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붕소함유 가교제를 기반으로 하는 겔형 고분자 전해질의
리튬이온전지로의 응용

**Gel Polymer Electrolyte
Based on Boron-Containing Crosslinking Agent
for High Performance Lithium-Ion Batteries**

2016년 2월

서울대학교 대학원

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Abstract

Gel Polymer Electrolyte Based on Boron-Containing Crosslinking Agent for High Performance Lithium-Ion Batteries

Ji Su Lee

Polymer Chemistry

Department of Chemical & Biological Engineering

Seoul National University

Boron-containing crosslinking agents having anion-trapping boron moieties and ion conducting poly(ethylene glycol) were synthesized and crosslinked with poly(vinylidene fluoride) (PVDF) with various composition to prepare gel polymer electrolyte for lithium-ion batteries. Dimensional stability at high temperature without any thermal shrinkage was obtained due to presence of PVDF. The gel polymer electrolyte having 80 wt % of boron-containing crosslinking agent and 20 wt % of PVDF exhibited high ionic conductivity ($\sim 4.2 \text{ mS cm}^{-1}$) at 30 °C which is about one order of magnitude higher than that of commercial Celgard separator (0.4 mS cm^{-1}), due to large amount of electrolyte uptake. Furthermore, anion-trapping boron moieties in the gel polymer electrolyte were found to improve lithium transference number, resulting in reduced concentration polarization. As a result, gel polymer electrolytes having boron-containing

crosslinking agents showed excellent cycle performance during 100 cycles.

Keywords: Lithium ion batteries, gel polymer electrolytes (GPEs), semi-IPN, boron, lithium transference number

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1. Introduction

Lithium-ion batteries (LIBs) which have been widely used in portable electronics are the most promising power sources for large-scale applications such as electric vehicles and energy storage system.^{1,2} Since the safety of LIBs is extremely important factor for the large-scale application, many studies concerning volatile and flammable organic solvent in electrolyte have been devoted to improving the safety of LIBs.³⁻¹⁰ Solid polymer electrolytes for all solid-state batteries can conduct lithium ion by mobility of polymer without leakage of liquid electrolyte, but the use is limited due to low ionic conductivity($10^{-8}\sim 10^{-4}$ S cm^{-1}) at room temperature.⁵⁻¹² Gel polymer electrolytes (GPEs), swollen polymer matrix in lithium salt solution, have advantages of high ionic conductivity and reliable safety, which combines liquid electrolyte and solid polymer electrolyte.¹³⁻¹⁵ Poly(methyl methacrylate) (PMMA)^{16,17}, poly(acrylonitrile) (PAN)¹⁸⁻²⁰, poly(vinylidene fluoride) (PVDF)^{21,22}, and poly(ethylene oxide) (PEO)^{17,20,23,24} are generally used for polymer matrix for GPEs and the GPEs based on the polar

polymers have different characteristics because the matrix has interaction between ions and constituent of liquid electrolyte. Among them, PVDF has good mechanical, electrochemical stability, and high electrical constant, but it is not able to hold large amount of liquid electrolyte unless specific strategy is introduced.²⁵ PEO can absorb large amount of liquid electrolyte due to high affinity between liquid electrolyte and PEO, but swollen PEO has low mechanical strength.^{20,26} Therefore, many researches to combine advantages of PVDF and PEO for high performance GPE have been reported.^{25,27}

Meanwhile, lithium ion transference number, defined as the fraction of the total current in an electrolyte by lithium ion, is significant parameter for high performance of LIBs.²⁸ It is ideal that the transference number of lithium ion is close to unity, however in practice most of electrolytes have lower lithium ion transference number than 0.5 causing concentration polarization during charge/discharge cycles.²⁹ In order to enhance the transference number, several studies have been reported; introducing 1) single ion conductor,^{30,31} 2) ceramic fillers (SiO₂, Al₂O₃, and TiO₂),^{32,33} 3) Lewis acids to polymer electrolyte.³⁴

Among them, boron moieties can trap anions through Lewis acid-base interaction between vacant p orbital of boron and anions.³⁵⁻³⁹ Therefore, boron moieties in electrolyte could enhance lithium ion transference number, resulting in reduced concentration polarization.

In this study, boron-containing crosslinking agents having anion-trapping boron moieties and ion-conducting PEO chains were synthesized by two-step reaction to improve ionic conductivity and transference number of lithium ion. In sequence, semi-interpenetrating polymer network (semi-IPN) polymer membranes composed of the boron-containing crosslinking agent and PVDF were immersed in liquid electrolyte to prepare gel polymer electrolyte. Thermal/mechanical properties, ionic conductivities, and lithium ion transference number were investigated depending on PEO chain length and content of boron-containing crosslinking agent, compared to liquid electrolyte or Celgard separator. Gel polymer electrolytes based on boron-containing crosslinking agent exhibited facile ionic conduction and high transference number of lithium ion, resulting in excellent cycle performance.

2. Experimental

2.1. Materials

Poly(ethylene glycol) methacrylate (average $M_n = 360 \text{ g mol}^{-1}$ and 500 g mol^{-1}), trimethyl borate (TMB, $\geq 99.8\%$), poly(vinylidene fluoride) (PVDF, average $M_w = 534,000 \text{ g mol}^{-1}$), 2-Hydroxyethyl methacrylate (HEMA), Trimethylolpropane ethoxylate triacrylate (ETPTA, average $M_n = 912 \text{ g mol}^{-1}$), 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP), and *N*-Methyl-2-pyrrolidone (NMP, 99.5%) were purchased from Aldrich and used as received. Acetonitrile was purchased from TCI and stored over molecular sieves before use. 1.0 M lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) electrolyte solution in a mixture of ethylene carbonate (EC) and diethylene carbonate (DEC) (1:1 vol %) was purchased from PANAXETEC. Co., Ltd.

2.2.Synthesis of boron-containing crosslinking agents (LBC and HBC)

Boron-containing crosslinking agents were synthesized via substitution reaction between TMB and PEGMA having molecular weights of 360 and 500 g mol⁻¹, respectively. Lower molecular weight boron-containing crosslinking agent (LBC) was prepared by the following procedure. PEGMA ($M_n = 360$ g mol⁻¹, 5.0 g, 13.9 mmol) and TMB (5.2 mL, 4.7 mmol) were dissolved in 50 mL of anhydrous acetonitrile and the solution was stirred at 50 °C for 3 h to equilibrate the reaction in dry nitrogen atmosphere. After that, the reaction temperature was raised to 70 °C and stirred for 2 h under nitrogen purge to eliminate methanol generated by the reaction. Unreacted TMB, methanol, and residual solvent were removed under reduced pressure by evaporation. The LBC was dried under vacuum at room temperature for several days. Higher molecular weight boron-containing crosslinking agent (HBC) was also prepared by the same procedure except using PEGMA ($M_n = 500$ g mol⁻¹). Boron-containing crosslinking agent without PEG chain (B-HEMA) was prepared from TMB and HEMA by the same procedure.

After dried under vacuum at room temperature for 2 days, LBC and HBC were obtained with 86.2 % and 83.1% of yield, respectively. Since B-O bond is known to vulnerable to small amount of water in the atmosphere, LBC and HBC were stored in Ar-filled glovebox to prevent possible hydrolysis.⁴⁰ ¹H NMR [300 MHz, CDCl₃, δ (ppm), TMS ref] of LBC and HBC: 6.13 (vinyl, CH), 5.58 (vinyl, CH), 4.31 (CH₂-O-C(O)), 4.05-3.88 (CH₂-O-B), 3.57-3.77 (CH₂-CH₂-O), 1.95 (isobutyl, CH₃). ¹H NMR [300 MHz, CDCl₃, δ (ppm), TMS ref] of B-HEMA: 6.13 (vinyl, CH), 5.58 (vinyl, CH), 4.31 (CH₂-O-C(O)), 4.07-4.05 (CH₂-O-B), 1.95 (isobutyl, CH₃).

2.3.Preparation of semi-IPN polymer membranes (IPMs)

The semi-IPN polymer membranes (IPMs) containing boron-containing crosslinking agent (LBC or HBC) and PVDF with various compositions were prepared by a solution casting and UV curing process. The weight ratios of boron-containing crosslinking agent (LBC or HBC) to PVDF were fixed as 20:80, 40:60,

60:40, and 80:20 and they are abbreviated as L-IPM and H-IPM, respectively. The numbers after the abbreviations represents the weight percent of LBC or HBC. PVDF, boron-containing crosslinking agent (LBC or HBC), and HMPP were dissolved in NMP and the homogeneous solutions were obtained. The injected mass of HMPP was fixed as 10 wt% of that of the boron-containing crosslinking agents. The solution was cast onto a glass plate and then it was exposed to UV light (OV-11 ultraviolet lamp, 60 Hz, FORCELAMP Co., LTD, Korea) for 5 min. The residual solvent was evaporated at 85 °C on a hot plate and the membrane was further dried at 60 °C under high vacuum for several days. Finally, the film was peeled off from the glass plate and the resultant film was placed in a high vacuum condition for a week at 60 °C. The thicknesses of the IPMs were in the range of 150-200 µm. The semi-IPN polymer membranes containing crosslinking agent (B-HEMA or ETPTA) were prepared by the same procedure. The weight ratio of B-HEMA to PVDF was fixed as 20:80 and the weight ratio of ETPTA to PVDF was fixed as 80:20.

2.4.Preparation of gel polymer electrolytes (GPEs)

The gel polymer electrolytes (GPEs) were prepared by immersing the IPMs into 1.0 M LiTFSI in EC:DEC (1:1 vol%) for 24 h. The excessive liquid electrolyte residue on the membrane surface was carefully wiped off with a tissue. The GPEs based on L-IPMs and H-IPMs are abbreviated as L-GPEs and H-GPEs, respectively. The numbers after the abbreviations represent the weight percent of LBC or HBC. The GPEs without boron or PEG chain were prepared from B-HEMA or ETPTA and they are abbreviated as N-GPE20 and E-GPE80.

2.5.Characterization

^1H NMR spectra were recorded on an AscendTM 400 spectrometer (300 MHz for ^1H NMR) and ^{11}B NMR spectra were recorded on a JeolJNM-LA400 spectrometer (400 MHz) with LFG. CDCl_3 (Cambridge Isotope Laboratories) was used as the solvent at room temperature, with TMS as a reference. HPLC analysis

was conducted by WATERS 2487 BREEZE to figure out difference of hydrophilicity between reactants and products. The boron-containing crosslinking agent and PEGMA were dissolved in acetonitrile and the solutions were filtered by 0.4 μm syringe filter. The elution was performed with acetonitrile as mobile phase, and the UV detector was set at 190 nm. The column used in the HPLC was C8 column. The Fourier transform infrared (FT-IR) spectra were recorded in the absorption mode on Nicolet 6700 spectrophotometer with a resolution of 4 cm^{-1} in the vibrational frequency range from 400 to 4000 cm^{-1} . The morphologies were imaged using JEOL JSM-6700F field-emission scanning electron microscope (FE-SEM) with an accelerating voltage of 10 kV. The x-ray diffraction (XRD) spectra were obtained using Rigaku SmartLab ($\text{Cu K}\alpha$) spectrometers. The liquid electrolyte contact angles were measured at room temperature and ambient relative humidity using a Krüss DSA 10 contact angle analyzer connected to drop shape analysis software. The contact angles for each sample were measured more than five times on five independently prepared membranes, and the values were averaged. The amount of liquid electrolyte uptake was determined by measuring

their changes in weight before/after immersion for 24 h. The electrolyte uptake is calculated as the following equation (1):

$$\text{Electrolyte uptake (\%)} = [(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}] \times 100 \quad (1)$$

where W_{dry} and W_{wet} are the weights of the dry IPMs and wet GPEs, respectively.

The glass transition temperatures of the polymers were examined by differential scanning calorimetry (DSC) using TA Instruments DSC-Q1000 under a nitrogen atmosphere. Samples were encapsulated in sealed aluminum pans. The samples were first heated to 150 °C and then quenched to -80 °C. This was followed by a second heating scan from -80 °C to 150 °C at a heating rate of 10 °C min⁻¹.

2.6. Electrochemical characterization

The ionic conductivity of the GPEs was determined using complex impedance spectroscopy with a Zahner Elektrik IM6 apparatus in the frequency range of 0.1 Hz to 1.0 MHz with an AC amplitude of 10 mV. The samples for the measurements were prepared by sandwiching the GPEs between two stainless-

steel electrodes. The ionic conductivity (σ) was calculated from the following equation (2):

$$\sigma = (1/R) \times (d/A) \quad (2)$$

where R is electrolyte resistance obtained from the impedance spectrum, d is the electrolyte thickness, and A is the area of the electrode. Lithium ion transference number (t_{Li^+}) was determined by DC polarization/AC impedance combination method.²⁸ The GPE was sandwiched between two non-blocking lithium metal disks to form a symmetrical Li/GPE/Li coin cell. The cell was polarized by a constant DC voltage of 10 mV and following current values were monitored until steady-state current was observed. The initial and steady-state resistances of the cell were also measured. From this method, t_{Li^+} was determined by following equation (3):

$$t_{Li^+} = \frac{I_s(V - I_i R_i)}{I_i(V - I_s R_s)} \quad (3)$$

where V is constant DC voltage applied to the cell and R_i and R_s are initial and steady-state resistances, respectively. I_i and I_s are initial and steady-state currents,

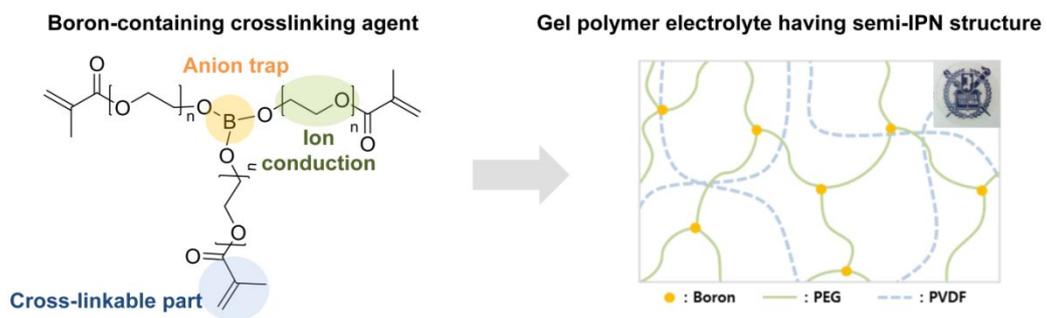
respectively. Electrochemical stability was evaluated by linear sweep voltammetry (LSV) using a potentiostat (VMP3, Biologics) at 30 °C at a scan rate of 1 mV/s. The cell for the measurement was assembled by sandwiching GPE between stainless steel (working electrode) and lithium metal (reference electrode) in 2032 coin cell. The cell was swept in a potential range from 3 V to 7 V (versus Li/Li⁺) at a scan rate of 1 mV/s at 30 °C. Charge/discharge test of lithium-ion battery was performed with a WBCS3000 battery cycler (WonATech) at 30 °C. LiV₃O₈ (70 wt%) prepared as previously described⁴¹ was used as cathode active material and dispersed in NMP with carbon black (20 wt%) and PVDF (10 wt%). The resultant slurry was deposited and cast onto Aluminium current collector using doctor blade. The residual NMP was completely removed under vacuum condition at 120 °C for 24 h. The obtained cathode sheet, lithium metal, and polymer composite electrolytes were punched into disks and assembled together in 2032 coin cell to form Li/GPE/LiV₃O₈ cell. All components were assembled in argon filled glove box (H₂O < 0.5 ppm, O₂ < 0.5 ppm). Charge/discharge test of lithium-ion battery was performed at cutoff voltages of 2.0 ~ 3.6 V versus Li/Li⁺ at 30 °C with a

current density of 1.0 C, where 1.0 C rate corresponds to a current density of 280 mA g⁻¹. Rate capability of Li/GPE/LiV₃O₈ cell was tested at the same cutoff voltages at 30 °C with various current densities.

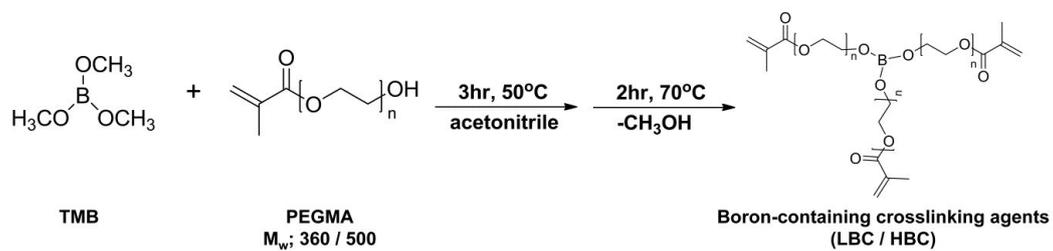
3. Result and Discussion

3.1.Synthesis and characterization of boron-containing crosslinking agent

Boron-containing crosslinking agents were synthesized to be used as gel polymer electrolyte having enhanced ionic conductivity, lithium transference number, and cycle performance of lithium ion batteries. Boron-containing crosslinking agents designed for the purpose have ion conducting PEG chains, anion trapping boron center, and cross-linkable methacrylate group. The concept of gel polymer electrolyte based on boron-containing crosslinking agent is illustrated on Scheme 1. Boron-containing crosslinking agent was obtained by substitution reaction of



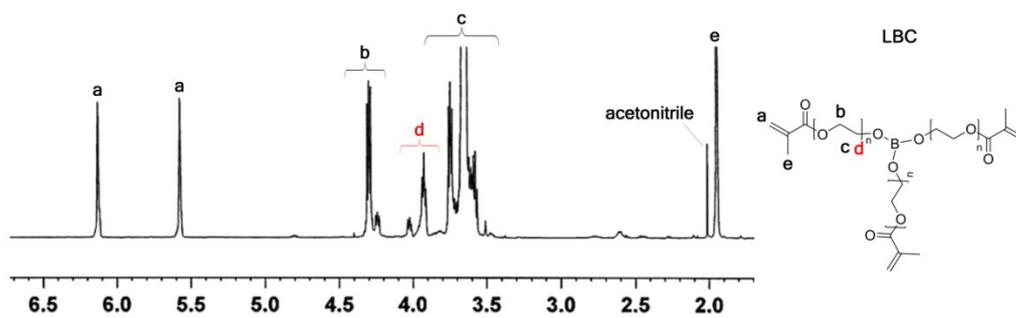
Scheme 1 Conceptual illustration of gel polymer electrolyte based on boron-containing crosslinking agents.



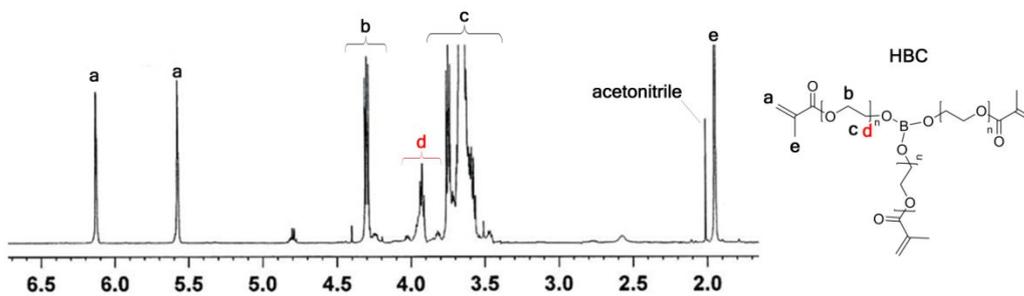
Scheme 2 Synthesis of boron-containing crosslinking agent.

trimethyl borate and PEGMA. (Scheme 2) As the reaction is reversible equilibrium reaction, two-step process is designed for increasing the conversion according to Le chatelier's principle. The reactant mixture reached equilibrium at 50 °C and then methanol, generated as by-product, was removed by raising reaction temperature to 70 °C and blowing out nitrogen gas to flask equipped outlet so that the equilibrium is forced to shift. In order to figure out effect of PEG chain length, two types of PEGMA with different molecular weight were used as reactant. Lower and higher molecular weight boron-containing crosslinking agents are abbreviated as LBC and HBC using PEGMA360 and PEGMA500, respectively. Structure of the boron-containing crosslinking agent was confirmed using ¹H NMR analysis (Fig. 1 (a) and (b)). Signals a and e are assigned to the methacrylate group and signals b and c are attributed to the ethylene oxide units. Peaks at 4.05 - 3.88 ppm (signal d) represent presence of protons near borate, verifying the successful incorporation of the boron moiety into PEGMA.³⁷ When hydroxyl groups are substituted by borate, the proton peaks of PEG chain-end are shifted to higher chemical shift due to electron deficient borate. The conversion of

(a)



(b)



(c)

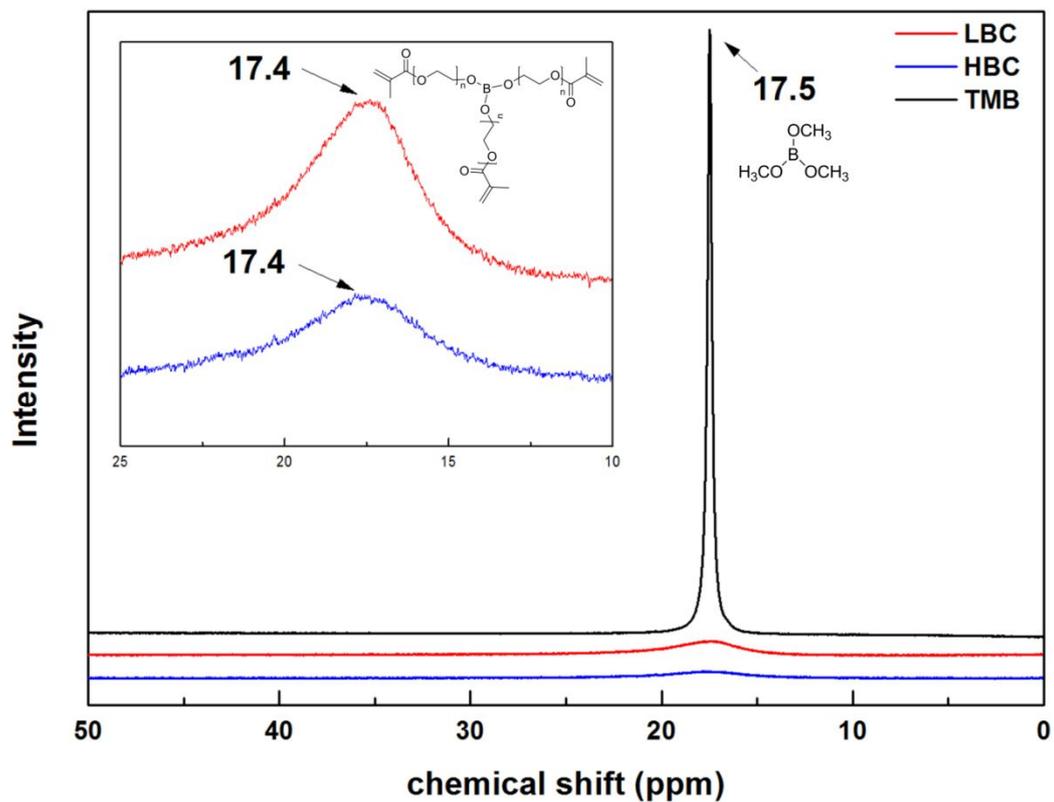


Fig. 1 ^1H NMR spectrum of (a) Low molecular weight boron-containing crosslinking agent (LBC) and (b) High molecular weight boron-containing crosslinking agent (HBC). (c) ^{11}B NMR spectrum of LBC, HBC, and trimethyl borate (TMB).

the reaction was calculated using the equation:

$$\text{Conversion (\%)} = [(I_d/2)/(I_e/3)] \times 100 \quad (4)$$

where I_d and I_e are the intensities of the f and e proton peaks, respectively. The conversions of LBC and HBC are 79 % and 77 %, respectively. Boron-containing crosslinking agents were further analyzed by ^{11}B NMR as shown in Fig. 1 (c). Trimethyl borate has sharp boron peak at 17.5 ppm, while LBC and HBC have broad peaks at 17.4 ppm corresponding to the characteristic signal of the tri-coordinate boron atoms. It can be explained due to effect of PEG chain. HPLC analysis was also conducted to confirm difference of hydrophilicity after the reaction (Fig. S1).

3.2.Preparation of semi-IPN polymer membranes (IPMs) and gel polymer electrolytes

To combine ion conduction properties of boron-containing crosslinking agent and thermal/mechanical/electrochemical stability of PVDF, a series of semi-IPN polymer membranes were prepared simply by drop casting of the mixture of

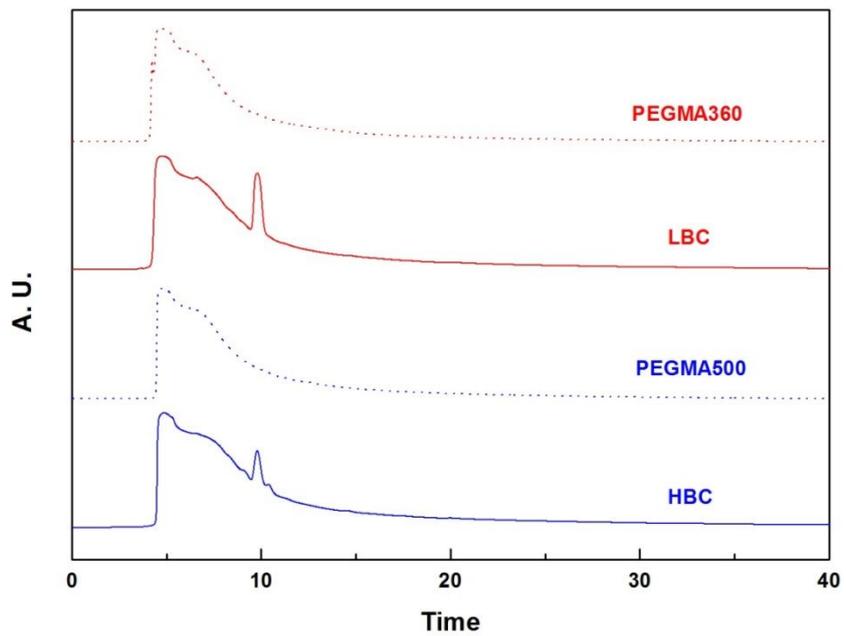


Figure S1. HPLC of PEGMA360, LBC, PEGMA500, and HBC.

boron-containing crosslinking agent, PVDF and photo-initiator in NMP followed by UV curing process. The polymerization of boron-containing crosslinking agent results formation of the cross-linked interpenetrating networks in the PVDF matrix. The semi-IPN polymer membranes (IPMs) are abbreviated as L- or H-IPM#, where L and H indicate that LBC and HBC used for the preparation of the IPMs respectively and # is the weight percentage of boron-containing crosslinking agent (LBC or HBC) in the IPMs. The crosslinking reactions were confirmed by the FT-IR spectra before and after crosslinking (Fig. 2). The peaks at 1637 cm^{-1} assigned characteristic vinyl (C=C) stretch peak appear from both LBC and HBC. After UV cross-linking for 5 min, the vinyl peaks significantly disappeared, demonstrating that the cross-linking reaction was completed for IPMs.^{15,42}

In order to evaluate the effect of boron-containing crosslinking agent content on the properties of polymer electrolytes, IPMs with different ratios of boron-containing crosslinking agent and PVDF were prepared. The IPMs containing different boron-containing crosslinking agent content (20, 40, 60, and 80 wt %) are flexible and free-standing films without aggregation (Fig. S2). All the IPMs

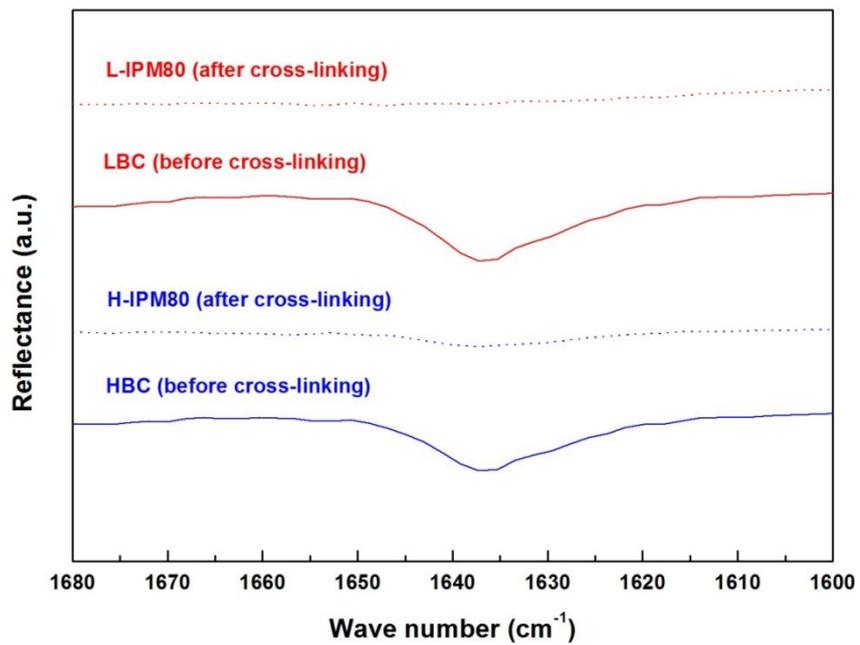


Fig. 2 FT-IR spectra of C=C double bonds of boron-containing crosslinking agent before and after UV cross-linking.

are flexible and dimensionally stable.

The morphologies of IPMs were further investigated by SEM analysis as shown in Fig. 3 (a)~(h). All IPMs show a porous and interconnected structure, which is advantageous for migration of lithium ions. It is well-known that high porosity is beneficial to improve electrolyte uptake and ionic conductivities, also pore diameters should be smaller than 1 μm to prevent movement of active materials, lithium dendritic growth, and electrolyte leakage.^{17,43-45} Pristine PVDF (Fig. 3(i)) has pores with diameters larger than 5~6 μm , while cross-linked LBC and HBC have wrinkled morphologies without pores. In L-IPMs and H-IPMs, highly porous structures with smaller pore size ($< 1 \mu\text{m}$) are observed. Therefore, it is expected safe and high-performance lithium ion batteries can be obtained using IPMs.

Fig. 4 presents XRD patterns for L-IPM80, H-IPM80 and pristine PVDF. The peaks of pure PVDF at $2\theta = 18.2^\circ$, 20.0° , and 26.6° corresponds to (100), (020), and (110) reflection of α -phase crystalline PVDF.⁴⁶ For L-IPM80 and H-IPM80, the diffraction intensity of crystalline peaks significantly decreased, indicating that crystallinity of PVDF reduced upon incorporation of boron-containing

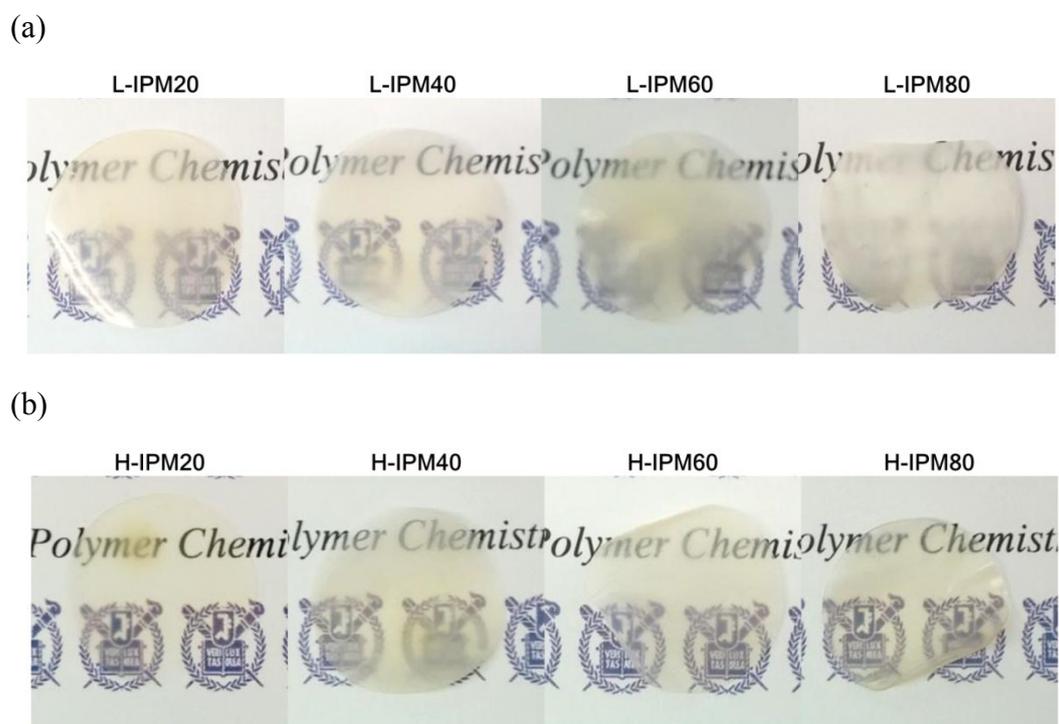


Figure S2. Photographs of semi-IPN polymer membranes (IPMs) having different amount of (a) LBC and (b) HBC after cross-linking and drying process.

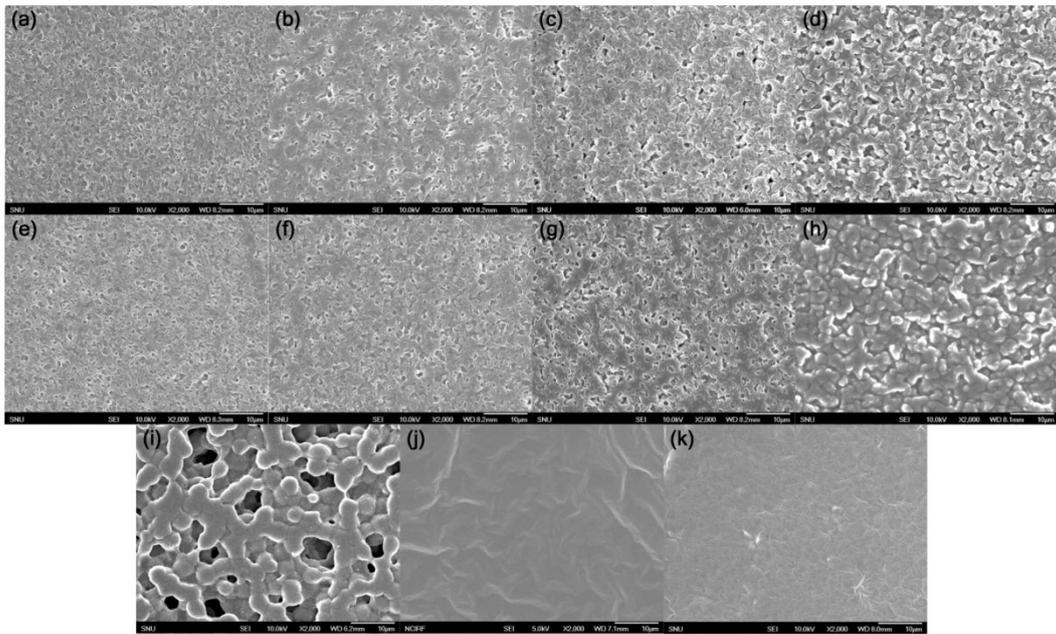


Fig. 3 SEM micrograph of (a) L-IPM20, (b) L-IPM40, (c) L-IPM60, (d) L-IPM80, (e) H-IPM20, (f) H-IPM40, (g) H-IPM60, (h) H-IPM80, (i) PVDF, (j) cross-linked LBC and (k) cross-linked HBC.

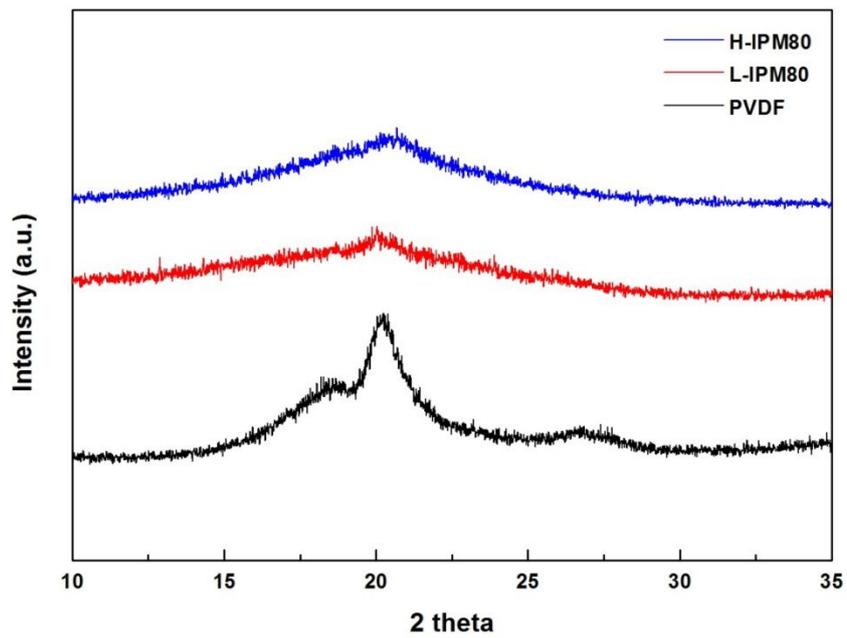


Fig. 4 XRD pattern of PVDF, L-IPM80, H-IPM80.

crosslinking agent. It can be explained because PEG chains in boron-containing crosslinking agent restrict crystallization of PVDF chains. Since amorphous PVDF phase can absorb liquid electrolyte,²⁵ IPMs would be able to obtain high electrolyte uptake which is essential for higher ionic conductivity.

3.3. Thermal and mechanical stability

Thermal stability of gel polymer electrolyte which separate anode and cathode plays an important role for battery safety. Thermal shrinkage test of commercialized Celgard 2320 separator, PVDF, L-IPM80, and H-IPM80 was conducted (Fig. 5). Celgard separator shrank uniaxially after heat treatment at 130 °C for 1 h, originated from internal stress formed historically during stretching process.^{47,48} The separator became transparent after heat treatment at 150 °C for 1h, indicating crystalline to amorphous transition of the separator.^{49,46} Thermal shrinkage of Celgard separator critically affects internal short-circuit failures of lithium-ion batteries.^{50,51} On the other hand, thermal shrinkage of L-IPM80 and

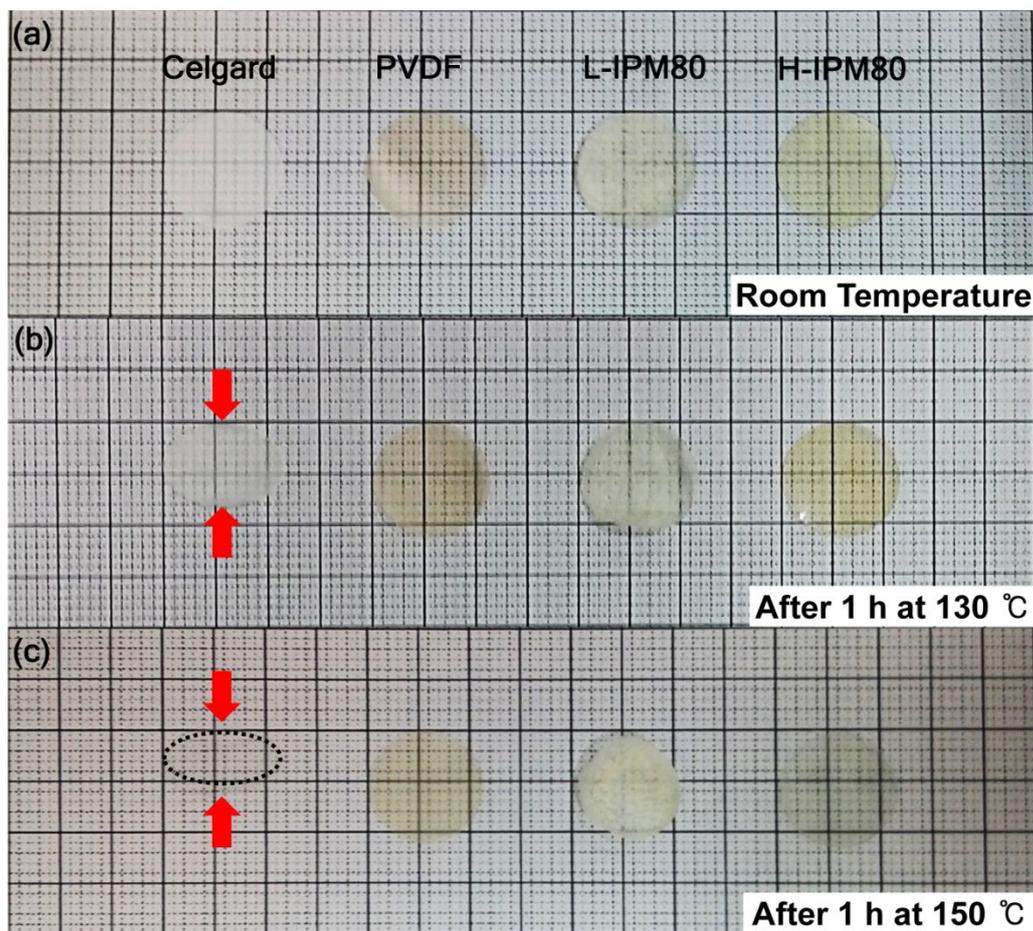


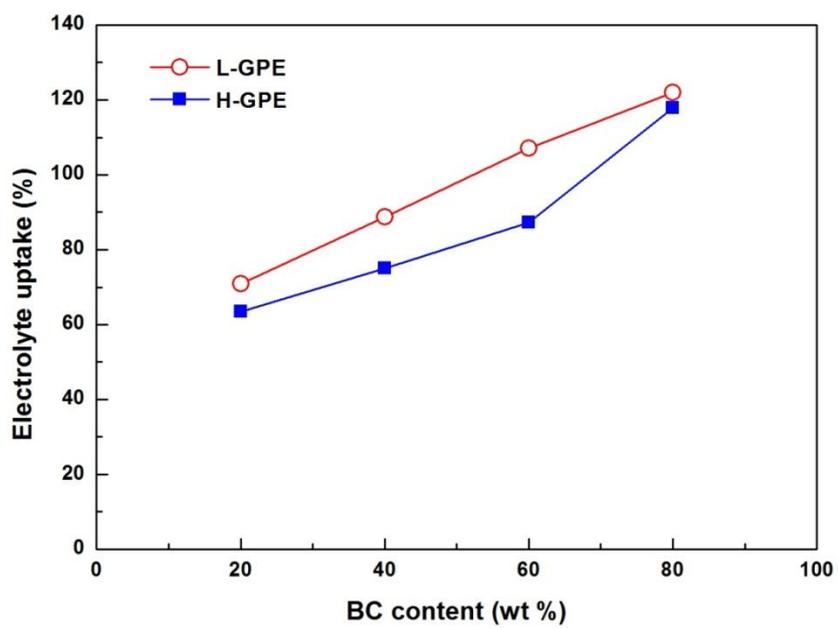
Fig. 5 Thermal shrinkage test of Celgard, PVDF, L-IPM80, and H-IPM80 (a) at room temperature, (b) after 1 h at 130 °C, (c) after 1 h at 150 °C.

H-IPM80 is negligible up to 150 °C due to thermally stable PVDF which has higher melting temperature than polyolefin. Also, improvement of thermal stability is attributed to formation of crosslinked networks.²⁷ Therefore when gel polymer electrolytes impregnated the IPMs are used for lithium-ion batteries, it is expected enhancement of battery safety.

3.4. Ion transport properties

To prepare L-GPEs and H-GPEs which are gel polymer electrolytes based on boron-containing crosslinking agent, the IPMs were impregnated in 1 M LiTFSI solution in EC/DEC (1:1 vol %). Fig. 6 (a) shows liquid electrolyte uptake of gel polymer electrolyte. Electrolyte uptake increases with the boron-containing crosslinking agent content. It can be explained by high porosity shown in SEM images (Fig. 3) and crystallinity reduction of PVDF which is beneficial to absorb liquid electrolyte (Fig. 4). Furthermore, good wettability is related to increasing electrolyte uptake. Photographs of liquid electrolyte (1 M LiTFSI solution in

(a)



(b)

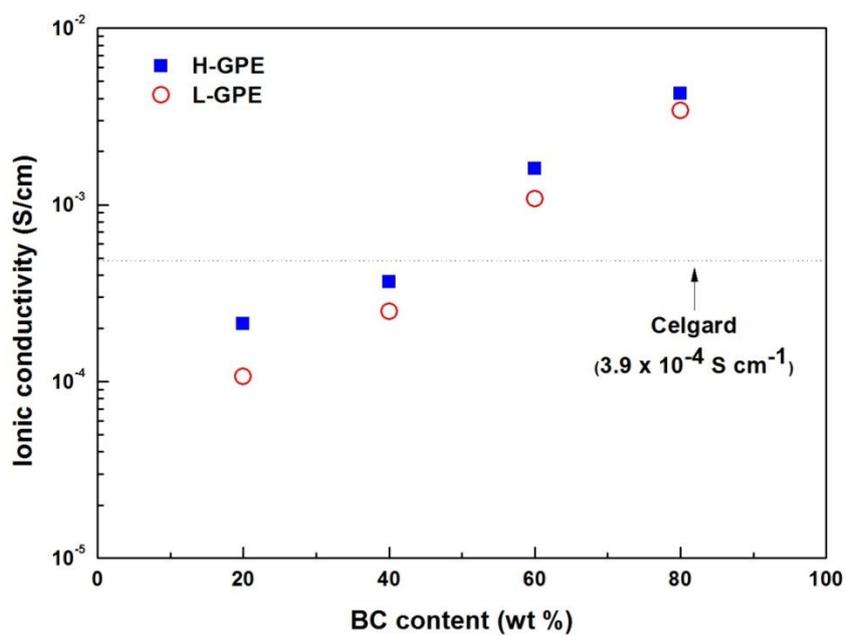


Fig. 6 (a) Liquid electrolyte (1M LiTFSI in EC/DEC) uptake and (b) ionic conductivities of L-GPEs and H-GPEs having different amount of boron-containing crosslinking agent.

EC/DEC) droplet and contact angle values of Celgard 2320 separator, L-IPM80, and H-IPM80 were shown in Fig. S3. Celgard separator consisted of hydrophobic polyolefins exhibited contact angle value of 52.6 °, while L-IPM80 and H-IPM80 having hydrophilic PEG exhibited low contact angle values of 16.2 ° and 15.0 ° respectively, indicating good wettability of the IPMs.

Ionic conductivities of L-GPEs and H-GPEs were plotted as a function of boron-containing crosslinking agent content in Fig. 6(b). Increase of the boron-containing crosslinking agent content increase the ionic conductivity values, which is the same behavior with increasing electrolyte uptake because ions are conducted by charge carriers in electrolyte uptake. As a result, high ionic conductivities (4.2×10^{-3} and 3.4×10^{-3} S cm⁻¹ at 30 °C for H-GPE80 and L-GPE80 respectively) were achieved when 80 wt % of the boron-containing crosslinking agent was incorporated, and this value is more than one order of magnitude higher than that of commercialized Celgard separator (3.9×10^{-4} S/cm at 30 °C). Interestingly, even though electrolyte uptake values of H-GPEs are lower than that of L-GPEs, ionic conductivities of H-GPEs are higher than L-

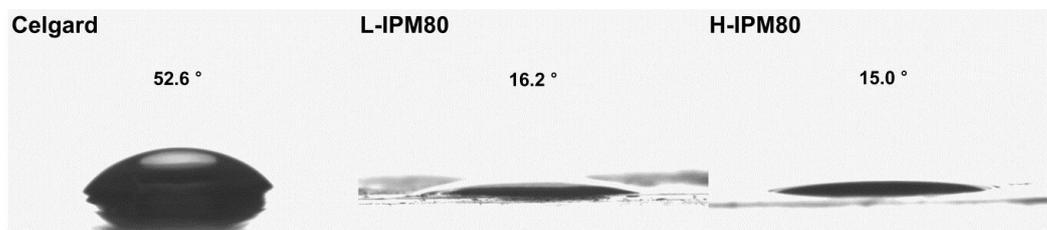


Figure S3. Contact angle of Celgard separator, L-IPM80, and H-IPM80.

GPEs. Glass transition temperatures (T_g) of polymer matrix, L-IPM80 and H-IPM80, were examined by DSC (Fig. S4). Since T_g values of PEG in L-IPM80 and H-IPM80 were -41.4 and -48.9 °C, respectively, IPMs have enough PEG chain mobility to conduct lithium ions. Therefore, lithium ion in gel polymer electrolyte can be conducted by not only solvent molecules but also PEG chain mobility, resulting that H-GPE80 having higher chain mobility has higher ionic conductivity than L-GPE80.

To evaluate Lewis acidic boron effect, lithium ion transference number was measured by DC polarization/AC impedance combination method using Li/electrolyte/Li coin cell. (Fig. 7) Lithium ion transference number in electrolyte systems, generally less than 0.5, is important factor particularly under a high current condition because the low value of transference number may cause a concentration polarization of electrolytes during charge/discharge step.²⁹ Since Lewis acidic boron can trap anions, it is expected that the increase in transference number induces by enhancing the dissociation of the lithium salts, resulting in reduced concentration polarization. Furthermore, it is reported that a significant

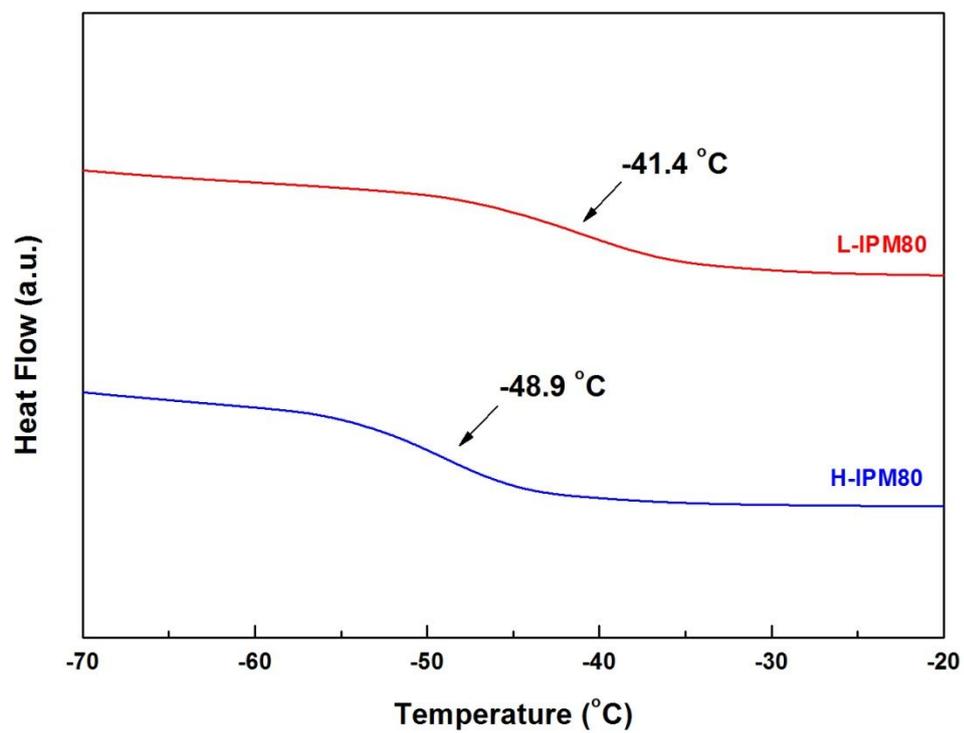


Figure S4. DSC curves of L-IPM80 and H-IPM80.

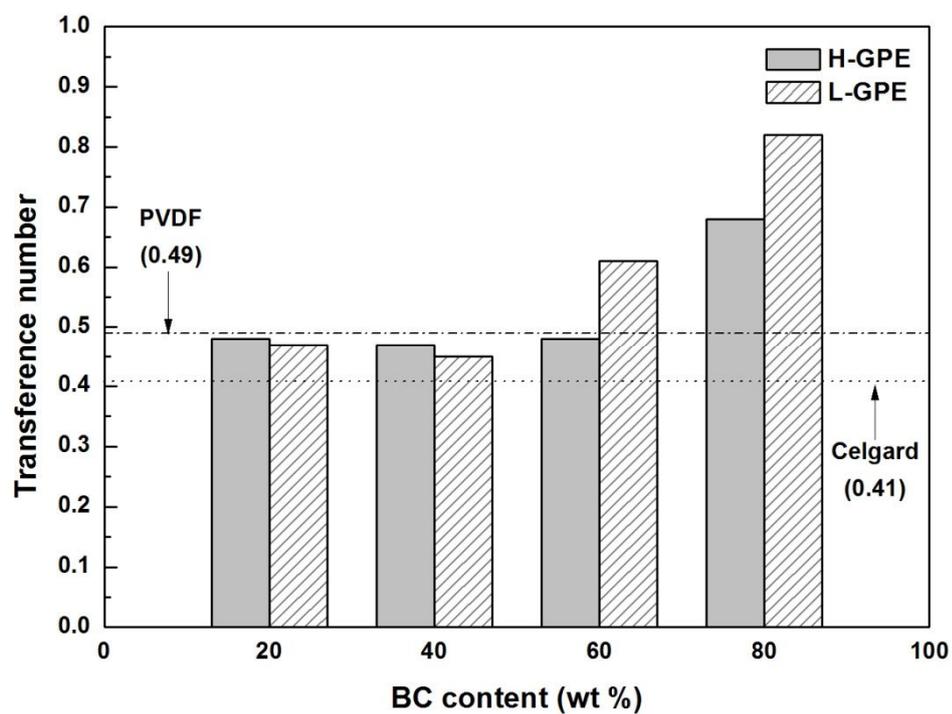


Fig. 7 Lithium transference numbers of L-GPEs and H-GPEs having different amount of boron-containing crosslinking agent at 30 °C.

enhancement of the charge-transfer reaction rate by addition of boron moieties was observed.³⁵

The transference number values were below 0.5 when boron-containing crosslinking agent content was low, while the transference number values gradually increase with boron-containing crosslinking agent content. Maximum transference number value of 0.82 was observed for L-GPE80, which is significantly higher than that of both pristine PVDF (0.49) and Celgard separator (0.41). Transference number values of H-GPEs also increase with the boron-containing crosslinking agent content, while the increase is less compared to that of L-GPEs due to relatively low concentration of boron moieties in the electrolytes. Enhancement of transference number with incorporation of boron-containing crosslinking agent may reduce concentration polarization.

In order to systematically evaluate the effect of boron and PEG content on the properties of gel polymer electrolytes, gel polymer electrolytes were prepared by using crosslinking agents without boron or PEG chain instead of boron-containing crosslinking agents (LBC or HBC). N-GPE20 without PEG chain was prepared by

semi-IPN membrane of PVDF and a crosslinking agent, synthesized from HEMA with same method to synthesize boron-containing crosslinking agent except PEGMA. E-GPE80 which has no boron moieties was prepared by semi-IPN membrane of PVDF and a well-known crosslinking agent, ETPTA. The ionic conductivities and transference numbers of gel polymer electrolytes are summarized in Table S1. The transference number values of L-GPE80 and N-GPE80 were quite close. Also, transference number value for L-GPE80 was nearly twice large than E-GPE80. Therefore, it is revealed that quantitative incorporation of boron moieties enhances lithium ion transference number.^{10,38}

3.5. Electrochemical performance

Electrochemical stability of polymer electrolyte limiting operating voltage for lithium-ion batteries is an imperative factor. Linear sweep voltammogram of L-GPE80 and H-GPE80 to evaluate electrochemical stability is shown in Fig. 8. The abrupt rise in current corresponds to electrochemical decomposition of TFSI

	L-GPE80	H-GPE80	N-GPE20	E-GPE80
Crosslinking agent structure				
PEG unit	6.2	9.4	1	4.7
Boron content (mol / 1g membrane)	5.8×10^{-4}	4.1×10^{-4}	4.4×10^{-4}	0
Ionic conductivity ($S\ cm^{-1}$)	3.4×10^{-3}	4.2×10^{-3}	1.6×10^{-5}	1.3×10^{-3}
Transference number of Li^+ ion	0.82	0.68	0.61	0.30

Table S1. Ionic conductivities and lithium ion transference number of gel polymer electrolytes (L-GPE80, H-GPE80, N-GPE20, and E-GPE80).

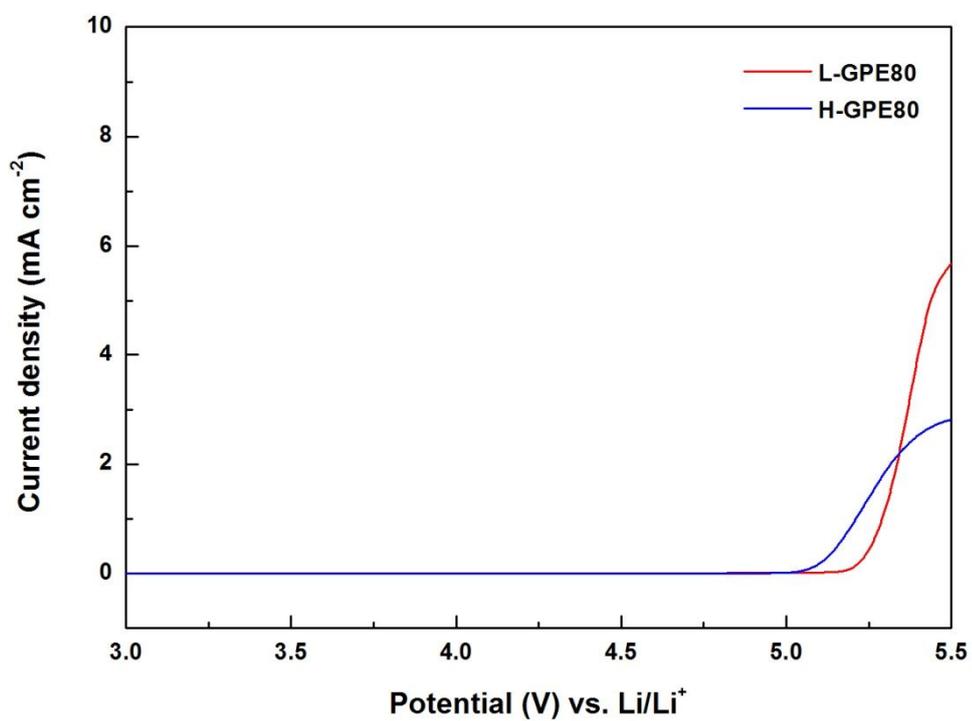
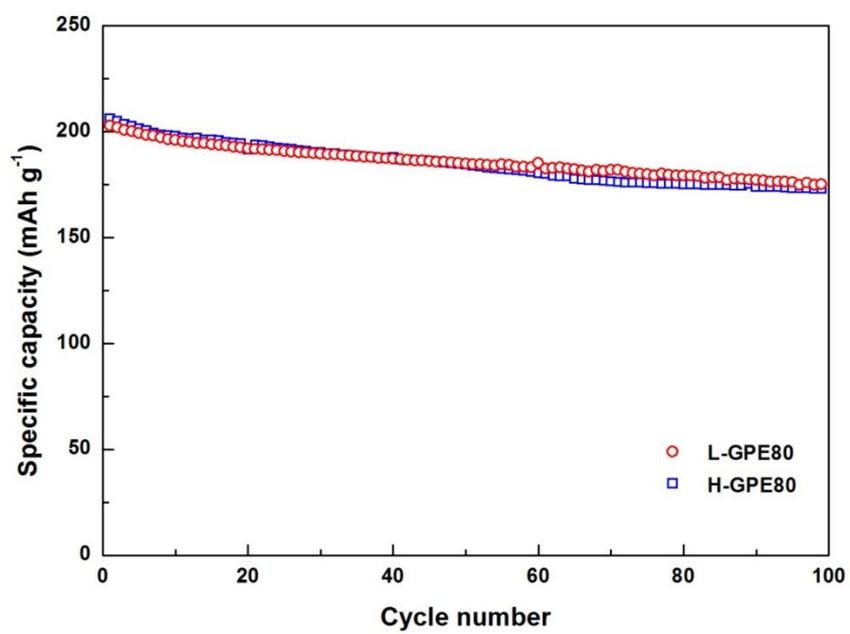


Fig. 8 Linear sweep voltammogram of L-GPE80 and H-GPE80 at 30 °C with a scan rate of 1 mV/s.

anions in electrolyte. The decomposition voltage of L-GPE80 and H-GPE80 were found to be close at about 5.3 and 5.1 V (vs. Li/Li⁺), respectively. It can be concluded that the gel polymer electrolytes based on boron-containing crosslinking agent are electrochemically stable up to 5.0V within the operation voltage range of the LiV₃O₈ cathode as well as high-voltage cathode materials. Electrochemical stability could be attributed to strong complexation between boron and TFSI anions that can retard decomposition of TFSI anions.^{36,38}

Cycle performance of Li/GPE/LiV₃O₈ cells with L-GPE80 and H-GPE80 were tested at 30 °C cycled at 1.0 C rate as shown in Fig. 9 (a). Severe concentration polarization can be induced by high charging/discharging current of 1.0 C, resulting in capacity decay.⁵² When anion-trapping boron moieties were introduced in the electrolyte, it is expected that concentration polarization by localized anions could be reduced and high capacity of the cell could be maintained even at high charging/discharging current density rate. As a result, the initial discharge capacity values of L-GPE80 and H-GPE80 are 203 and 206 mAh g⁻¹ respectively. The capacity values after 100 cycles of 175 and 173 mAh g⁻¹ are

(a)



(b)

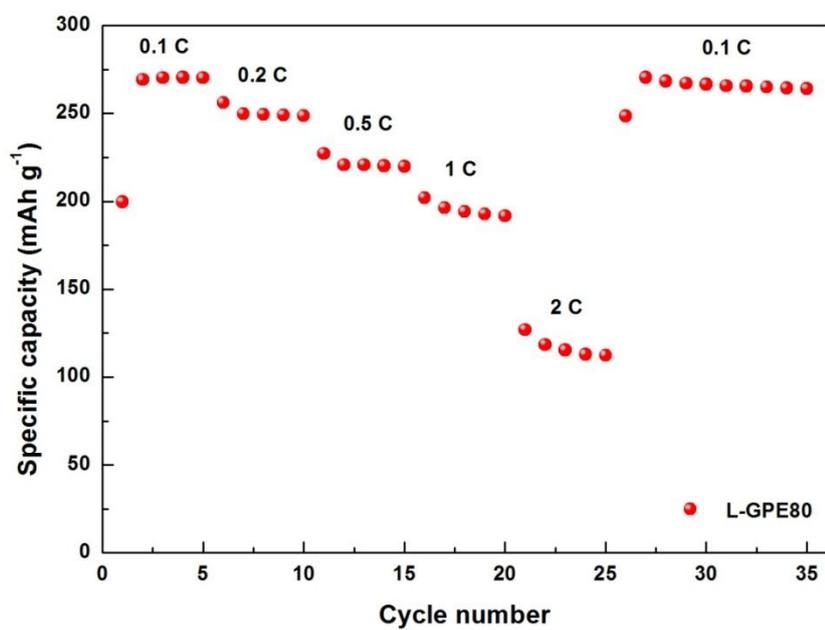


Fig. 9 (a) Discharge capacity profiles of Li/LiV₃O₈ cell cycled at 30 °C with scan rate of 1 C using L-GPE80 and H-GPE80. (b) Rate capability of Li/LiV₃O₈ cell with L-GPE80.

observed, which indicating capacity retentions are 86.2 and 84.0 % for L-GPE80 and H-GPE80 respectively. It was demonstrated that H-GPE80 having larger PEG content has higher initial capacity due to high ionic conductivity, whereas L-GPE80 having larger boron content has higher capacity retention due to high lithium ion transference number. Fig. 9 (b) shows discharge capacity of Li/L-GPE80/LiV₃O₈ cycled at various charging/discharging current density of 0.1 – 2.0 C. The discharge capacity value at 0.1 C is 270 mAh g⁻¹, which is very close to the theoretical capacity of the LiV₃O₈. Even though discharge capacities gradually reduced when discharging current density rate increased, high capacities (> 100 mAh g⁻¹) even at high current density of 2 C and cycle reversibility when current density was recovered from 2 C to 0.1 C was observed.

4. Conclusions

In this study, boron-containing crosslinking agents with ion-conducting poly(ethylene glycol) and anion-trapping boron moieties were synthesized and

used for matrix of gel polymer electrolyte having semi-IPN structure with poly(vinylidene fluoride). Dimensional stabilities of the polymer matrix maintained even at the elevated temperature up to 150 °C, preventing internal short-circuit. Maximum ionic conductivity of 4.2×10^{-3} S/cm at 30 °C was achieved when 80 wt% of the boron-containing crosslinking agents were incorporated and this value is one order of magnitude higher than that of the commercialized Celgard separator because of high electrolyte uptake and ion-conducting poly(ethylene glycol). It was found that lithium ion transference number was increased due to incorporating anion-trapping boron moieties, resulting reduced concentration polarization. Furthermore, electrochemical stability was observed since strong complexation between boron moieties and anions retarded electrochemical oxidative decomposition of electrolyte. Charge/discharge test revealed that gel polymer electrolyte based on boron-containing crosslinking agents could deliver high specific capacity and good cycling performance at high charging/discharging current density.

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국문 요약

음이온을 잡아당기는 붕소와 이온전도성 PEG을 포함하는 붕소함유 가교제를 합성하였고 이를 PVDF와 함께 다양한 조성을 가지도록 함께 가교시켜 겔형 고분자 전해질로 응용하였다. PVDF의 존재로 인해 고온에서도 열 수축이 없는 치수안정성이 얻어졌다. 붕소함유 가교제 80 wt %와 PVDF 20 wt%를 가지는 겔형 고분자 전해질은 높은 액체전해질 함침량으로 인해 30도에서 높은 이온전도도 ($\sim 4.2 \text{ mS cm}^{-1}$) 를 보였으며, 이는 상용화된 Celgard separator ($\sim 0.4 \text{ mS cm}^{-1}$) 보다 10배 높은 수치이다. 또한, 겔형 고분자 전해질 내 음이온을 잡아당기는 붕소는 리튬 운반율을 향상시켜 농도분극 현상을 완화시키는 것으로 나타났다. 결과적으로, 붕소함유 가교제를 포함하는 겔형 고분자 전해질은 100 사이클 동안 훌륭한 충방전 특성을 보였다.

주요어: 리튬 이온 전지, 겔형 고분자 전해질, 준상호침투형 가교구조,

붕소, 리튬 운반율