °C	50 °C	60 °C	70 °C
SPEC	$2.2 \times 10^{-5}$	$4.6 \times 10^{-5}$	$1.3 \times 10^{-4}$	$3.6 \times 10^{-4}$	$5.3 \times 10^{-4}$	$1.0 \times 10^{-3}$
SPE01	$4.1 \times 10^{-5}$	$7.3 \times 10^{-5}$	$1.9 \times 10^{-4}$	$4.5 \times 10^{-4}$	$6.9 \times 10^{-4}$	$1.1 \times 10^{-3}$
SPE02	$4.3 \times 10^{-5}$	$8.4 \times 10^{-5}$	$2.0 \times 10^{-4}$	$4.6 \times 10^{-4}$	$7.8 \times 10^{-4}$	$1.2 \times 10^{-3}$
SPE03	$5.5 \times 10^{-5}$	$9.1 \times 10^{-5}$	$2.4 \times 10^{-4}$	$5.2 \times 10^{-4}$	$8.3 \times 10^{-4}$	$1.3 \times 10^{-3}$

The films composed of SPEC and SPEB03 were subjected to the DSC measurements from  $-100$  to  $150$  °C to observe the changes in glass transition temperature. The heating rate was  $10$  °C per minute.

## Results and discussion

### Borate ester plasticizer

The plasticizer was synthesized by esterification of boric acid anhydride with an end-capped glycol in good yield (Fig. 1). The plasticizer was fairly thermostable and decomposed near  $250$  °C. The borate ester was characterized by FTIR,  $^1\text{H-NMR}$  and elemental analysis. The IR peaks at  $2,898$  and  $2,868$   $\text{cm}^{-1}$  are attributed to the alkyl C–H stretching frequencies and the  $1,126$   $\text{cm}^{-1}$  absorption was due to C–O stretching. The  $^1\text{H-NMR}$  and elemental analysis data also correspond to the structure of this compound.

### Conductivity

Ionic conductivity was measured at several temperatures in the range of  $25$  to  $70$  °C for four SPE films. The data obtained are shown in Table 2. The trend toward higher conductivity with increasing concentration of plasticizer was readily apparent. The highest conductivity was observed for the film SPE03, where the ratio of polymer and plasticizer was 1:0.4. This ratio, the highest attainable while retaining a free-standing film, exhibited a very favorable ionic conductivity ( $9.1 \times 10^{-5}$  S/cm) at  $30$  °C.

### Thermal and electrochemical stability

In general, all PEO-based electrolytes exhibit good chemical, mechanical, and electrochemical stabilities, as they

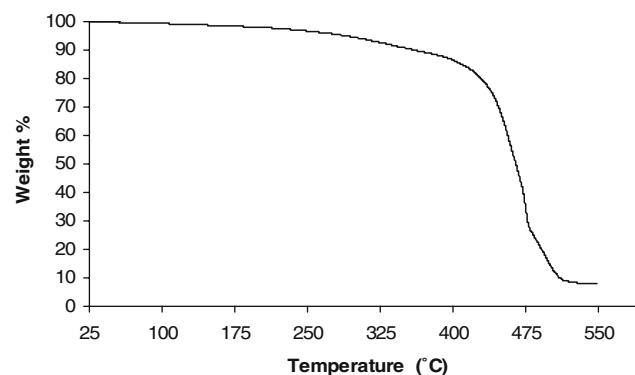
contain only strong unstrained C–O, C–C, and C–H bonds [1]. All the films exhibited excellent thermal stability up to  $300$  °C. A representative TGA thermogram of SPE03 is depicted in Fig. 2. For practical application, it is essential that an electrolyte does not degrade at the melt-processing temperature, which is  $80$ – $90$  °C for PEO. The thermogram of SPE03 indicates suitability of its melt processing capability because of a very nominal weight loss (less than 1%) in the temperature range of  $100$  to  $150$  °C, which is ascribed to absorption of moisture during preparation of the sample for TGA.

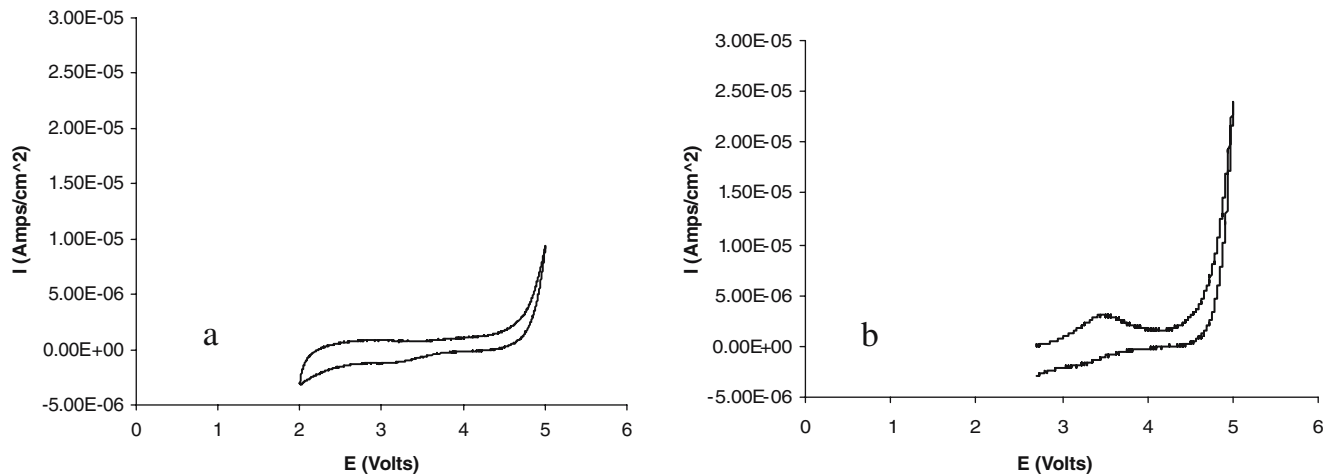
As mentioned above, PEO-based electrolytes exhibit good electrochemical stability. Therefore, as a representative example, we tested SPE03, which contains 40 wt% of borate ester plasticizer. As shown in Fig. 3, the plasticized SPE possesses very good electrochemical stability between the voltage window of  $2.5$  to  $4.5$  V. For most practical applications, especially for constant current cycling, it is essential that the electrolytes be stable within the potential limits of  $3.2$ – $4.2$  V at current densities between  $0.1$  and  $0.2$   $\text{mA}/\text{cm}^2$  [1].

### DSC measurements

The DSC curves for two films were compared (Fig. 4), and a clear shift to lower  $T_g$  for the plasticized polymer film was observed. The onset of glass transition for SPEC is  $-41$  °C and the midpoint  $-39$  °C (enthalpy at  $39$  °C is  $6.53$  J/g), while the onset for glass transition of the plasticized SPE03 polymer electrolyte film is  $-57$  °C and the midpoint  $-52$  °C (enthalpy at  $52$  °C is  $16.9$  J/g).

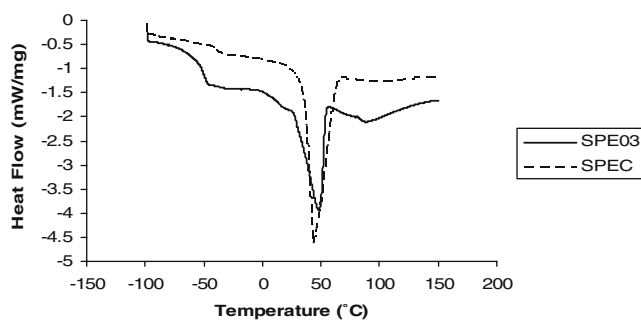
The glass transition temperature of the polymer is directly related to the flexibility of the polymer chains, which also affects the ionic conductivity of the electrolyte.

**Fig. 2** TGA thermogram of SPE03 polymer electrolyte film



**Fig. 3** Cyclic voltammograms of SPEC and SPE03 polymer electrolyte films: **a** without plasticizer, **b** with plasticizer

The lower the  $T_g$ , the higher the flexibility and conductivity. PEO is very flexible ( $T_g = -65^\circ\text{C}$ ) because of the presence of swivel ether linkages and the repeat unit,  $-\text{CH}_2\text{CH}_2\text{O}-$ , provides just the right spacing for maximum solvation, which decreases the energy of coordination with lithium ion. PEO electrolyte behaves like a rubbery material due to the presence of sufficient interchain entanglement and contains both crystalline and amorphous regions. Lithium ion conduction is believed to occur in the amorphous phase via diffusion, which occurs through a complex mechanism involving the PEO segmental mobility [9]. While incorporation of the electrolyte salts raises the  $T_g$  of the polymer, addition of plasticizer effectively compensates by playing a significant role in lowering the  $T_g$  of the polymer by enhancing the mobility of its chain segments. This trend is prominent in our studies.



**Fig. 4** DSC curves for SPEC and SPE03 polymer electrolyte films

## Conclusion

The conductivity data clearly demonstrate that increasing the concentration of a star-shaped borate ester plasticizer in the polymer matrix results in a substantial enhancement of ionic conductivity of the SPE film. This plasticizer facilitates ionic mobility, leading to a best value of  $9.1 \times 10^{-5}$  at  $30^\circ\text{C}$ . The SPE films also exhibited impressive thermal and electrochemical stabilities.

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