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Copolymer-assisted Polypropylene Separator for Fast and Uniform Lithium Ion Transport in Lithium-ion Batteries

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Electronic Supplementary Information

Abstract In lithium-ion batteries (LIBs), separators play a vital role in lithium-ion (Li^+) transport, and thus affect rate performance, battery life, and safety. Here, a new kind of multifunctional copolymer poly(acrylonitrile-co-lithium acrylate-co-butyl acrylate) (PAAB-Li) is synthesized through soap-free emulsion polymerization, and is used to form homogeneous-covered separator based on PP matrix by a simple dip-annealing process. Compared to the bare PP separator, the modified separators with PAAB-Li enable higher ionic conductivity, higher lithium ion transference number (increased from 0.360 to 0.525), and lower interface impedance (reduced from 155 Ω to 34 Ω). It has been indicated that PAAB-Li functional layer significantly promotes the fast transport of Li^+ and improves the compatibility of the separator/electrolyte-electrode interface. The LiCoO_2 /graphite cells with the PAAB-Li-assisted separator demonstrate excellent cycle stability and rate performance. In addition, the Li symmetric cells with the modified separator stably cycle over 800 h, indicating the functional layer effectively suppresses the lithium dendrite growth. This facile strategy can be easily applied to LIBs requiring high safety and even be scalable to Li metal batteries. Moreover, the possible mechanism of the PAAB-Li functional layer promoting fast and uniform Li^+ transport is discussed in this paper.

Keywords Polyelectrolytes; Polypropylene separator; Lithium ion transport; Dendrite-free; Lithium-ion battery

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INTRODUCTION

With more widespread use of lithium-ion batteries (LIBs) in portable devices, it is also hoped that LIBs will be used as efficient clean energy in large-scale energy storage devices such as electric vehicles and mobile base stations. To meet the needs in these scenarios, LIBs with high power density, long cycle life, and excellent safety are highly desired.^[1–3] However, the slow and uneven transport behavior of lithium (Li) ions in the battery severely hurt LIBs performance, which limits the application of LIBs in large-scale energy storage devices. Specifically, slow Li ions transport will reduce the power density of LIBs, and uneven Li ion transport will lead to the proliferation and growth of Li dendrites, causing the capacity attenuation and internal short circuit, which damage the cycle life and safety.^[4–8]

In general, the transport behavior of Li ions occurs in three spaces, including the inside of the electrodes, the separator/electrolyte-electrode interface, and the inside of the separator.

It is obvious that the separator will deeply affect the transport behavior of Li ions at the separator/electrolyte-electrode interface and inside the separator through its surface chemical composition and porous structure.^[9,10] Therefore, optimizing the separator is an effective strategy for achieving high power density, long cycle life, and excellent safety of LIBs by improving Li ion transport properties.^[11] In recent research, Zhu *et al.* have prepared carboxylated polyimide separators to improve Li ion transport properties by producing a large number of $-\text{COOH}$ groups on the separator surface. After simulation and calculation, they concluded that the COOH group increased the Li ion transport rate by more than six times.^[12] Furthermore, poly(methyl methacrylate) (PMMA),^[13] poly(ethylene oxide) (PEO),^[14,15] polyethyleneimine (PEI), and polyphenols^[16–18] all have been used to improve electrochemical properties of separators. Based on the results of these studies, it is concluded that acrylate polymer has great affinity with the liquid electrolyte as they have similar ester groups, and other polymers containing oxygen-supplying atoms (such as oxygen atom and nitrogen atom) have considerable effects on increasing ionic conductivity

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and reducing interfacial resistance.^[19–21] These strategies focused on the improvement of the macro-electrochemical performance of the LIBs. In contrast, less attention was paid to the effect of materials on Li ion transport behavior. Moreover, these strategies were dedicated to improving the wettability to the electrolyte for remarkable electrochemical performance, and little effort has been made to address the Li dendrite issue in LIBs.

Notably, materials affect Li ion transport behavior by affecting the hydrodynamic volume of Li ions and the quality of Li ions migration space. Therefore, the key points for the Li ions to achieve fast and uniform transport are desolvated Li ion, homogeneous separator/electrolyte-electrode interface, and good wettability. In this work, a multifunctional copolymer poly(acrylonitrile-co-acrylic acid-co-butyl acrylate) (PAAB) was synthesized through soap-free emulsion polymerization, which was used for fast and uniform Li ions transport. Considering that the gel electrolyte tends to cause undesirable low-temperature ionic conductivity and low mechanical strength,^[22–24] we decided to adhere the multifunctional copolymer on the PP skeleton to build an ultra-thin functional layer instead of directly using it as polyelectrolyte. The reason for choosing PP as the skeleton is to take advantage of its attractive properties, such as reliable electrochemical stability, excellent mechanical strength, proper pore structure, and low cost.^[22,25] The ultra-thin functional layer well retained the proper pore structure from commercial PP skeleton. Besides, the multifunctional copolymer can form a stable system with PP matrix through strong intermolecular forces with PP and retain the flexibility of PP skeleton, which meet the needs of large-scale industrial production.

The copolymer achieved fast and uniform transport of Li ions by reducing hydrodynamic volume of Li ions and providing the separator with electrolyte-filled pore network and compatible interphase interfaces. The AA and AN units containing —COOH groups and —CN groups, respectively, can improve Li ions transport rate by interacting with solvated Li ions and desolvating the Li ions.^[12,26,27] The BA units can help to yield a homogeneous separator/electrolyte-electrode interface and reduce the migration resistance of Li ions through the interface.^[28,29] Furthermore, all functional units containing polar groups can help the separator obtain great wettability to the liquid electrolyte. Moreover, Aurbach *et al.* have used lithium polyacrylate (LiPAA) as a kind of binder for high-voltage LIBs, and believe that LiPAA can compensate Li-ion loss in full LIBs by acting as an extra Li source.^[30] Inspired by this thought, we decided to lithiate the copolymer and introduce —COOLi groups as a supplement to the Li source.

In the charge-discharge process, some Li ions will produce irreversible deposition of metallic Li on the anode, during which the electrolyte is consumed and Li dendrites are formed, resulting in low coulomb efficiency. Further growth of Li dendrites may even pierce the separator and incur internal short circuits, causing thermal runaway of the battery.^[31,32] In this work, we also studied the positive effect of multifunctional copolymer on the suppression of Li dendrite growth, and proposed possible mechanisms, which is important for cycle life and safety of LIBs.

EXPERIMENTAL

Materials

The commercial monomers acrylonitrile (AN, > 99.0%), acrylic acid (AA, > 99.0%), and butyl acrylate (BA, > 99.0%) were purchased from Aladdin Chemistry Co. (Shanghai, China). In order to remove the polymerization inhibitor, AN and AA were distilled in vacuum, and BA was filtered and separated by means of alumina column before use. Dibenzoyl peroxide (BPO, > 99.0%) was provided by Macklin Biochemical Technology Co. (Shanghai, China) and recrystallized before use. Deionized water (DI water) was obtained by a Millipore water purification system (18.2 M Ω , Millipore, USA). Lithium hydroxide, dimethyl acetamide (DMAc), and ethanol (EtOH) were provided by Sinopharm Chemical Reagent Co. (Shanghai, China) and were directly used. The liquid electrolyte of 1 mol·L^{−1} LiPF₆ in a mixed solvent [V(EC):V(DME):V(EMC) = 1:1:1 (mL:mL:mL)], LiCoO₂ cathode, graphite anode and other battery materials were obtained from Kejing Materials Technology Co. (Shenzhen, China). The PP separator (Celgard 2500, thickness 25 μm) was supplied by Celgard Company (North Carolina, USA).

Synthesis of Poly(acrylonitrile-co-acrylic acid-co-butyl acrylate)

Poly(acrylonitrile-co-acrylic acid-co-butyl acrylate) (PAAB) was synthesized through soap-free emulsion polymerization (Scheme S1 in the electronic supplementary information, ESI) and the procedure is simply described as follows. First, 70 g of DI water was added into a 250 mL flask and bubbled with nitrogen gas for 30 min. Meanwhile, the mixed monomers containing 10 g of AN, 10 g of AA, and 10 g of BA [$m(\text{AN}):m(\text{AA}):m(\text{BA}) = 1:0.74:0.41$ (mol:mol:mol)] were stirred at room temperature for 10 min and then 0.19 g of BPO was added into the mixture. After that, the monomer mixture was added dropwise into DI water under vigorous mechanical stirring after heating this flask to 65 °C. The polymerization was continued at 65 °C for 6 h. PAAB was obtained by precipitation of the emulsion in ethanol and freeze-dried under vacuum for further use. Finally, the copolymer sample was purified by dissolving in DMAc, precipitated in water, and freeze-dried.

Preparation of PAAB-Li-assisted PP Separators

The PAAB-Li-assisted separators were prepared by dip-annealing method. A homogeneous PAAB solution, as a non-lithiated control group, was formed by dissolving PAAB in a mixed solvent of DMAc and EtOH (V(DMAc):V(EtOH) = 1:1) with copolymer concentration of 1 wt% at 60 °C for 6 h. A PAAB-Li solution was prepared by the same method after PAAB and the equimolar lithium hydroxide were added into the mixed solvent. PP separators pre-wetted by ethanol were immersed into PAAB solution and PAAB-Li solution for 1 h, respectively, and subsequently dried under ambient temperature for 1 h to evaporate the solvent. PAAB-full-coated PP and PAAB-Li-full-coated PP were finally acquired by annealing at 60 °C in a vacuum for 24 h. The as-prepared separators made with PAAB and PAAB-Li were named as PP-1 and PP-2 (coating solution viscosities of 13.21 and 40.14 mPa·s, respectively). The specific preparation process is displayed in Fig. 1.

Characterization

The structure of the copolymer was characterized by ¹H-NMR

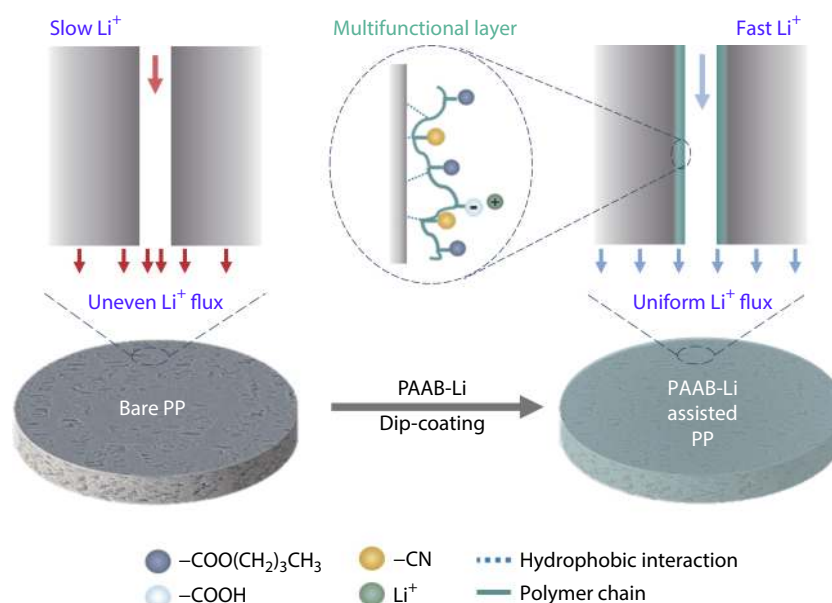


Fig. 1 Schematic illustration of the preparation process. By introducing PAAB-Li copolymer on the PP skeleton, Li^+ achieved fast and uniform transport across the separator.

and ^{13}C -NMR (500 MHz, Bruker, Billerica, MA) using dimethyl sulfoxide- D_6 ($\text{DMSO}-\text{D}_6$) as solvent. To characterize the functional groups on the surface of separators, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet 6700, Madison, Wisconsin, USA) was performed in a wavenumber range of $3900\text{--}1000\text{ cm}^{-1}$. The surface chemical composition of the separators was analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5000, ULVAC-PHI, Chigasaki, Japan). To analyze the pore structure properties of the separators, mercury intrusion meter (AutoPore IV 9510, McMurritique, USA) was employed. To observe the surface and cross section morphologies of the separators, a field emission scanning electron microscope (FE-SEM, Hitachi S4800, Tokyo, Japan) was used. Element mappings were obtained by energy dispersive X-ray (EDX, equipped with the FE-SEM). The Li content in the modified separator was estimated by the ion exchange capacity (IEC, in $\text{mmol}\cdot\text{g}^{-1}$). The NaCl solution ($5\text{ mol}\cdot\text{L}^{-1}$) was used to fully equilibrate PP-2 and the acidified PP-2, and the number of protons released from the separator was determined by using the classical titration technique (NaOH, $0.1\text{ mol}\cdot\text{L}^{-1}$), which was recorded as IEC. The IEC was calculated with the following Eq. (1):

$$\text{IEC} = (\Delta V_{\text{NaOH}} \times c_{\text{NaOH}}) / W_s \quad (1)$$

where ΔV_{NaOH} is the amount of NaOH solution consumed during titration, c_{NaOH} is the concentration of the NaOH solution ($0.1\text{ mol}\cdot\text{L}^{-1}$), and W_s is the weight of the dry separator.

The wettability of the separator in liquid electrolyte was estimated by the electrolyte contact angle (ECA) and the electrolyte uptake (U). ECA was measured by a contact angle goniometer (OCA20, Dataphysics, Germany) equipped with video capture (the drop volume was $3\text{ }\mu\text{L}$). U was calculated with the following Eq. (2):

$$U(\%) = (w_1 - w_0) / w_0 \times 100\% \quad (2)$$

where w_0 and w_1 represent the weights of the dry and the electrolyte-soaked separators, respectively.

Electrochemical Characterization

To verify the electrochemical stability of the modified separators, linear sweep voltammetry (LSV) was performed from 1.0 V to 6.0 V (versus Li/Li^+) at a scan rate of $10\text{ mV}/\text{s}$ by assembling stainless steel (SS)/separator-liquid electrolyte/lithium foil (Li) cells. The ionic conductivities and interface impedances of the separators were determined by using an electrochemical workstation (CHI660D, CH Instruments, China) in an AC impedance measurements mode, which was conducted over a frequency range of 0.01 Hz to 100 kHz with an amplitude of 5 mV . The ionic conductivity was measured with the SS/separator-liquid electrolyte/SS cell, and calculated according to the following Eq. (3):

$$\sigma = L / (R_b \times A) \quad (3)$$

where L , R_b , and A are the thickness ($24\text{ }\mu\text{m}$), bulk resistance (ohm), and effective area (1.96 cm^2), respectively. R_b was determined by applying electrochemical impedance spectroscopy (EIS). The interfacial resistance (R_{int}) was measured in the same way as that of R_b , with the assembly of Li/separator-liquid electrolyte/Li (Li symmetric cells).

Lithium ion transference number (t_+) was determined by combining chronoamperometry and EIS analysis using Li symmetric cells. t_+ was calculated according to the following Eq. (4):

$$t_+ = \frac{I_s (\Delta V - I_0 R_0)}{I_0 (\Delta V - I_s R_s)} \quad (4)$$

where I_0 and I_s are the initial current and steady-state current, R_0 and R_s are the interfacial resistance before and after polarization, respectively, ΔV is the potential difference (10 mV). Moreover, galvanostatic cycling test (Neware, CT-3008, China) was applied on the Li symmetric cells to obtain the change of overpotential with time.

The battery performance of separators was examined by using the charge/discharge testing system (Neware, CT-3008,

China) after assembling LiCoO₂/separator-liquid electrolyte/graphite coin-type cell. All cells were assembled in a dry, argon-filled glove box. To activate cells and form a stable solid electrolyte interface, the coin cells were rested for 12 h and then galvanostatic charged/discharged for 3 cycles at 0.05 C. The charge/discharge current density was fixed at 1 C/1 C (100 mAh·g⁻¹) with the voltage range of 2.75 V to 4.20 V for testing cycle stability. Additionally, the rate discharge test was conducted at the rates varying from 0.2 C to 5.0 C.

RESULTS AND DISCUSSION

Structure of Copolymer

The molecular structure of PAAB was determined by ¹H-NMR spectrum as shown in Fig. 2(A). The signal at 12.48 ppm is attributed to the proton of COOH group in AA unit, and the signal at 4.02 ppm is assigned to the proton of CH₂ near the ester in BA unit. The responses at 1.56, 1.32, and 0.80 ppm demonstrate the presence of the *n*-butyl group in PAAB. It was further analyzed by ¹³C-NMR spectrum (Fig. 2B). The narrow signal at 120.61 ppm arises from the CN group in AN unit, which proves the successful polymerization of AN monomers. NMR results show that all three monomers (AN, AA, and BA) participated in the polymerization to form a multifunctional

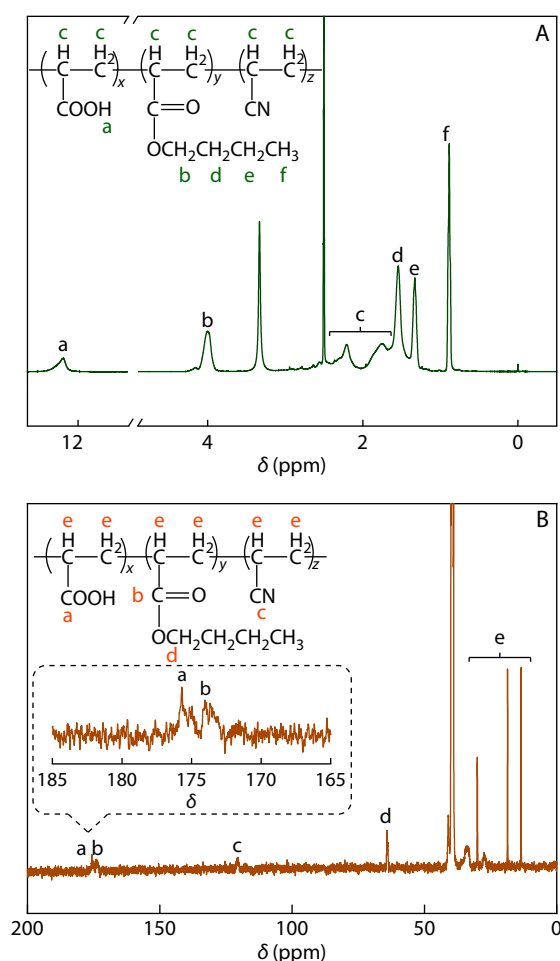


Fig. 2 (A) ¹H-NMR and (B) ¹³C-NMR spectra of PAAB in DMSO-D₆.

copolymer PAAB. According to the results of elemental analysis (Table S1 in ESI), the actual molar ratio of three monomers (AN:AA:BA) in PAAB is calculated to be about 1:0.67:1.69, different from the ratio of raw materials (AN:AA:BA = 1:0.74:0.41). The above results indicated that AN and AA monomers partly participated in the polymerization, which is because both AN and AA monomers are hydrophilic, of which AA is extremely hydrophilic. Therefore, AN and AA monomers tend to polymerize in the aqueous phase, and only a portion of the monomers enter the micelles. According to the results of our previous experiments, PAAB with the above structure has opportune molecular rigidity, great processability, and excellent adhesion.

Surface Chemical Composition and Morphology Structure

The surface chemical composition and pore structure of the separator have an important effect on the transport behavior of lithium ions. The surface chemical composition of the separators was characterized by ATR-FTIR and XPS. As shown in Fig. 3(a), compared to the bare PP separator, new characteristic absorption bands at 2253 cm⁻¹ (C≡N stretching vibration) and 1730 cm⁻¹ (C=O stretching vibration) appear in the FTIR spectra of PP-1, which certifies the existence of PAAB on the PP-1 surface. And new absorption bands at 1580 cm⁻¹ (O=C—O—Li asymmetric stretching vibration) appear in the FTIR spectra of PP-2, which certifies the —COOH from PAAB on the PP-2 surface was converted into a carboxylate. As shown in Fig. 3(b), there is only C 1s for the bare PP separator. By comparison, new peaks assigned to N 1s and O 1s appear in the XPS spectra of the modified separators, indicating the presence of CN and oxygen-containing groups on the surface of the modified separators. Moreover, Li 1s peak observed from the spectra of PP-2 confirms that the proton of the carboxyl group has been replaced by lithium ion. The results of XPS spectra demonstrate that the copolymers are well adhered onto the surface of PP separator. In order to measure the adsorption of PAAB and PAAB-Li on the PP skeleton, the quality change of the PP separator before and after coating was tested. The content of PAAB on PP is 0.68 g·m⁻², and the content of PAAB-Li is 0.75 g·m⁻². IEC can characterize the —COOH content in the PP-2 separator by ion exchange reaction. Thus, the Li content in PAAB-Li is evaluated by the difference values of IEC before and after PP-2 acidification. The IEC before and after acidification were 0.58 and 1.56 mmol·g⁻¹, respectively. It can be calculated that about 63% carboxyl groups in PAAB are converted to lithium carboxylates (—COOLi).

In order to analyze the pore structure of the modified separators, FE-SEM was used. As exhibited in Fig. 4(a), the pore size of the modified separators on both the surface and the cross section decreases, and the skeleton thickness of the modified separators increases, compared with those of the bare PP separator. The result indicates that PAAB and PAAB-Li adhere to both the surface and the cross section of PP skeleton to form a homogeneous-covered network. However, the modified separators still retain the porous structure of the bare PP separator, and no obvious plugging is found. It should be pointed out that PP-1 shows lower porosity compared with PP-2 (Table S2 in ESI) because the coating solution with lower viscosity is more likely to penetrate and re-

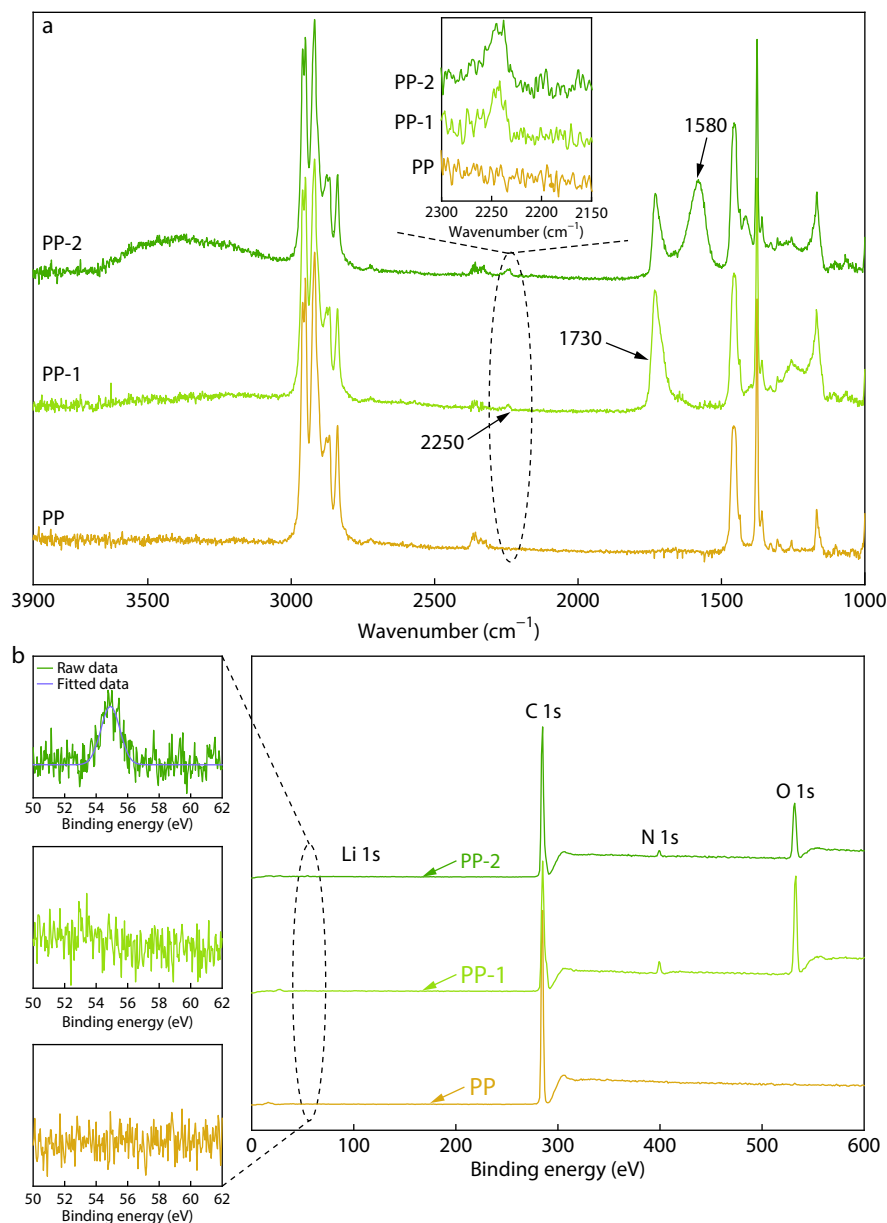


Fig. 3 (a) ATR-FTIR spectra of the separators. (b) XPS spectra of the bare PP and modified separators (PP-1 and PP-2).

main in the internal channels. Additionally, the EDX element mappings of the modified separator surface and section are shown in Figs. 4(b) and 4(c), respectively. The homogeneous distribution of N and O element suggests that both PAAB and PAAB-Li are uniformly adhered to the PP skeleton, forming a uniform homogeneous-coated functional layer.

Electrochemical Stability

The electrochemical stability of the modified separators was examined by linear sweep voltammetry (LSV) testing. Fig. 5(a) shows the LSV curve of the modified separators and the bare PP separator when the voltage is less than 5.5 V (versus Li/Li^+). It is seen that no redox peak appears between the modified separators and the bare PP separator in the voltage range of 2.8–4.8 V (versus Li/Li^+), indicating that no obvious electro-

chemical decomposition of any components in the cell occurs within this voltage window. The redox peak at 5.0–5.5 V (versus Li/Li^+) is ascribed to the decomposition of the liquid electrolyte.^[33,34] Notably, the redox peak of the modified separator appears at higher voltages compared to the bare PP separator, indicating that the modified separators show a bit better electrochemical stability. This is because the copolymer uniformly distributed on the PP skeleton absorbs the electrolyte to form a gel layer, which reduces the electrolyte at the electrode surfaces, and suppresses the decomposition of electrolyte.^[35,36] This reliable electrochemical stability guarantees that the modified separator is suitable for most commercial battery systems.

Effect of PAAB-Li on Lithium Ion Transport Behavior

It is well known that the transport behavior of Li ion in relation

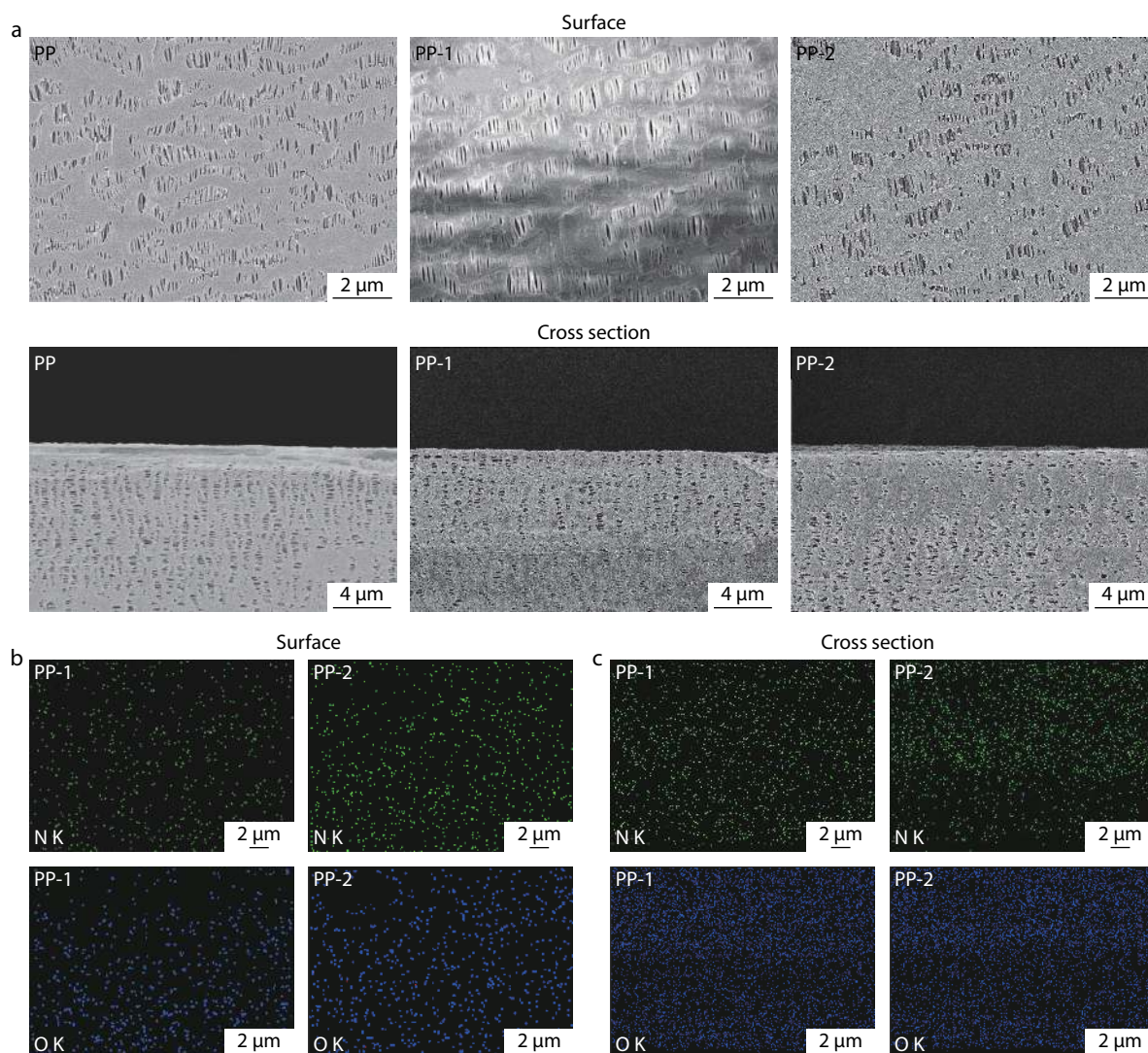


Fig. 4 (a) Surface and cross-sectional SEM images of the separators; (b) EDX mappings for the surfaces of PP-1 and PP-2 separators; (c) EDX mappings for the cross sections of PP-1 and PP-2 separators.

to the separator occurs in two spatial ranges, namely inside the separator and at the separator/electrolyte-electrode interface. More attention is first paid to the influence of the PAAB-Li functional layer on the transport properties of Li ions inside the separator. In general, the Li ion transport behavior mainly occurs in liquid electrolyte filled in the internal network of the separator. Therefore, the wettability of the separator has a significant effect on the transport behavior of Li ions.^[33] In an attempt to determine the effect of PAAB-Li functional layer on the wettability, electrolyte contact angle and electrolyte uptake were measured. As shown in Fig. 5(b), the bare PP separator displays a contact angle of 41.9° due to its inherently low surface energy. The contact angle of PP-1 is 29.6°, and the contact angle of PP-2 further is 18.4°, indicating that PP-2 separator possesses better affinity with the liquid electrolyte. It is considered that PAAB-Li significantly improves the wettability of the separator due to a lot of polar groups derived from it. It is worth noting that $-\text{COOLi}$ is more polar than $-\text{COOH}$, so PP-2 has better affinity for polar electrolytes than PP-1. In addition, the

electrolyte uptake of the bare PP separator is just only 110.0%, whereas those of PP-1 and PP-2 separators reach up to 165.5% and 195.8%, respectively (Fig. 5c). The results reflect that PAAB-Li improves the ability of the PP separator to adsorb and retains the electrolyte, which means that there are wider Li ion transport channels inside the PAAB-Li-assisted separator.

To illustrate the transport behavior of Li ion inside the separator comprehensively, both ionic conductivity (σ) and Li ion transference number (t_+) of the separators were tested. As shown in Fig. 5(c), the ionic conductivity of the separator was studied by assembling SS/separator-electrolyte/SS blocking cells without any ions from crossing the separator/electrolyte-electrode interface. The PP-2 separator containing cell possesses the highest ionic conductivity ($0.96 \text{ mS}\cdot\text{cm}^{-1}$), while the bare PP containing cell shows the lowest ($0.60 \text{ mS}\cdot\text{cm}^{-1}$). According to the calculation, it can be inferred that there is $2 \times 10^{-3} \text{ mmol}$ of $-\text{COOLi}$ and $18 \times 10^{-3} \text{ mmol}$ of LiPF_6 on each square meter of the pore wall surface in the channel of PP-2. Therefore, the change of Li^+ concentration in the EIS test

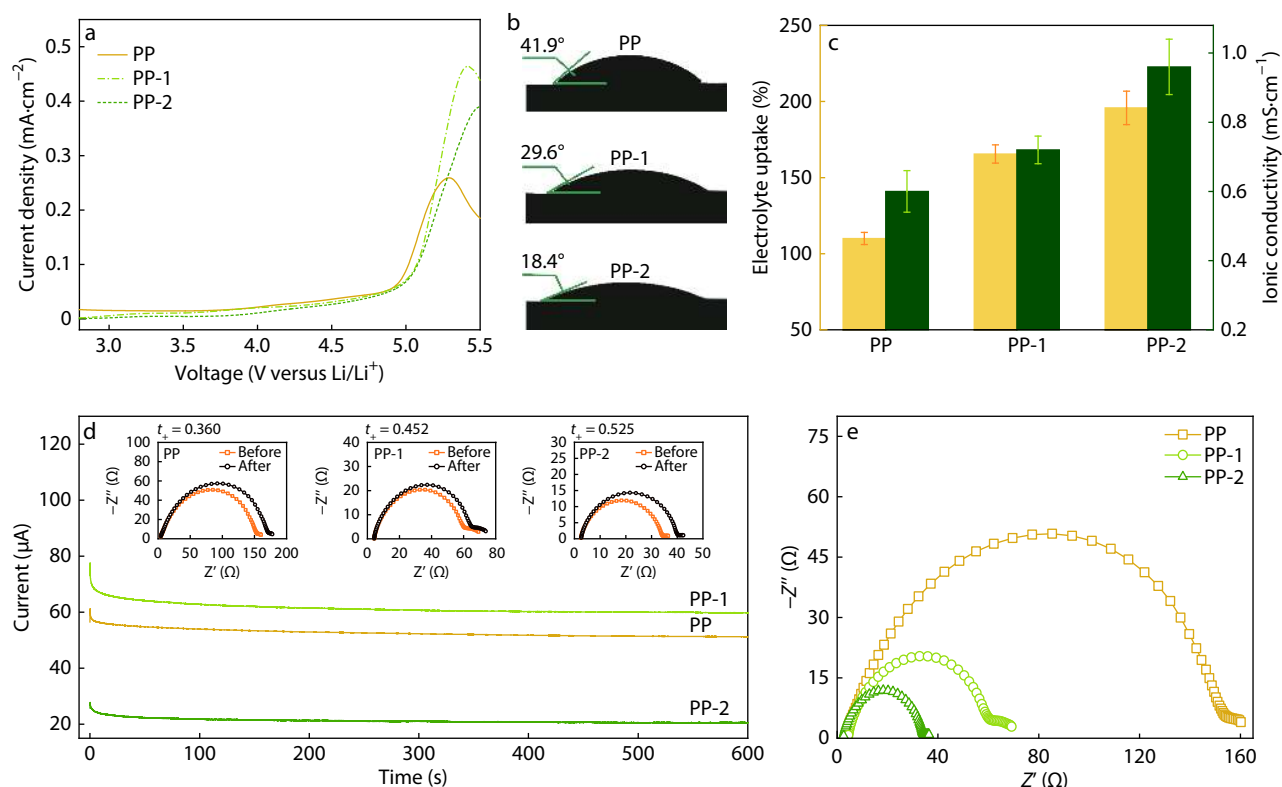


Fig. 5 Lithium ion transport properties for the bare PP and modified separators: (a) LSV curves of SS/separator-liquid electrolyte/Li cells; (b) Electrolyte contact angles; (c) The electrolyte uptakes (yellow) and ionic conductivities (green); (d) Chronoamperometry profiles and the corresponding EIS analyses (before and after the chronoamperometry) for the Li symmetric cells; (e) Nyquist plots for the Li symmetric cells.

of different separators is very small. Given this, the results reveal that PAAB-Li functional layer weakens the migration resistance of ions inside the separator and increases the ionic transport rate. Further, the Li ion transference number (t_+) represents the effective electrochemical process caused by Li ion transport (Fig. 5d). Compared with the bare PP separator (t_+ , 0.360), the modified separators have much higher t_+ (PP-1, 0.452; PP-2, 0.525). This proves that the PAAB-Li functional layer improves the transport efficiency of Li ions, thereby reducing the effects of the concentration gradient and internal polarization of the battery, ensuring the power density of the cell.^[34]

The lithium ion transmission channel in the pore of the PP-2 separator can be divided into two parts: one is the bulk channel not affected by the PAAB-Li functional layer, and the other is the modified channel affected by the PAAB-Li functional group, which is close to the surface of the pore wall area. According to the ion conductivity and lithium ion transference number, the Newman's model^[35] is used to calculate the ion transport rate of Li^+ in the bulk channel and the modified channel, respectively. As shown in Fig. S4 (in ESI), the Li^+ transport rate in the bulk channel is 0.22k, while the rate in the modified channel is increased to 0.79k, where k is a constant related with electron charge, pore area, and electric field intensity (the specific calculation process is shown in ESI). The Li^+ transport rate in the modified channel is increased by 3.6 times. The results prove that PAAB-Li can assist to establish a fast channel on the surface of the PP pore wall for Li^+ to

quickly transfer between the electrodes.

In addition, the activation energy is deduced by measuring conductivity of PP and modified separators as a function of temperature. The results are shown in Fig. 6, where the solid line represents fits of data, k_1 is the slope of the solid line and E_a (eV) is the activation energy. Comparison of the results for PP and PP-2 separators clearly shows that there is a reduction in activation energy when PAAB-Li is present. This observation further proves that the channel walls to which PAAB-Li layer adheres facilitate Li^+ conduction.

In order to research the effect of the PAAB-Li functional lay-

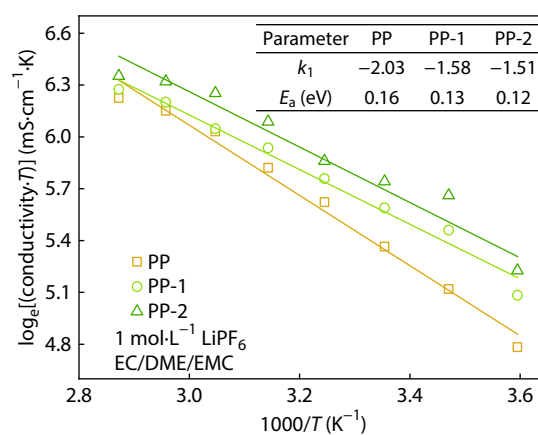


Fig. 6 Conductivity as a function of temperature for different separators (1 mol·L⁻¹ LiPF₆, EC/DME/EMC).

er on the transport properties of Li ions at the separator/electrolyte-electrode interface, the interface impedance (R_{int}) was determined. Fig. 5(e) displays the Nyquist plots of the Li symmetric cells with the bare PP and the modified separators. The high frequency semicircle relates to R_{int} of the separators.^[36] It is obvious that the modified separators exhibit much lower R_{int} (~60 Ω for PP-1, ~34 Ω for PP-2), while that of the PP separator is 155 Ω . It is mainly caused by the numerous BA units from PAAB-Li, which provide strong adhesion between the separator and the electrode to yield a more compatible and stable separator/electrolyte-electrode interface.^[28,29,37] Simultaneously, the better affinity of PAAB-Li with the electrolyte helps to form a uniform electrolyte adsorption layer, thereby reducing interface impedance and promoting the fast and uniform transport of Li ions at the interphase interfaces.

According to the influence of PAAB-Li on lithium ion transport behavior mentioned above, we propose a possible explanation in Fig. 7 from the perspective of molecular structure. PAAB-Li improves the transport efficiency of lithium ions in cells through the synergy effect of two factors. On the one hand, the cyano, ester, and lithium carboxylate groups ($-\text{COOLi}$) in PAAB-Li provide abundant donor atoms (nitrogen and oxygen). The unshared electron pairs of these donor atoms interact with strongly solvated lithium ions in the modified channel, leading to breakup of the solvation sheath of lithium ion. Desolvated lithium ions migrate faster compared to strongly solvated lithium ions because of their smaller hydrodynamic volume.^[38] On the other hand, the donor atoms weaken the electrostatic interaction between lithium ion (Li^+) and hexafluorophosphate (PF_6^-), and promote the dissoci-

ation of ion pairs, while the $-\text{COOLi}$ groups from the PAAB-Li are also dissociated in the electrolyte, thereby increasing the concentration of free Li^+ and finally affording high lithium ion transference number.^[39] Furthermore, the lithium ions dissociated from $-\text{COOLi}$ groups are expected to be a supplemental lithium source to make up for the capacity loss in actual battery applications.^[30] Overall, PAAB-Li can accelerate lithium ion migration and improve lithium ion transport efficiency.

Effect of PAAB-Li on Lithium Dendrite Growth

It is generally believed that the formation and growth of dendrites is caused by the uneven deposition of Li ions.^[32,40] PAAB-Li is expected to alleviate this problem by improving the transport performance of Li ions in the cell. Profiles of prolonged galvanostatic cycling performance for the Li symmetric cells are shown in Fig. 8. For the cell equipped with bare PP separator, the overpotential between the stripping and plating decreases consistently from 110 mV to 39 mV, and finally stabilizes at 39 mV in the first four cycles. It gradually increases after the 150th cycle, which was the result of the growth of Li dendrites.^[41] Then, the overpotential for PP suddenly drops from 360 mV to 97 mV at the 227th cycle, which was an indication of internal short-circuits as Li dendrites pierced separator.^[4,41,42] In contrast, the overpotentials for PP-1 and PP-2 stabilize at 85 and 43 mV, respectively, after the 227th cycle without short-circuit signals detected. It was proved that the modified separator effectively inhibits the growth of Li dendrites. However, for PP-1, the overpotential suddenly drops from 350 mV to 105 mV at the 328th cycle, while the overpotential of

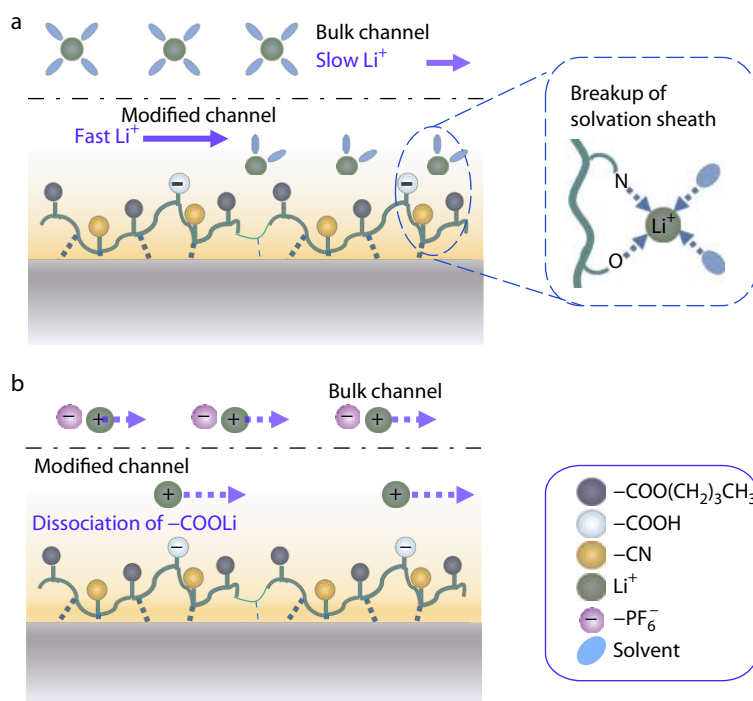


Fig. 7 The schematic of the effect of the PAAB-Li layer on Li^+ transport behavior: (a) N and O atoms from PAAB-Li layer break the solvation sheath of Li^+ by competing with solvents for the coordination of Li^+ . The hydrodynamic volume of Li^+ is thus reduced, which in turn causes fast migration of Li^+ . (b) LiPF_6 dissociates more fully affected by N and O, and $-\text{COOLi}$ also dissociates in the electrolyte, resulting in an increase in free Li^+ in the system and an increase in the Li ion transference number.

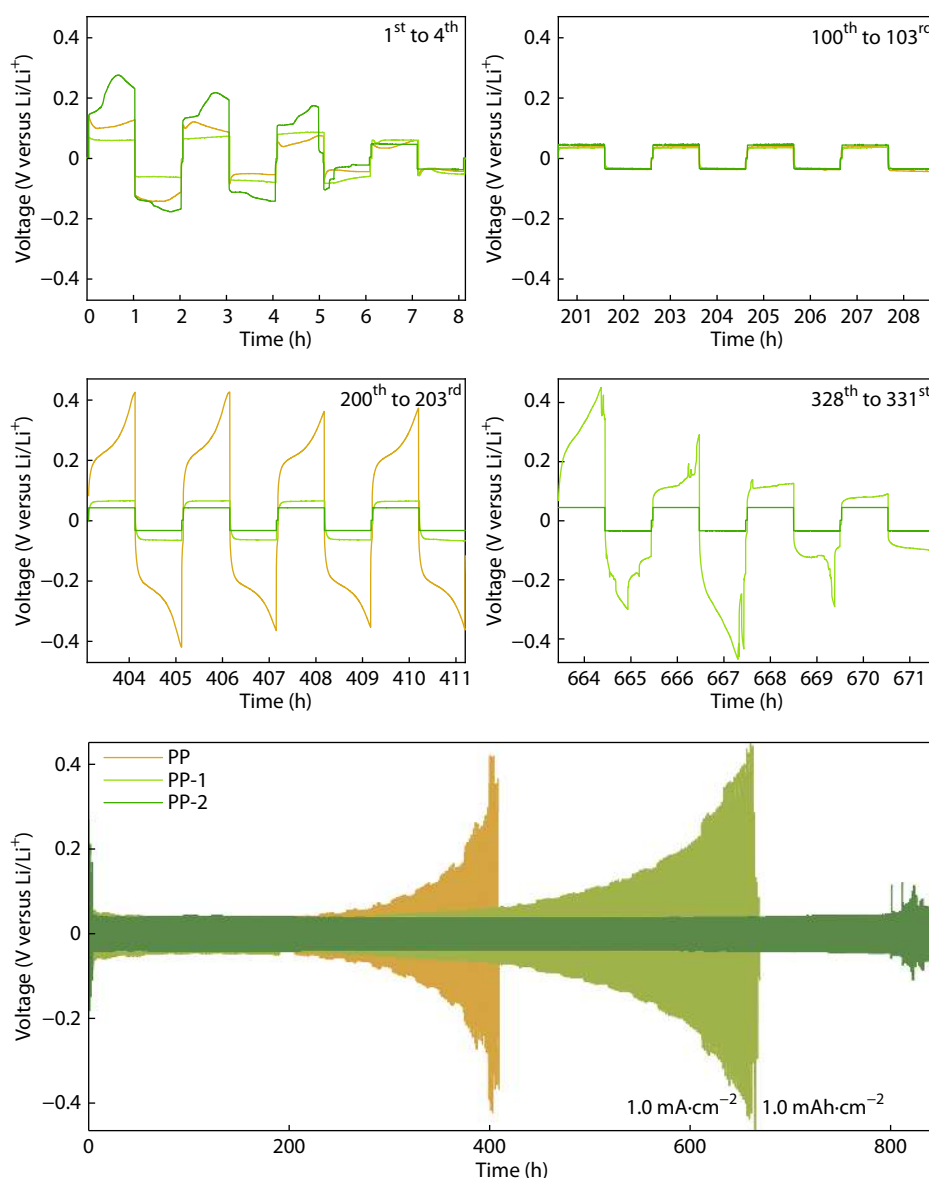


Fig. 8 Galvanostatic cycling performance for Li symmetric cells with different separators cycled at the current density of $1.0 \text{ mA}\cdot\text{cm}^{-2}$ with a stripping/plating capacity of $1.0 \text{ mAh}\cdot\text{cm}^{-2}$.

PP-2 remains stable until the 401st cycle (800 h). It demonstrates that the lithiated separator has a better performance in inhibiting the growth of Li dendrites. In theory, overpotential is generated partly due to kinetic hindrances of Li ions transport process in electrolyte-separator.^[43–45] PAAB-Li helps PP improve the interfacial interphase compatibility, further facilitates rapid and uniform transport of Li ions in the cell, and ultimately suppresses uneven deposition of Li ions on the anode and delays the growth of dendrites effectively. The test results mean that PAAB-Li assist commercial separators to meet the requirements of high safety and long service life, and has great potential for use in next-generation Li metal batteries. The role of PAAB-Li in inhibiting the growth of Li dendrites is further demonstrated by the battery performance of NCM523/Li metal cells. The cell performance is susceptible to the growth of Li dendrites. Compared with bare PP, the cycle stability and coulombic efficiency of PP-2 are significantly improved during

70 cycles (shown in Fig. S3 in ESI), which is consistent with the cycle performance for the Li symmetric cells. It helps to further prove that PAAB-Li assists PP separator to inhibit dendrite growth effectively.

We propose a possible mechanism in Fig. 9 for the effect of PAAB-Li-assisted PP separator on Li ion deposition at the interface of Li electrode. Due to the inert surface of the bare PP separator, the electrolyte cannot fully infiltrate the channels inside the separator. As a result, an air gap is formed between the separator and the electrolyte, thereby forming a heterogeneous interface. The transport space of Li ions inside the separator is confined, which results in concentrated deposition of Li ions on the surface of the Li electrode.^[40] In addition, the slow transport of Li ions inside the PP separator is not conducive to the uniform dispersion of Li ions at the interphase interface, which also exacerbates the concentrated deposition of Li ions. Then, the unevenly deposited lithium

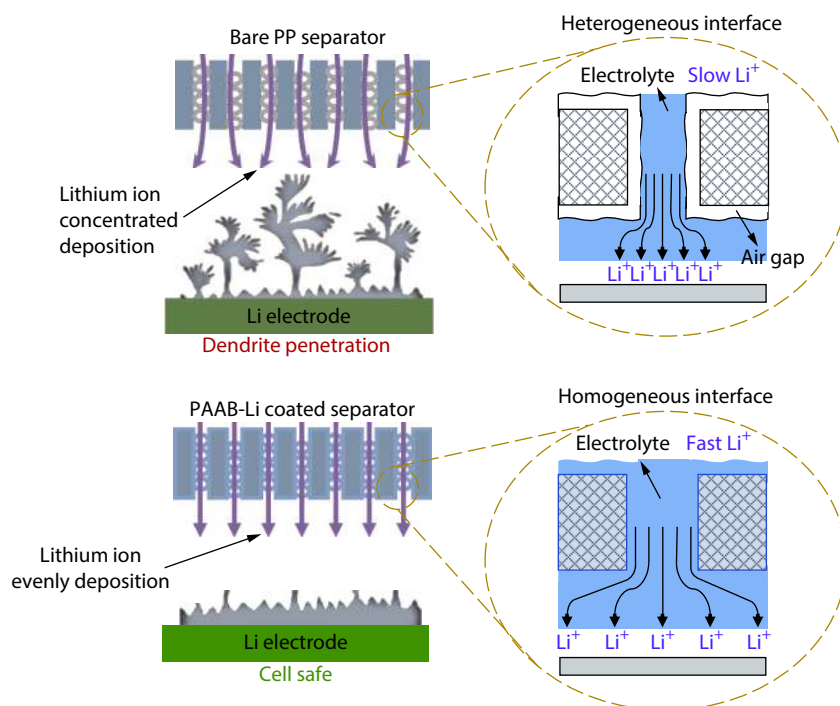


Fig. 9 The possible strategies for PAAB-Li to assist in inhibiting lithium dendrite growth. PAAB-Li achieves the evenly deposition of Li^+ on the lithium electrode by improving the migration rate and transmission space of Li^+ in the separator, which in turn inhibits the growth of dendrites. Great wettability leads to a homogeneous interface at the separator-electrolyte interface, resulting in an expansion of the transmission space.

will be preferentially consumed in the next dissolution process. Subsequently, the repeated dissolution/deposition process accelerates the growth of dendrites.^[31] However, PAAB-Li not only improves the wettability of the separator to the electrolyte and forms a homogeneous interface, but also accelerates the transport of Li ions. Therefore, Li ions tend to deposit evenly on the electrode surface in the PP-2 separator, which effectively inhibits Li dendrite growth.

Battery Performance

Taking into account practical application of the modified separators, the battery performance was measured by assembling full cells (LiCoO_2 /liquid electrolyte-separator/graphite) with different separators. The charge-discharge cycle tests were conducted at 1 C. The Coulombic efficiency and discharge capacity curves of different separators assembled coin cells are presented in Fig. 10. The initial discharge capacities of cells with PP-1 ($119.5 \text{ mAh}\cdot\text{g}^{-1}$) and PP-2 ($119.4 \text{ mAh}\cdot\text{g}^{-1}$) are similar to that of cell with bare PP ($118.4 \text{ mAh}\cdot\text{g}^{-1}$) (Fig. 10a). However, the discharge capacity of the cell assembled with PP separator retains only 40.8% after 250 cycles (compared to the 1st cycle), which decreases significantly as the cycle number increases. In contrast, the capacity retention of PP-1 is 56.2% after 250 cycles, and that of PP-2 is even up to 78.0%, far higher than that of the cell with bare PP separator. The modified separator exhibits better cycle stability, and PP-2 displays the best performance.

In addition, the initial Coulombic efficiencies of the modified separators PP-1 (99.7%) and PP-2 (99.3%) are significantly higher than that of the bare PP separator (97.3%). During the initial cycle, the formation of solid electrolyte interphase (SEI) consumes Li ions, resulting in a loss of discharge

capacity and low Coulombic efficiency. The above result demonstrates that PAAB helps to form SEI more efficiently and reduce capacity loss. Furthermore, the cells containing the modified separator consistently comport higher Coulombic efficiency. Although PAAB-Li and unlithiated PAAB show similar Coulombic efficiency, PAAB-Li has better cycle performance. It is explained as follows. Polar groups such as cyano and ester groups help to form a better separator/electrolyte-electrode interface, which has a more important impact in the SEI formation and stabilization. Li ions that gradually dissociate from $-\text{COOLi}$ under the electric field are used as a supplemental Li source to make up for capacity loss, which is more pronounced in cycle performance.

The separator affects the rate performance of the battery by affecting the ion transport, which is important for adjusting the battery kinetics and achieving high power density of the battery. Fig. 10(b) exhibits the discharge capacity of cells with different separators at various current densities (from 0.2 C to 5 C). For all cells with different separators, the discharge capacity gradually decreases as the discharge current density increases; however, PP-2 always exhibits a higher level of discharge capacity. At relatively low current density, the difference in the discharge capacity between PP and PP-2 is not obvious. As the current density increases, the gap in the capacity between PP and PP-2 gradually widens. The PP-2 separator still keeps 72.9% of the discharge capacity when the current density reaches up to 5 C, while the PP separator retains only 15.2% of the capacity and almost loses its ability to discharge. The satisfactory rate performance is partially explained by better Li ion transport efficiency from PAAB-Li,

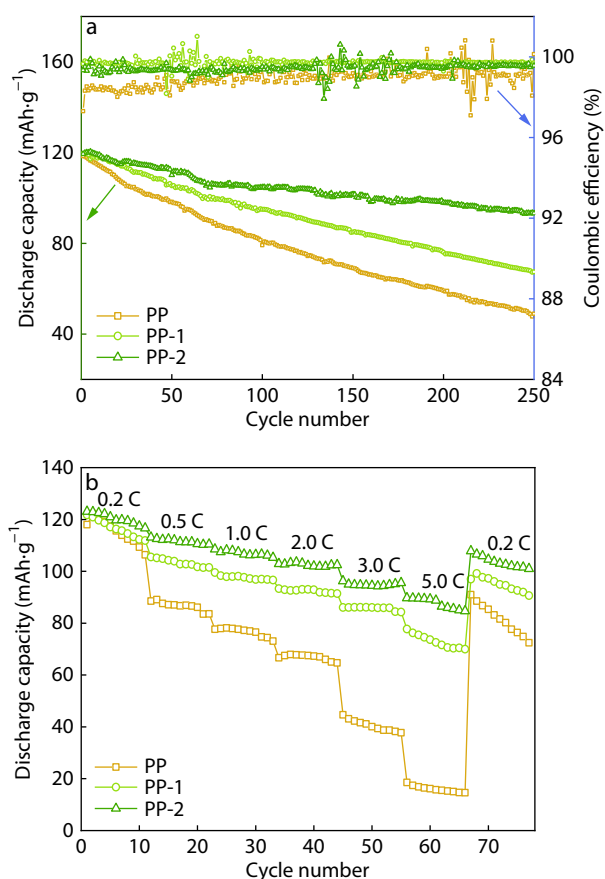


Fig. 10 (a) Cycle performance and Coulombic efficiencies of the batteries at 1 C and (b) rate capability of the cells at the current densities range from 0.2 C to 5 C.

which reduces capacity loss due to polarization arising from the counterion. Meanwhile, PAAB-Li provides a homogeneous separator/electrolyte-electrode interface, creating excellent conditions for Li ion diffusion and migration, which also helps to improve the rate performance.

CONCLUSIONS

In summary, a new kind of multifunctional copolymer PAAB-Li has been synthesized through soap-free emulsion polymerization. By using PP as a matrix to form a PAAB-Li homogeneous-covered modified separator, Li ions achieve fast and uniform transport in LIBs. It should be mentioned that the modified separator covered with PAAB-Li enables a higher ionic conductivity, a higher t_+ (increased from 0.360 to 0.525), and lower interface impedance (reduced from 155 Ω to 34 Ω) compared to those of the bare PP separator. It indicates that rich functional groups from PAAB-Li significantly promote the fast transport of Li ions and improve the compatibility of the separator/electrolyte-electrode interface. It is worth noting that a homogeneous interphase interface is the key point to ensure the uniform transport of Li ions in LIBs. The LiCoO₂/graphite cells with the PAAB-Li-assisted PP separator demonstrate excellent cycle stability and rate performance. The superior rate capability from the modified separator surely results in the potential application in LIBs requiring high power

density. In addition, the Li symmetric cells with the modified separator stably cycled over 800 h with a constant overpotential of 43 mV (1 mAh·cm⁻²), indicating the modified separator effectively suppresses the Li dendrite growth. This facile strategy can be easily applied to LIBs requiring high safety and even be scalable to Li metal batteries.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-020-2455-1>.

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