Facile Fabrication of Functionalized Separators for Lithium-Ion Batteries with Ionic Conduction Path Modifications via the γ -Ray Coirradiation Grafting Process

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ABSTRACT: Separators play a vital role in electronic insulation and ionic conduction in lithium-ion batteries. The common improvement strategy of polyolefin separators is mostly based on modifications with a coating layer, which is simple and effective to some extent. However, the improvement is often accompanied by negative effects such as the increase of the thickness and the blockage of the porous structure, resulting in the decrease of energy density and power density. The porous structure of the separators serves as a conduction path for ions to travel back and forth between the anode and cathode, which has an important impact on the performance of lithium-ion batteries. If the porous structure of the separators can be modified, it will essentially affect the ionic transport behavior through the whole conduction path. Herein, we provide a simple and effective method to functionalize the porous polyolefin separator via the γ -ray coirradiation grafting process, where high-energy γ -ray is used to generate active sites on the polymer chain to initiate the grafting polymerization of chosen monomers with



selected functional groups. In this work, 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane, a kind of borane molecule with an electrondeficient group, was chosen as the grafting monomer. After the γ -ray co-irradiation grafting process, both the surface and pores of the polyolefin separators were functionalized by electron-deficient groups in the borane molecule and the whole electrolyte conduction path within the separator was activated. Due to the electron-deficient effect of the B atom, the lithium-ion conduction is promoted and the lithium-ion transference number can be increased to 0.5. As a result, the half-cell assembled with the functionalized separator shows better cycle stability and better capacity retention under high current rate.

KEYWORDS: ion conduction path modification, γ -ray co-irradiation, separator, lithium-ion transference number, lithium-ion batteries

1. INTRODUCTION

With the rapid development of human society and the threat to the environment due to fossil energy, the demand for renewable and clean energy represented by solar energy, wind energy, and hydropower to generate electricity is increasing. However, those kinds of renewable energy often have the problem of a mismatch between the electricity supply and demand in time and space. As a result, the application of energy storage technologies is an essential component to solve the problem.^{1–3} Among them, electrochemical energy storage systems, which are mainly represented by lithium-ion batteries (LIBs), have become a focus of attention due to their long cycle life, high energy density, and so on.^{4–6}

A cell of the LIBs consists of a cathode and an anode isolated from each other by a separator, typically a kind of microporous polyolefin membrane, which contains the liquid electrolyte within the pores and allows the conduction of lithium ions. Although the separator does not participate in the electrochemical reaction, the function it provides to prevent direct contact between two electrodes in principle is the foundation of energy conversion in the cell.^{7–9} Furthermore, from the practical application view, the isolation between two electrodes at any condition is the first importance to keep the battery away from the internal short circuit, which is thought to be the root cause of most safety issues. Therefore, the separator plays quite an important role in LIBs. Porous polypropylene (PP) and polyethylene (PE) separators are still mostly applied in commercial LIBs due to their excellent properties based on polyolefin materials such as chemical/ electrochemical stability, mechanical strength, low cost, and so on.^{10,11} However, those polyolefin separators also suffer from some disadvantages including low thermal stability, poor wettability with the electrolyte, and low lithium-ion trans-

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Scheme 1. (a) Process of Introducing a Borane Molecule into the Polymer Chain of PE Separators by the γ -Ray Co-irradiation Grafting Process; (b) Interaction between a Borane Molecule and Various Species in the LB301 Electrolyte



ference number. Obviously, overcoming the shortcomings of polyolefin separators is of benefit to better LIBs.^{12–16}

Constant efforts have been dedicated to improving the performance of separators by introducing various modification lavers onto one or two sides of the separators. For example, by coating polyolefin separators with a 2–3 μ m layer of Al₂O₃ or SiO₂, a kind of ceramic-coated separator with improved dimensional stability at elevated temperatures has been widely applied in LIBs for electric vehicles. Additionally, Rahman et al.¹⁷ combined thermally and chemically stable boron nitride nanotubes (BNNTs) onto a PP separator through a dip coating process and successfully prepared a new type of BNNT-modified separator. This separator showed further improved thermal stability, and with it, the cell assembled could work stably under temperatures as high as 150 °C. Our group designed a heatproof-fireproof bifunctional separator by coating a flame-retarded ammonium polyphosphate (APP) layer and a phenolic-resin-reinforced ceramic layer on each side of a PE separator. The heat-resistant and fire-resistant dual-function separator was assembled within a Li-Ni_{0.8}Co_{0.1}Mn_{0.1}O₂|SiO_x graphite full battery, which can burn for 30 s without catching fire and can be kept at 300 °C for 10 min without any thermal shrinkage.¹⁸

It is known that a separator works as a partition to separate two electrodes, and most research has focused on how to strengthen the function of "separate" to ensure the safety of the battery. Besides ensuring safety, it is also an effective strategy to improve the electrochemical performance of the battery by simply introducing some functional compounds as a coating layer on the separator.⁹ We coated the PP separators with a layer of magnesium borate fiber (MBO) as a functional ceramic, where MBO acts as a Lewis acid and coordinates with anions in the electrolyte; thereby, the movement of anions was restricted and the lithium-ion transference number could be increased to 0.57.¹⁹ By the coating modification of the separator, the real lithium ionic conductivity was improved and the kinetics of liquid transport was accelerated. Wang et al.²⁰ used plasma treatment to build an ultrathin poly(acrylic acid) (PAA) and ZrO₂ composite-functional-modified film on a PE separator. This modified PE separator showed good physical and electrochemical performance. Kang et al.²¹ produced Ag-nanoparticle-modified porous carbon fibers (Ag-PCNFs) and coated them on the surface of PP separators. Because silver nanoparticles could guide the nucleation of lithium ions onto the surface of the pores inside the fiber, the growth of lithium dendrites was greatly inhibited. This is also thought to provide a positive application prospect of separator improvement for lithium metal anodes.

It should be pointed out that the common method of modified separators is mostly based on the coating layer strategy. It is simple and effective enough to some extent. However, the modification function depends largely on the thickness of the layer. The question is that the improved performance is usually accompanied by increased thickness, whereas clogged pores might hinder the ionic conduction. Furthermore, the increased thickness also reduces the volumetric energy density of the battery, where the loss is thought to outweigh the gain.

How to realize the functionalization of separators without changing their characteristics as much as possible should be taken into further consideration. Actually, as the matrix for the electrolyte, a separator with a porous structure also provides an ionic conduction path. The physical parameters of the porous structure like porosity, curvature, and the diameter of pores could evidently influence the conduction behavior of the electrolyte. It should be keenly noted that the interaction

between a separator and species in the electrolyte would further act upon the electrochemical performance of the battery. The point is that if the porous structure inside the separators can be modified, it is essentially a modification of the ion transport path, which could thus enhance the interaction between the separator and electrolyte. In this way, when the electrolyte passes through the pores of the separators, the species as ions and solvents in the electrolyte can more fully contact the modified functional groups.

Here, we reported a separator modification method to introduce some functional groups onto the backbone of polyolefin by a simple γ -ray co-irradiation grafting process. The irradiation grafting process is a mature polymer modification technology where the irradiation as γ -ray is used to generate active species (free radicals or ions) on the polymer chain, and then the active species initiate the grafting polymerization of chosen monomers with selected functional groups. In this work, 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane, a kind of borane molecule, was chosen as the grafting monomer. After the γ -ray co-irradiation grafting process, both the surface and pores of the polyolefin separators were functionalized by electron-deficient groups in borane molecules and the whole electrolyte conduction path within the separator was activated. Thus, the separators can selectively participate in electrochemical reactions because the ionic conduction behavior could be promoted through the interaction between the modified conduction path within the separator and the species in the electrolyte. The electron-deficient effect of boron atoms makes them act as Lewis acids to coordinate with Lewis bases in the electrolyte such as the carbonate solvent and anions. Thereby, without changing the structure of the polyolefin separators, the lithium-ion transference number was effectively increased and the cell with the modified separator showed improved rate performance. It provides a potential solution to realize the functionalization of the separators and improve the electrochemical performance of LIBs.

2. EXPERIMENTAL SECTION

2.1. Preparation of Modified PE Separators. Scheme 1. shows the preparation process of co-irradiation grafting to prepare boranefunctionalized PE separators. We added 5, 15, and 30 g of 4,4,5,5tetramethyl-2-vinyl-1,3,2-dioxaborolane ($M = 154.02 \text{ g} \cdot \text{mol}^{-1}$, Energy Chemical) into a certain amount of absolute ethanol. After stirring at a speed of 500 rpm for 6 h, ethanol solutions of borane with mass fractions of 5, 15, and 30% were obtained. Then, the PE separators (16 μ m, Asahi Kasei) washed with acetone and dried at 60 °C for 6 h were immersed in the solution. After the inert gas argon was introduced to remove the dissolved oxygen (polymerization inhibition), the solution was placed in the γ -ray radiation field to induce the co-irradiation grafting process. The radiation source was 60 Co γ -ray, and the radiation dose was optimized to be 10 kGy. Followed by washing with ethanol three times to remove the unreacted borane monomers and drying in a vacuum oven at 60 °C for 6 h, the borane-grafted PE separators (marked as PE-g-B separators) were finally obtained.

2.2. Material Characterization. A Fourier transform infrared spectrometer (FT-IR, Nicolet IS5 spectrometer, Thermo Fisher Scientific Inc.) was used to analyze the molecule structure of pristine PE separators and modified PE separators. Thermogravimetric (TG) analysis was performed using an STA449F3 Jupiter thermogravimetric analyzer (NETZSCH Company, Germany) under an Ar atmosphere with a heating rate of 5 °C min⁻¹ from 25 to 800 °C. The surface and cross-sectional morphology and element distribution of the separators were studied using scanning electron microscopy (SEM; Zeiss GeminiSEM 500) and energy-dispersive X-ray spectroscopy (EDS).

The porosity test of the separator was conducted by weighing the mass change of the separator before and after the adsorption of n-butanol (BuOH), and the porosity statistical formula is shown as follows

porosity (%) =
$$\frac{M_{\text{BuOH}}}{\rho_{\text{BuOH}} \times \left(\frac{M_{\text{BuOH}}}{\rho_{\text{BuOH}}} + \frac{M_{\text{m}}}{\rho_{\text{p}}}\right)} \times 100\%$$
(1)

where $M_{\rm BuOH}$ and $\rho_{\rm BuOH}$ are the mass and density of *n*-butanol, respectively, and $M_{\rm m}$ and $\rho_{\rm P}$ are the mass and density of the PE separator, respectively.

NMR spectroscopy of ¹⁹F and ¹¹B was performed on Bruker Avance Neo 500 at 25 °C. To add deuterated reagents and internal standard substances without contaminating the tested substance, the capillary internal standard method was applied in this work, in which a capillary filled with the internal standard solution was inserted into the NMR tube and the tested substance was placed in the NMR tube. The drift of chemical shift was recorded after confirming that the peaks of the internal standard were aligned. The internal standard solution chosen in this work was 0.1 M NaF in D₂O for ¹⁹F NMR and 0.1 M HBO₃ in D₂O for ¹¹B NMR.

2.3. Electrochemical Characterization. Electrochemical impedance spectroscopy (EIS) conducted on an electrochemical workstation (Solartron, SI-1260, U.K.) was used to test the ionic conductivity by assembling a stainless steel/separator/stainless steel blocking cell. The frequency range was 0.1 Hz to 1 MHz, and the formula for calculating ionic conductivity is

$$\sigma = d/R_{\rm b}S\tag{2}$$

where σ is the ionic conductivity, d (16 μ m) is the thickness of the separator, $R_{\rm b}$ is the bulk resistance, and S (2 cm²) is the area of the stainless steel sheet.

The alternating current (AC) impedance and steady-state current method (Metrohm Autolab PGSTAT-302N) was used to test the polarization current and polarization resistance of the separator assembled into a Li/separator/Li coin cell, to calculate the lithium-ion transference number. The calculation formula is shown as follows

$$t_{\rm Lf} = \frac{I_{\rm s}(\Delta V - I_{\rm o}R_{\rm o})}{I_{\rm o}(\Delta V - I_{\rm s}R_{\rm s})}$$
(3)

where $I_{\rm o}$ and $I_{\rm s}$ are the initial current and steady-state current measured by chronoamperometry, respectively; $R_{\rm o}$ and $R_{\rm s}$ are the interface impedance before and after the polarization by the AC impedance method, respectively; and ΔV is the applied polarization voltage (10 mV).

The CHI electrochemical workstation (Chenhua660E) was used to test the electrochemical stability window by linear sweep voltammetry (LSV). A coin cell with different separators was assembled using stainless steel as the working electrode and lithium foil as the counter and reference electrode. The scan rate was 1 mV s⁻¹ between 0 and 5 V (vs Li/Li⁺).

To compare the cycle performance of the pristine PE separators and the modified PE-g-B separators, different separators were used to assemble LiFePO4 half-cells and cycled at different rates. The Nmethyl pyrrolidone (NMP) slurry composed of 80 wt % LiFePO₄ (Guoxian co. Ltd, China), 10 wt % poly(vinylidene fluoride) (PVDF, Sigma-Aldrich), and 10 wt % carbon black was coated on an aluminum foil, which was put in a vacuum oven at 80 °C to dry for 24 h to obtain the LiFePO4 cathode plate. The LiFePO4 cathode, separators, and lithium metal foil were placed in a dry glovebox (Mbraun, Germany) filled with argon gas to assemble the half-cell, where the electrolyte was the mixed solution of 1 mol·L⁻¹ LiPF₆ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) at a ratio of 1:1 (v/v) (LB301, Zhangjiagang Guotai Huarong Co., Ltd). Under different current densities ($1C = 150 \text{ mAh g}^{-1}$), the cycle test of the battery was carried out on the Xinwei battery test system, and the voltage ranged from 2.5 to 3.8 V (vs Li/Li⁺). The AC impedance data of the LiFePO4 half-cell after 100 cycles was

measured in a frequency range of 0.1 Hz to 100 kHz on an electrochemical workstation (Solartron, SI-1260, U.K.).

2.4. Density Functional Theory (DFT) Calculations. DFT calculations were performed by Gaussian09 E.01²² software. The geometries of all of the molecules were optimized using the B3LYP-D3^{23,24} density functional with the def2-SVP²⁵ basis set. Frequency analysis was performed using the same theoretical level to ensure that all structures were at the minimum energy points. The high-precision single-point energy of the optimized structures was further calculated at M06-2X-d3²⁶/def2-TZVP levels.²⁵ Binding energy was calculated by high-precision single-point energy. The molecular surface electrostatic potential (ESP) and bond level were calculated using Multiwfn^{27,28} software at the B3LYP-D3/def2-SVP level. The visualization of surface ESP and molecular structure was performed using VMD²⁹ and CYLview9³⁰ software.

3. RESULTS AND DISCUSSION

The molecular structure of 4,4,5,5-tetramethyl-2-vinyl-1,3,2dioxaborolane ($C_8H_{15}BO_2$) is shown in Figure 1. It is a kind of



Figure 1. Structure of 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane.

organic borane monomer containing a vinyl group and a B atom with the O–B–O triangle structure. Because it contains unsaturated double bonds, it is easily grafted onto the chosen polymer chain induced by the γ -ray co-irradiation process, and the boron atom with the O–B–O triangle structure in the molecule has an obvious electron-deficiency effect.

To confirm whether this borane monomer was successfully grafted onto the PE separators, the pristine PE separator and modified PE-g-B separators grafted with different borane concentrations (5, 15, 30%) were first analyzed by FT-IR. The spectra of PE-g-B separators grafted with different borane concentrations and the pristine PE separator are shown in Figure 2a. It can be clearly seen that all of the infrared peaks of separators before and after the γ -ray co-irradiation grafting process show the characteristic bands of polyethylene separators:^{31,32} the stretching vibration of C-H at 2850- 3000 cm^{-1} and the bending vibration of C-H at 1465 cm⁻¹. This tells that the basic structure of the PE separators has not been changed even after γ -ray treatment. In addition, it can be clearly observed that compared with pristine PE separators, all of the modified PE-g-B separators grafted with different borane concentrations have several obvious newly formed characteristic peaks. The absorption peaks at 1145 and 1310 cm⁻¹ correspond to the stretching vibration of the C-O bond and the asymmetric stretching vibration peak of the B-O bond, respectively.^{33,34} The absorption peak at 1370 cm⁻¹ belongs to the stretching vibration of the -CH₃ bond introduced by the borane molecule. It can be concluded that borane has been successfully grafted onto the -CH2-CH2- chain of PE separators.

The actual grafting ratio of PE-g-B separators grafted with different borane concentrations was tested by TG measurements. As shown in Figure 2b,c, due to the breakage of the C–C main chain, the PE separator was decomposed at about 400 °C. For the modified PE-g-B separators, the weight loss started at about 200 °C, which was mainly caused by the decomposition of the borane molecule grafted on the PE separators. In addition, as the concentration of borane (5, 15, 30%) increased, the weight loss percentage also gradually increased (2.0, 5.9, 9.0%). This also further proves that the borane molecule was successfully grafted onto the PE separators. Furthermore, the degree of grafting could be adjusted by the concentration of the borane monomer in the grafting solution. This is a significant advantage of the radiation



Figure 2. (a) FT-IR spectra of modified PE-g-B separators grafted with different concentrations of borane and pristine PE separators. (b) TG curves of modified PE-g-B separators grafted with different concentrations of borane and pristine PE separators. (c) Enlargement of the marked part in (b).

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Figure 3. (a-d) SEM images of the pristine PE separator and modified PE-g-B separators grafted with different borane concentrations (5, 15, 30%). (e-h) EDX elemental mapping of B and O for the whole surface of the modified PE-g-B separator. (i-l) EDX elemental mapping of C, B, and O for the cross section of the modified PE-g-B separator.

grafting method, with which ready-made polymers with chosen properties such as high chemical stability could be easily modified. This is the advantage that the normal chemical grafting method had to realize.

To observe the microstructure of the modified PE-g-B separators, the surface and cross-sectional morphology of different separators were characterized by SEM. As shown in Figure 3a-d, the surface morphology of the modified PE-g-B separators remained almost the same porous structure as that of the pristine PE separator. Even when the concentration of borane in the grafting solution was increased to 30% and the grafting ratio of the obtained PE-g-B separator was increased to 9.0%, there was no significant decrease in the porosity of the membrane and the diameter of the pores. This result indicates that the well-constructed porous structure of the commercial polyolefin separators can be maintained after the irradiation grafting process. Meanwhile, the compositional distribution of the borane molecule on the PE-g-B separators was further investigated by energy-dispersive X-ray spectroscopy (EDX) mapping. It can be seen in Figure 3e-h that there is a quite uniform distribution of B and O elements on the whole surface of the separator and each fiber of the porous structure is evenly wrapped on the B and O atoms, forming an ultrathin and homogeneous functional molecular modification layer. In addition, elemental analysis was performed on the cross section of the modified PE-g-B separator (Figure 3i-l). It can also be identified that the B and O elements are evenly distributed across the whole cross section of the membrane. This shows the successful introduction of borane to both the surface and inside of the pores of the separators by coirradiation grafting. This is attributed to the significant advantage of the irradiation grafting process. Since energy absorption has nothing to do with the temperature and

molecular structure, the polymer chain can be uniformly activated to form a grafting site by the γ -ray irradiation, and the chosen monomer molecule could be uniformly grafted onto the polymer chain by this convenient γ -ray irradiation process. Once the commercial PE separator with a well-constructed porous structure was immersed into the grafting solution and induced by the γ -ray irradiation, all of the surface of the membrane or inside the pores could be modified with a functional monomer. Furthermore, because the electrolyte was contained in the pores of the separator, the essence of the modification within the porous structure was the functionalization of the ionic conduction path. Here, a typical wet process PE separator with appropriate porosity and a smaller pore size was chosen as the grafting substrate, which is beneficial to enlarge the contact area between the electrolyte and the separator. Therefore, when the various species in the electrolyte pass through the separators, the functional groups modified on the internal pores of the separators can more fully interact with the electrolyte.

However, the modification on the surface of the pores will inevitably occupy the internal space of the separator and reduce the porosity. Therefore, to verify the influence of the molecular modification layer on the porous structure, the change in the porosity of different separators was tested by the *n*-butanol adsorption method. It can be found that the porosity of the modified PE-g-B separator decreases from 43.3 to 41% with the increasing grafting ratio of borane molecules (Table 1). Although the porosity would decrease slightly, it was still in the acceptable range. It is also further proved that an ultrathin modification layer was introduced onto the surface of the porous structure in the separator.

The ionic conduction properties of modified PE-g-B separators were carefully studied through various character-

 Table 1. Physical and Electrochemical Properties of Different Separators

separator	PE	PE-g-B-5%	PE-g-B-15%	PE-g-B-30%
$t_{\rm Li}^{+}$	0.27	0.32	0.5	0.49
ionic conductivity $(mS \ cm^{-1})$	0.63	0.61	0.57	0.53
Li ⁺ ionic conductivity (mS cm ⁻¹)	0.17	0.20	0.29	0.26
porosity	43.5%	43.0%	41.9%	41.0%

izations. Figure 4 shows the Nyquist plots of the SS/separator/SS cells assembled with different separators at 25 $^{\circ}$ C. The bulk



Figure 4. Impedance measurements recorded for SS/separator/SS cells based on different separators at 25 $^\circ$ C.

resistance (R_b) was reflected by a high-frequency intercept on the real axis, while the ionic conductivity can be calculated using R_b . It can be found that the calculated ionic conductivity of all of the modified PE-g-B separators is slightly lower than that of the pristine PE separator, and as the grafting ratio increases, the ionic conductivity gradually decreases (Table 1). This is probably because the porosity of the modified PE-g-B separator decreases slightly after the grafting process as well as the uptake of the electrolyte.³⁵

The ionic conductivity of an electrolyte is thought to be quite important for the stable electrochemical performance of LIBs. However, because only lithium ions could participate in the electrochemical reaction in the energy conversion process, the real lithium ionic conductivity is the determinant parameter of ionic conduction. Figure 5 shows the test results of the lithium-ion transference number, which determines the contribution of lithium ions in the whole ionic conduction. The lithium-ion transference number of all modified PE-g-B separators assembled into Li/separator/Li coin cells is significantly improved compared with that of the pristine PE separator (Table 1), and the lithium-ion transference number can reach as high as 0.5 when the borane concentration is 15% (grafting rate is 5.9%). It is known that in the ordinary electrolyte system, the movement speed of anions is much higher than that of lithium ions due to the coordination of lithium ions and oxygen atoms of organic solvents with lone pair electrons. As a result, the lithium-ion transference number in the liquid electrolyte system is generally less than 0.3.^{20,36,37} Nevertheless, after irradiated grafting of the borane-modified ionic conduction path, the lithium-ion transference number can reach 0.5. Although the ionic conductivity decreased slightly after the grafting modification, it can be easily found that the real lithium-ion conductivity of the electrolyte with the modified PE-g-B separators has been significantly improved. This indicates that lithium ions contribute more to the whole ionic conduction and are thus beneficial for high rate performance with improved mass transfer in the electrolyte. This may be rooted in the B atom in the borane molecule grafted into the ionic conduction path acting as a Lewis acidic site and interacting with the electrolyte. On the one hand, B atoms provide Lewis acid sites to interact with organic solvents such as EC and DMC in the electrolyte, reducing the solvation



Figure 5. Chronoamperometry profiles and AC impedance curves of Li/separator/Li cells assembled with different separators.

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Figure 6. Interaction between borane and various species in the electrolyte. (a) ¹⁹F NMR spectra of LB301 and LB301 + borane. (b) ¹¹B NMR spectra of borane, borane + DMC, borane + EC, and borane + LB301.

between organic solvents and lithium ions.^{38,39} On the other hand, B atoms could attract the anion in the electrolyte^{34,40} with an electrostatic force to restrict the movement of PF_6^- . The synergy effect promotes the conduction of lithium ions; thereby, the lithium-ion transference number increases. In addition, since borane is modified on the ion conduction path, the functional group can be more fully contacted with the electrolyte.

To further explore the interaction between borane molecules and anions, other two kinds of electrolytes with different anions such as 1 mol·L⁻¹ LiTFSI and 1 mol·L⁻¹ LiClO₄ in EC/ DMC (v/v = 1) were applied to measure the lithium-ion transference number. The result is shown in Figure S1. It can be seen that compared with that of the pristine PE separators, the measured lithium-ion transference number of LiClO₄ and LiTFSI electrolytes with the modified PE-g-B-15% separators were increased to a certain extent, from 0.24 to 0.55 and 0.25 to 0.45, respectively. This indicates that a borane molecule has certain Lewis acid and base interactions with anions due to the B atom with the electron-deficient effect. In addition, according to the Lewis acid-base pairing theory,⁴¹ the boron atom plays a role of the "hard" Lewis acid center and also inclines to have a stronger interaction with the hard Lewis base ion like ClO₄⁻. Therefore, it can be concluded that the borane molecule modification layer on the surface of the ionic conduction path can achieve a sufficient interaction effect through direct contact between the functional group and the electrolyte, thereby increasing the lithium-ion transference number. Furthermore, it has general applicability to different lithium electrolyte systems with various salts.

A liquid NMR experiment was carried out to further verify the interaction mechanism. Figure 6 shows the ¹⁹F NMR spectrum of the LB301 electrolyte and the ¹¹B NMR spectrum of borane. Figure 6a shows the ¹⁹F NMR spectrum of the LB301 electrolyte before and after the addition of the borane monomer. According to the principle of resonance coupling and splitting, for PF_6^- , the coupling of six F nuclei and one P nucleus causes the ¹⁹F spectrum to split into double peaks, so there are two ¹⁹F NMR signals in the LB301 electrolyte, which are reflected in Figure 6a as $\delta = -73.53$ and -75.03 ppm.⁴² Compared with the ¹⁹F NMR signal of the LB301 electrolyte, the ¹⁹F NMR signal of the LB301 electrolyte after the addition of the borane monomer shifts by 0.15 ppm (the signals are δ = -73.38 and -74.88 ppm, respectively). Figure 6b shows the NMR spectrum of ¹¹B in the borane monomer before and after being mixed with EC, DMC, and the LB301 electrolyte. It can be seen that, compared with the NMR signal of ¹¹B in the borane monomer (δ = 29.85 ppm), after being mixed with EC,

DMC, and the LB301 electrolyte, the NMR signal of ¹¹B shifts by 0.17 ppm (δ = 29.68 ppm), 0.01 ppm (δ = 29.84 ppm), and 0.17 ppm (δ = 29.68 ppm), respectively. The experimental results of NMR show that the chemical environment change of 19 F reflects the interaction between PF₆⁻ and the borane monomer. When PF_6^- is used as a Lewis base to coordinate with the borane molecule, PF_6^- loses a certain amount of electrons, which reduces the electron cloud density outside the F core, and the shielding effect is weakened. The NMR signal of ¹⁹F shifts to a low field as a result. In this way, when the B atom in borane interacts with various species in the electrolyte, the B atom as a Lewis acid gets a certain amount of electrons, which increases the density of the outer electron cloud of the B atom; the shielding effect is enhanced, and the NMR signal of ¹¹B shifts to the high field.⁴³ It can be proved that a borane molecule can not only carry out Lewis acid-base pairing with PF_6^- to restrict the movement of anions but can also combine with organic solvents in the electrolyte to weaken the solvation between organic solvents and lithium ions. The synergy of the two effects promotes the improved conduction of lithium ions. Therefore, the lithium-ion transference number is increased.

Density functional theory (DFT) calculations were also performed to study the interaction between the LB301 electrolyte and the grafted borane molecule at the molecular level (Figure 7). The results show that the binding energies of



Figure 7. Result of density functional theory (DFT) calculations.

EC, PF_6^- , and DMC with the borane molecule are -36.5, -30.4, and -28.9 kJ·mol⁻¹, respectively, under vacuum, indicating that the borane molecule will attract electron-rich species in the LB301 electrolyte, which is consistent with the NMR spectroscopy. To analyze this interaction deeply, the bond levels in the complex were calculated and the van der Waals surface penetration diagram of the complex was drawn. The Mayer bond levels of the coordination atom (O atom or F atom) to the B atom in the three complexes were 0.02, 0.11, and 0.01, respectively, much less than 1, which indicates that the complex does not form a new covalent bond but combines by intermolecular interaction. The van der Waals surface



Figure 8. (a) Discharge C-rate capabilities of LiFePO₄ half-cells assembled with pristine PE separators and borane-modified PE separators. (b, c) Discharge-C-rate-capability-related discharge profiles of cells. (d, e) Cycle performance of the LiFePO₄ half-cell assembled using the pristine PE separators and the modified PE separators at 1C rate and the corresponding AC impedance spectra in the 2nd and 100th cycles. (f) Cycle performance of the LiFePO₄ half-cell assembled using pristine PE separators at 5C discharge rate.

penetration diagram shows that the positively charged B atom surface (red) of the borane molecule combines with the negatively charged O or F atom (white or blue) surface. The van der Waals surface has penetrated, indicating that the intermolecular interaction contains electrostatic and van der Waals interactions. From the perspective of the Lewis acid– base interaction, it can be described as a hard acid combined with a hard alkali.

The electrochemical stability of the separators itself plays a very important role in the electrochemical and safety performance of the battery. The electrochemical windows of the pristine PE separators and the modified PE-g-B-15% separator were tested by linear sweep voltammetry (LSV) (Figure S2). It can be seen that the pristine PE separator and the modified PE-g-B-15% separator did not undergo obvious oxidation and decomposition until 4.4 V, which shows that the introduction of a borane molecule does not cause side reactions. This result indicates that the electrochemical window of the modified separator can be suitable for applications in LIBs.

To fully understand the impact of the co-irradiation-grafted boron-modified PE separators on the electrochemical performance of the battery, the half-cell was assembled with the $LiFePO_4$ cathode, a lithium metal foil anode, and different

separators to test the cycle and rate performance. The result of the rate test is shown in Figure 8a. It is worth noticing that when the discharge rate is lower than 2C, the discharge capacities of the cells assembled with the pristine PE separator and the modified PE-g-B-15% separator are almost at the same level, around 150 mAh·g⁻¹(0.5C), 142 mAh·g⁻¹ (1C), and 136 mAh g^{-1} , (2C). However, when the rate increases above 5C, the LiFePO₄ cells assembled with the modified PE-g-B-15% separator show a higher discharge capacity than that of the cell with the pristine PE separator. Especially under 10C discharge conditions, the discharge capacity of the half-cell assembled with the modified PE-g-B-15% separator (100 mAh·g⁻¹) is significantly higher than that of the half-cell with the pristine PE separator (80 mAh·g⁻¹). This may be due to the promoted lithium-ion conduction caused by the interaction between the borane molecule grafted onto the surface of the ion conduction path and species in the electrolyte. The ionic conductivity measured for the modified PE-g-B-15% separator by EIS is slightly lower than that for the pristine PE separator. However, in combination with the lithium-ion transference number, the real lithium-ion conductivity of the modified PE-g-B-15% separator is significantly improved compared to that of the pristine PE separator. This indicates that lithium ions contribute more to the ionic conduction and benefit in

achieving a fast electrochemical reaction. The increase in the lithium-ion transference number promotes the electrochemical reaction of LIBs and reduces the concentration polarization.^{19,20} Lithium ions are easier to transport and therefore have a higher discharge capacity. A similar situation can also be found from the corresponding capacity-voltage curve (Figure 8b,c). As can be seen from the discharge capacity-voltage curves, when the current is lower than 2C, there are similarities between the discharge voltage platforms of the modified PE-g-B-15% separator and the pristine PE separator, meaning no obvious polarization during the cycling. However, when the current density continues to increase, the discharge platform of the LiFePO₄ half-cell assembled with the modified PE-g-B-15% separator (3.30 V at 5C, 3.21 V at 10C) has a significant improvement compared to that of the pristine commercial PE separator (3.20 V at 5C, 3.10 V at 10C). Therefore, the polarization of the LiFePO4 half-cell equipped with the modified PE-g-B-15% separator is smaller, especially at a high current density, and therefore has a higher discharge platform and discharge capacity.⁴⁰ After that, LiFePO₄ was used to assemble the half-cell to test its cycle performance under the condition of 1C and 5C charge and discharge. The results are shown in Figure 8d,e. It can be seen that the pristine PE separator and the modified PE-g-B separator-15% have similar discharge specific capacities (143 mAh g^{-1}) and Coulomb efficiencies (99%) under the condition of 1C charge and discharge (Figure 8d). However, the impedance of the modified PE-g-B-15% separator before and after the cycle is significantly lower than that of the pristine PE separators (Figure 8e). It can be concluded that a borane molecule introduced into the ion conduction path by the co-irradiation grafting process can reduce the interface impedance between the separators and the LiFePO₄ electrode, which is beneficial for the reversibility and stability under long cycling. The long cycle performance of LiFePO₄ half-cells with different separators was tested under the condition of 5C rate. After 500 cycles (Figure 8f), the modified PE-g-B separator can also maintain the capacity of 113 mAh·g⁻¹, which is much higher than that of cells with the pristine separator.

4. CONCLUSIONS

In summary, the electron-deficient effect of borane was introduced into the porous structure of the PE separator by the γ -ray co-irradiation grafting process. Without changing the morphology of the porous structure, the ionic conduction path was modified by a functional molecular layer. The interaction between borane and various species in the electrolyte was carefully studied and explored. The specific interactions of this internal modification and the electrolyte increased the lithiumion transference number, thereby promoting the electrochemical reaction of LIBs and reducing the concentration polarization at fast cycling rates. This work introduces a functional monomer to modify the ion conduction path and applies a universal strategy to develop a functionalized separator. The effect of other functional monomers with different functional groups is worthy of further investigation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c06460.

Chronoamperometry profiles and AC impedance curves of Li/separator/Li cells assembled with pristine PE separators and modified separators; LSV curves of Li/ separator/SS cells assembled with pristine PE separators and modified PE separators; results of density functional theory (DFT) calculations; internal standard method: ¹¹B NMR spectra of borane, borane + DMC, borane + EC, and borane + LB301; ¹⁹F NMR spectra of LB301 and LB301 + borane (PDF)

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Notes

The authors declare no competing financial interest.

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