Amphiphilic Bottlebrush Polymeric Binders for High-Mass-Loading Cathodes in Lithium-Ion Batteries

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In contrast to noteworthy advancements in cathode active materials for lithium-ion batteries, the development of cathode binders has been relatively slow. This issue is more serious for high-mass-loading cathodes, which are preferentially used as a facile approach to enable high-energy-density Li-ion batteries. Here, amphiphilic bottlebrush polymers (BBPs) are designed as a new class of cathode binder material. Using poly (acrylic acid) (PAA) as a sidechain, BBPs are synthesized through ring-opening metathesis polymerization. The BBPs are amphiphilic in nature owing to the hydrophilic PAA sidechains and hydrophobic polynorbornene (PNB) backbones. The PNB backbone allows process compatibility with nonaqueous solvent-based commercial cathode fabrication, while the PAA sidechain provides strong adhesion between cathode active layers and metallic current collectors. Moreover, the PAA sidechain simultaneously chelates transition metal ions dissolved from cathode active materials (LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NCM811)) particles which are chosen as a model material. Driven by the well-balanced amphiphilicity and bottlebrush-based structural uniqueness of the BBP binder, the resulting NCM811 cathode exhibits uniform electron/ion conduction networks and dimensional stability. Notably, a high-mass-loading (27 mg cm⁻², corresponding to 5.2 mAh cm⁻²) NCM811 cathode with stable cyclability is achieved with an extremely low content (1 wt%) of the BBP binder.

1. Introduction

To meet the ever-increasing demand for high-energy-density lithium-ion batteries, significant efforts have been devoted to developing cathode active materials that can fulfill high-capacity/

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the advancements of cathode active materials are overshadowed by the slow development of cathode binders, which should not be underestimated in terms of enabling practical cathode sheets. This issue becomes more stringent for the development of high-mass-loading cathode sheets, which have garnered considerable attention as a facile and scalable way to construct high-energy-density Li-ion batteries.^[5-7] Major challenges facing the high-massloading cathode sheets include nonuniform electron/ion conduction networks in their through-thickness direction,[8-12] insufficient adhesion (between electrode active layers and current collectors) under electrolyte-soaked states,[13-15] and dissolution of transition metal (TM) ions from cathode active materials.^[8,16,17] Notably, these challenges are closely dependent on cathode binders. Several previous studies on cathode binders have focused on the synthesis and engineering of new materials, with particular attention to replacing

high-voltage requirements.^[1-4] However,

polyvinylidene fluoride (PVdF) binders that have been predominantly used in commercial cathodes. For example, gum materials^[18,19] such as xanthan and guar gums with hydroxyl groups enhance the structural stability and electrochemical performance of overlithiated layered oxide (OLO) cathodes by chelating the dissolved TM ions. Carboxymethyl cellulose (CMC) exerted a strong binding force on OLO and mitigated the phase transition of OLO during cycling.^[20,21] Owing to its hydroxyl groups, lignin enhanced the adhesion between LiNi_{0.5}Mn_{1.5}O₄ (LNMO) active materials and current collectors, and contributed to the formation of uniform cathode–electrolyte interphase (CEI).^[22] In addition to these biomaterials, polyacrylic acid (PAA)^[23] and Li–PAA^[24] were explored as binders for the OLO and LNMO cathodes, which formed stable CEI layers and suppressed the dissolution of TM ions.

However, these cathode binders were only suitable for aqueous slurry-based cathode fabrication processes due to their hydrophilic functional groups. More notably, these aqueous binders were not suitable for moisture-sensitive Ni-rich cathode active materials, which have gained considerable attention for high-energy-density Li-batteries used in long-range electric vehicles. The Ni-rich cathode active materials often undergo structural disruption when exposed to water molecules,^[25] thus generating unwanted residual Li compounds such as LiOH and SCIENCE NEWS ______ www.advancedsciencenews.com

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 Li_2CO_3 .^[26] To overcome these problems triggered by aqueous slurry for the Ni-rich cathode active materials, nonaqueous binders have been investigated. Fluorinated polyimide maintained the structural integrity of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811) cathode active materials and improved their thermal stability.^[27,28] A recent study reported that elastic spandex binders form hydrogen bonds with NCM811 particles and suppress the interfacial side reactions with liquid electrolytes.^[29]

Most of the previously reported binders mentioned above failed to resolve the longstanding trade-off issue, that is, simultaneously achieving strong binding forces enabled by the polar groups of binders and low electrolyte swelling enabled by the nonpolar groups of binders. Moreover, these binders have limitations in terms of active material content (in many cases, \leq 94 wt%) and areal capacities (\leq 1.0 mAh cm⁻²) of cathode sheets, resulting in formidable obstacles to the development of practical high-energy-density Li-ion batteries.

Here, we propose a new cathode binder design based on amphiphilic bottlebrush polymer (BBP) chemistry. The BBPs, which belong to a class of comb-like macromolecules, feature 3D architecture consisting of densely grafted sidechains attached to the polymer backbones.^[30-32] Using ring-opening metathesis polymerization (ROMP) allows the precise control of the architecture and chemical functionalities of the BBPs. The BBPs synthesized herein are composed of hydrophobic polynorbornene (PNB) backbones and hydrophilic PAA sidechains. The densely grafted hydrophilic PAA sidechains enable the BBPs to provide strong adhesion forces through hydrogen bonding and chelate TM ions, which are dissolved from cathode active materials. The hydrophobic PNB backbones in the BBPs are hardly swollen with liquid electrolytes; hence, they contribute to the structural integrity and allow process compatibility with nonaqueous solventbased cathode fabrication used for commercial Li-ion batteries, particularly for moisture-sensitive Ni-rich layered cathodes. In addition, the amphiphilicity of the BBP binder allows uniform dispersion of cathode slurries. As a proof of concept for this approach, NCM811 cathode active materials were chosen.

Benefiting from the well-balanced amphiphilicity and bottlebrush-based structural uniqueness, the BBP binder enhances: i) formation of highly developed electron/ion conduction pathways in the through-thickness direction of the resulting cathode sheets; ii) adhesion between NCM811 layers and current collectors, even in electrolyte-soaked state of the cathode sheets; and iii) chelation of the TM ions dissolved from NCM811, thereby preventing phase transition of NCM811. These advantageous effects of the BBP binder on the NCM811 cathode sheets are schematically presented in **Scheme 1**a. As a result, a high-mass-loading (27 mg cm⁻², corresponding to 5.2 mAh cm⁻²) NCM811 cathode sheet with stable cycling retention is achieved with an extremely low content (1 wt%) of the BBP binder, which lies far beyond those achievable with previously reported cathode binders.

2. Results and Discussion

2.1. Design and Synthesis of the BBPs

The BBPs with well-defined architecture and amphiphilicity were synthesized using a grafting-through method of ROMP

with Grubb's catalyst. A linker with six carbon atoms was attached to the norbornene monomer to avoid a steric hindrance of densely grafted sidechains, and hence to achieve a high conversion of macromonomers during the ROMP reaction.^[33–35] For the sidechains, poly(*tert*-butyl acrylate) (PtBA) was synthesized through general Cu(0)-mediated atom transfer radical polymerization (ATRP), and the norbornene-functionalized macromonomer, NB-PtBA, was obtained after nitroxide-radical coupling of a norbornene-functionalized nitroxide radical with PtBA.^[36] To compare the effect of the length of a sidechain on the electrochemical and physical properties of the BBP binders, we controlled the molecular weights (M_n) of PtBA (detailed information is summarized in Table S1 in the Supporting Information). These polymers are characterized through gel permeation chromatography (GPC) (Figure S1, Supporting Information). The end modification of PtBA with norbornene moiety was confirmed through nuclear magnetic resonance (NMR) analysis (Figures S2 and S3, Supporting Information). The BBPs were then synthesized through the ROMP reaction of the fully functionalized norbornene macromonomers with Grubb's catalyst. The degree of polymerization (DP) of the BBP backbone was fixed to 100 and nearly complete conversion of NB-PtBA was achieved, as confirmed from the results of GPC and NMR. The PNB-g-PtBA BBPs of different sidechain lengths were synthesized with total M_n 's of 133, 436, and 732 kDa, which were represented as BBP-1, BBP-2, and BBP-3, respectively. Finally, the PNB-g-PAA BBPs were obtained after removing the tert-butyl groups in the PtBA sidechains through acid hydrolysis, in which the *k* and *m* values represent the degree of polymerization of PNB backbone and PAA sidechains, respectively. The calculated M_n 's of PNB-g-PAA BBPs correspond to 76, 244, and 407 kDa for BBP-1, BBP-2, and BBP-3, respectively (Table S1, Supporting Information). Since the BBPs were synthesized via ROMP reaction using norbornene-functionalized macromonomers, each repeating unit contains one sidechain from macromonomer, leading to the same grafting density of sidechains regardless of the sidechain length. It is worth noting that all reactions employed for the BBP synthesis resulted in high yields, which could be suitable for large-scale synthesis.

2.2. Electrochemical/Physical Properties of the BBP as a Cathode Binder

The electrochemical/physical properties of the BBP were investigated and compared with those of a commercial PVdF (chosen as a control sample, weight average molecular weight $(M_w) = 280$ kDa, Kureha) to explore its potential use as a cathode binder. The linear sweep voltammetry (LSV) profile of a BBP film (Figure S4, Supporting Information) showed that its electrochemical stability was comparable to that of a PVdF film. Adhesion between electrode active layers and Al current collectors can significantly affect the electrochemical performance of cathode sheets. Various BBP films with different sidechain lengths under a fixed DP (=100) of the PNB backbone were laminated with Al current collectors and subjected to a 180° peel-off test. The adhesion force increased with the increasing sidechain length (Figure S5, Supporting Information). Meanwhile, the electrolyte swelling of the cathode binders should be



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Scheme 1. a) Schematic representation depicting structural superiority of the BBP cathode over the PVdF cathode and advantageous effects of the BBP binder on the formation of electron/ion conduction networks, adhesion with Al current collectors, electrolyte swelling, and chelation of TM ions, with focus on the roles of hydrophilic PAA sidechain and hydrophobic PNB backbone. b) Synthetic route of the BBP (i.e., PNB-g-PAA). The *k* and *m* values indicate the degree of polymerization of backbone and sidechains, respectively.

minimized because it weakens the adhesion forces during the cell operation and dries out the electrolytes in the electrodes, resulting in the structural disruption of the electrodes and loss of cycling performance.^[37] The BBP films with relatively short sidechain lengths (BBP–1 and BBP–2) were hardly swollen with a liquid electrolyte (1 $\,\mathrm{M}$ lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC)/diethyl carbonate (DEC) = 1/1 (v/v)) (Figure S6, Supporting Information). However, further increase in the sidechain length (BBP–3) led to the increase in the volume of the BBP film, thereby revealing that the BBP–3 film was severely swollen with the electrolyte.

Considering these observations, we chose the BBP–2 as an optimal sample. The BBP film showed the higher adhesion force of 3.76 N cm⁻¹ with the Al current collector compared to the PVdF film (0.18 N cm⁻¹) (Figure 1a). This result indicates that the hydrophilic PAA groups of the BBP play a significant role in forming strong hydrogen bonds with the Al current collector, whereas PVdF forms weak van der Waals bonds with the Al current collector. In addition to this higher adhesion force, the BBP film was hardly swollen with the liquid electrolyte, whereas the PVdF film showed an increase in the volume change (Figure 1b). This result indicates that the BBP, owing to



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Figure 1. Characterization of the BBP binder and cathode slurries. a) Adhesion force between the BBP film (vs PVdF film) and Al current collector, which was estimated using 180° peel-off test. b) Volume change of the BBP film (vs PVdF film) in a liquid electrolyte (1 \bowtie LiPF₆ in EC/DEC = 1/1 (v/v)) as a function of elapsed time. Insets show the photographs after the swelling test, in which the red lines indicate area of the films before the swelling test. c) Amount of Mn²⁺ trapped by the BBP film (vs PVdF film), which was estimated using ICP-MS analysis. d) Micro-CT images of the NCM811 cathode slurries with the PVdF binder (left) and BBP binder (right).

its well-balanced amphiphilicity, can resolve the trade-off issue of electrode binders, that is, between adhesion force and electrolyte swelling.

A formidable challenge facing high-capacity/high-voltage cathode active materials, such as NCM811, is the dissolution of TM ions in electrolytes, resulting in interfacial side reactions with cathode active materials and consequent metallic deposition on anodes. To examine the TM-ion-chelating capability, the BBP film was immersed in a model liquid electrolyte (10×10^{-3} M manganese perchlorate [Mn(ClO₄)₂]-containing liquid electrolyte ($1 \ M \ LiPF_6$ in EC/DEC = 1/1 (v/v)) for 2 h, and then the trapped Mn²⁺ was quantitatively estimated using inductively coupled plasma mass spectrometry (ICP-MS). Figure 1c shows that the amount of Mn²⁺ (180 ppm) trapped by the BBP film is substantially higher than that (15 ppm) of the PVdF film, verifying that the PAA sidechains of the BBP

effectively chelate Mn²⁺ by the formation of metal ion–PAA complexes. The polar acrylic acid groups are known to strongly interact with metal ions via the formation of metal ion–organic complexes.^[38]

From the structural point of view, the dispersion state of electrode slurries plays a crucial role in constructing uniform electron/ion conduction networks in the electrodes. As described above, the hydrophilic PAA sidechains of the BBP have affinity toward NCM811 particles. The PAA sidechains adsorbed on the NCM811 particles could change surface charge of the particles. The increased surface charge of the particles tend to generate electrostatic repulsion between the particles, thereby facilitating the dispersion.^[39,40] The BBP slurry of this study, due to the PAA sidechains adsorbed on the NCM811 particles, showed the higher zeta potential (–50.08 mV) than the control PVdF slurry (–36.27 mV) (Figure S7, Supporting Information). This result

indicates a strong electrostatic repulsive force among the particles, which can prevent the aggregation of the particles and contribute to the better dispersion state of slurry. In addition, it has been well known that the BBPs are less entangled compared to linear polymers owing to their nonlinear architecture of densely grafted sidechains that prevents chain entanglement.^[41] These features of the BBPs are expected to prevent the aggregation of cathode components in the slurries. As a supplementary experiment to examine the dispersion state, the NCM811 particles were mixed with the BBP binder at a NCM811/BBP composition ratio of 80/20 (w/w) in *n*-methyl-2-pyrrolidone (NMP) solvent. Subsequently, the supernatants were obtained by centrifugation, and then ultraviolet-visible (UV-vis) spectroscopy was performed for these supernatants. The BBP-bindercontaining solution showed stronger absorbance than the PVdF-binder-containing solution (Figure S8, Supporting Information), indicating the better dispersion state. This beneficial effect of the BBP binder was verified through microcomputed tomography (CT) of the cathode slurry (Figure 1d), in which the composition ratio of the slurry was NCM811/carbon black/BBP binder = 97/2/1 (w/w/w). The NCM811 particles and carbon black additives were uniformly dispersed in the BBP slurry, whereas some aggregates of the particle mixtures were observed in the PVdF slurry. This result underscores a viable role of the amphiphilic BBP binder in achieving the well-dispersed cathode slurry. Furthermore, the process compatibility of the BBP binder with the commercial cathode fabrication process based on the NMP solvent demonstrates its facile application and viability for practical applications.

2.3. Structural/Electrochemical Characterization of the BBP Cathodes

Effects of the BBP binder on the morphology and electrochemical performances of the NCM811 cathodes were investigated. The NCM811 cathode was fabricated by casting a cathode slurry (NCM811/carbon black/binder (BBP or PVdF) = 97/2/1 (w/w/w)) on an Al current collector. The obtained NCM811 cathodes had an areal mass loading of 16 mg cm⁻² and a thickness of $62 \ \mu m$ for both the BBP and PVdF binders (Figure S9, Supporting Information). The NCM811 cathode with the PVdF binder (hereinafter referred to as PVdF cathode) showed that the particles were not homogeneously dispersed, along with some aggregates (Figure 2a (left)). By comparison, the NCM811 cathode with the BBP binder (referred to as BBP cathode) exhibited uniform dispersion state of the components (Figure 2a (right)). This morphological difference between the two cathodes was further examined by analyzing transmission emission microscopy (TEM) images (Figure S10, Supporting Information). The BBP binder covered the surface of NCM811 particle with a thin, uniform, and conformal film, whereas the PVdF binder provided a thicker and irregular coverage. Polar binders such as PAA are known to establish hydrogen bonds with oxygen-containing groups existing on the cathode active particle surface, thereby showing the film-forming ability together with inducing strong particle-to-particle cohesion.^[23,29] This result underlines a vital role of the hydrophilic PAA sidechains of the BBP binder. This result was verified by comparing the surface electrical resistivities of the NCM811 cathodes (Figure 2b). Owing to the highly developed electron conduction networks achieved by the well-dispersed slurry, the BBP cathode showed lower electrical resistivity than the PVDF cathode with the same cathode composition ratio.

For the practical application of electrode binders in Li-ion batteries, the electrolyte swelling of the electrode binders should be suppressed because it often weakens the adhesion forces.^[15] We conducted a 180° peel-off test for the BBP cathode after soaking in the liquid electrolyte. The BBP cathode maintained its structural integrity compared to the PVdF cathode, thereby exhibiting severe detachment of its components (Figure S11a, Supporting Information). This result was confirmed by measuring the contact resistance between the cathodes (taken after the peel-off test) and Li metals. The BBP cathode had higher resistance than the PVdF cathode (Figure 2c; Figure S11b, Supporting Information). This result indicates that the cathode active layer in the BBP cathode was maintained, thus preventing direct contact of the Al current collector with the Li metal. As an additional evidence, the interfacial contact resistance between the cathode active layer and Al current collector was analyzed by electrochemical impedance spectroscopy (EIS) using a symmetric cell comprising two identical cathodes.^[42] The Nyquist plot of the BBP cathode showed a smaller semicircle arc (Figure 2d), indicating the lower interfacial resistance. This result demonstrates that the BBP binder enables the strong interfacial adhesion between the cathode active layer and Al current collector in the electrolyte-soaked state.

The uniform dispersion state of the BBP cathode contributes in developing electron/ion conduction networks. We performed galvanostatic intermittent titration technique (GITT) analysis of a half cell (BBP cathode/Li metal). Figure 2e shows that the BBP cathode effectively alleviated the rise in cell polarization upon repeated current stimuli (applied at a current density of 1C with an interruption time of 1 h between the pulses), in which the obtained internal cell resistances were provided as a function of the state of charge (SOC) and depth of discharge (DOD) (Figure 2f). From these GITT results, we calculated Li⁺ diffusion coefficients using the following equation^[7]

$$D = \frac{4}{\pi \Delta \tau} \left(\frac{m_{\rm B} V_{\rm M}}{M_{\rm B} S} \right) \left(\frac{\Delta E_{\rm S}}{\Delta E_{\rm \tau}} \right)^2 \tag{1}$$

The BBP cathode had higher diffusion coefficient (4.67 \times 10⁻⁸ cm² S⁻¹) than the PVdF cathode (3.50 \times 10⁻⁸ cm² S⁻¹), indicating that Li ion movement was facilitated in the BBP cathode.

2.4. Cell Performance of the BBP Cathode and Postmortem Analysis

The electrochemical performance of the BBP (or PVdF) cathodes (under a fixed areal mass loading of 16 mg cm⁻²) was investigated using a 2032-type coin cell (cathode/polyethylene separator/Li metal anode, liquid electrolyte of 1 \mbox{M} LiPF₆ EC/ethylmethyl carbonate (EMC)=3/7 (w/w) with 10 wt% fluoroethylene carbonate (FEC) and 2 wt% vinylene carbonate (VC)). www.advancedsciencenews.com

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Figure 2. Structural/electrochemical characterization of the BBP cathode. a) Surface SEM images of the PVdF (left) and BBP (right) cathodes. b) Surface electrical resistivity of the BBP cathode (vs PVdF cathode). c) Contact resistance between the NCM811 electrodes (taken after the peel-off test) and Li metals: BBP cathode versus PVdF cathode. d) Nyquist plots of the symmetric cells (comprising two identical cathodes): BBP cathode versus PVDF cathode. e) GITT profiles obtained upon the repeated current stimuli (at a current density of 1C, where the interruption time between the pulses is 1 h). f) Change in the internal cell resistance at a function of SOC and DOD.

The BBP cathode showed slightly higher initial discharge capacity, which almost reached a theoretical value of NCM811 (190 mAh g^{-1}),^[43] than the PVdF cathode (Figure S12, Supporting Information). The discharge rate capability of the BBP cathode was compared to that of the PVdF cathode, in which the discharge current densities varied from 0.2C to 3.0C under a constant charge current density of 0.2C (**Figure 3**a). The BBP cathode presented faster discharge rate capability than the PVdF cathode, exhibiting its facile redox kinetics. In addition, the cycling performance of the BBP cathode was investigated at a charge/discharge current density of 0.5C/0.5C (Figure 3b). Notably, the BBP cathode showed the higher cycling retention (80.6% after 240 cycles), whereas the PVdF cathode failed to maintain its capacity (0% after 240 cycles). The sharp decay in the cycling retention of

the PVdF cathode was consistent with the result of the previous study. $\ensuremath{^{[29]}}$

To further elucidate the superior cycling performance of the BPP cathode, we conducted the postmortem analysis of the electrodes after the cycling test. The results of the ICP-MS analysis showed that the amount of metallic Ni, Co, and Mn deposited on the Li metal anode (coupled with the BBP cathode) was lower than that on the Li metal anode (coupled with the PVdF cathode) (Figure 3c). This result was attributed to the excellent chelating ability of the PAA sidechain of the BBP binder, as shown in Figure 1c. The TM ions trapped by the BBP binder can mitigate the additional metal dissolution according to the Le Chatelier's principle.^[44] As a supplementary evidence, the surface morphologies of the cycled Li metal anode were analyzed (Figure S13, Supporting Information). The Li metal anode







Figure 3. Cell performance and postmortem analysis of the BBP cathode. a) Discharge rate capability (BBP cathode vs PVdF cathode) over a wide range of discharge current densities (0.2C–3.0C) at a fixed charge current density of 0.2C. b) Cycling performance (BBP cathode vs PVdF cathode) at a charge/discharge current density of 0.5C/0.5C under a voltage range of 3.0–4.2 V. c–e) Postmortem analysis after the cycling test (BBP cathode vs PVdF cathode). c) Amount of metallic Ni, Co, and Mn deposited on the Li metal anodes (estimated by ICP-MS analysis). d) XPS F1s spectra of NCM 811 cathodes. e) TEM images with fast Fourier transform patterns of NCM811 particles.

assembled with the BBP cathode showed smooth and uniform surface, whereas the Li metal anode with the PVdF cathode had random and irregular surfaces.

In addition to the cycled Li metal anodes, the structural changes in the cycled BBP (and PVdF) cathodes were investigated. The NCM811 particles of the cycled BBP cathode were relatively clean and less contaminated with the byproducts compared to the PVdF cathode (Figure S14, Supporting Information). The surface of the cycled NCM811 particles was further identified by X-ray photoelectron spectroscopy (XPS) (Figure S15, Supporting Information). The F1s spectra (Figure 3d) showed that the characteristic peak at 684.7 eV assigned to LiF/MF₂

(M: transition metal such as Ni, Mn, and Co) was weaker at the BPP cathode. The LiF/MF₂ are the unwanted byproducts occurring between M²⁺ ions dissolved from cathode active materials and hydrofluoric acid (HF) generated by PF₆⁻ and residual water in electrolytes.^[45,46] Furthermore, the BBP cathode showed lower peak intensities, including that of the Li_xPO_yF_z peak at 686.7 eV (assigned to a typical CEI layer), compared to the PVdF cathode since the side reactions were prevented.^[47,48] Meanwhile, Ni-rich NCM active materials tend to show the repeated anisotropic volume change accompanying phase transition, resulting in unwanted microcrack generation along the grain boundaries.^[49–52] The morphology of the cycled NCM811



particles was investigated using focused ion beam-scanning electron microscopy (FIB-SEM). The cycled NCM811 particles of the BBP cathode were stably maintained without severe structural disruption and cracks, as compared to the result of the PVDF cathode (Figure S16, Supporting Information).

To gain better understanding of the cycled NCM811 particles, their crystalline structures were analyzed (Figure 3e). In the delithiated state of NCM811, divalent Ni ions (Ni²⁺) tend to migrate from transition-metal slabs to Li slabs, resulting in a structural transformation from the layered phase to the spinel phase and the formation of the rock-salt phase.^[53] The TEM image showed that the cycled NCM811 particles in the PVdF cathode has the rock-salt phase and amorphous region, revealing the occurrence of structural change. By comparison, the cycled NCM811 particle of the BBP cathode maintained its layered phase together with the formation of a thin NiO rock-salt phase (≈10 nm). This result indicates that the BBP binder suppresses the dissolution of Ni²⁺, thereby maintaining the structural stability of NCM811. Moreover, the ex situ X-ray diffraction (XRD) patterns (Figure S17, Supporting Information) showed that the (006)/(102) and (108)/(110) peaks corresponding to the layered phase^[54] were slightly changed before/after the cycling test at the BBP cathode, whereas the peaks of the PVdF cathode almost disappeared after the cycling test. These results demonstrate the beneficial role of the BBP binder in preventing the interfacial side reactions and dissolution of TM ions.

In addition to the aforementioned electrochemical performance, thermal stability of cathode active materials should be secured to enable their practical applications. It is known that delithiated NCM811 could release oxygen gas upon exposure to high-temperature conditions, thereby accelerating interfacial side reactions between NCM811 and electrolytes.[55] The interfacial exothermic reaction of the delithiated NCM811 cathodes (charged to 4.2 V at a charge current density of 0.1C) was examined through differential scanning calorimetry (DSC) (Figure S18, Supporting Information). The delithiated PVdF cathode exhibited larger exothermic heat generation and lower exothermic peak temperature ($\Delta H = 493.5 \text{ Jg}^{-1}$ and T_{peak} = 209.4 °C). However, the BBP cathode presented substantially enhanced thermal stability ($\Delta H = 307.5 \text{ J g}^{-1}$ and T_{peak} = 211.9 °C). This result exhibited that the BBP binder effectively suppresses the oxygen gas release and the interfacial exothermic reactions of the NCM811 cathodes.

2.5. High-Mass-Loading NCM811 Cathodes Enabled by the BBP Binders

The strong adhesion and good slurry dispersion achieved by the BBP binder were expected to beneficially contribute to the fabrication of cathodes with low binder contents. The BBP cathode maintained the uniform dispersion state and structural stability even at a binder content of 0.5 wt% (NCM811/carbon black/BBP binder = 97.5/2.0/0.5 (w/w/w)), which was difficult to attain with the PVdF binder (Figure S19, Supporting Information). The obtained BBP cathode with areal mass loading of 15.5 mg cm⁻² showed stable cycling performance (Figure S20, Supporting Information).

Subsequently, the BBP cathodes (NCM811/carbon black/BBP binder = 97/2/1 (w/w/w)) with areal mass loadings of 16 mg cm⁻² (62 μ m), 23 mg cm⁻² (85 μ m), and 27 mg cm⁻² (95 μ m) were successfully fabricated. Figure 4a shows cross-sectional morphologies of the BBP cathodes as a function of their thickness, that is, areal mass loadings. The uniform dispersion state, along with the structural stability, was observed over the whole BBP cathodes. The PVdF binder failed to fabricate a high-mass-loading (≥ 23 mg cm⁻² or $\geq 85 \mu$ m) cathode compared to the BPP binder (Figure S21, Supporting Information). The areal discharge capacities of the BBP cathodes increased with the increasing areal mass loading (Figure 4b), while the specific capacity (190 mAh g⁻¹ at 0.1C/0.1C) of NCM811 in the BBP cathodes remained almost unchanged (Figure 4c). This result indicates that the BBP cathode facilitates full realization of theoretical specific capacity of NCM811 over the entire range of areal mass loadings. In addition, the BBP cathodes with higher mass loadings (i.e., 16, 23, and 27 mg cm⁻²) exhibited stable cycling performance (Figure 4d). It is noteworthy that the mass loading of 27 mg cm⁻² (corresponding to 5.2 mAh cm⁻²) enabled by the low BBP binder content (1 wt%) far exceeded those of the previously reported cathode binders (Table S2, Supporting Information; Figure 4e).

3. Conclusion

In summary, we presented a new binder strategy based on amphiphilic BBP to develop high-mass-loading cathodes. The amphiphilic BBP was designed to have hydrophobic PNB backbone and hydrophilic PAA sidechain. The PAA sidechain enabled good adhesion with Al current collectors and chelated TM ions dissolved from NCM811. Moreover, the PNB backbone allowed the process compatibility with NMP-based commercial cathode fabrication, particularly for moisturesensitive Ni-rich layered cathodes such as NCM811. The wellbalanced amphiphilicity of the BBP binder played a viable role in achieving the uniform dispersion state of cathode slurries. Owing to its chemical functionalities and structural uniqueness, the BBP binder enabled the formation of welldeveloped electron/ion conduction pathways in the throughthickness direction of the NCM811 cathode, strong adhesion between NCM811 layers and Al current collectors even in electrolyte-soaked state, and chelation of TM ions dissolved from NCM811. More notably, the high areal mass loading of 27 mg cm⁻² (corresponding to 5.2 mAh cm⁻²) was achieved with stable cycling retention at a very low BBP binder content (1 wt%). This was difficult to achieve with previously reported cathode binders. This study opens new routes for designing advanced cathode binders, which should keep pace with the progress of cathode active materials for sustainable highenergy-density batteries.

4. Experimental Section

Materials: *tert*-Butyl acrylate (*t*BA), methyl 2-bromopropionate, Cu(0) (gauge 0.25 mm) wire, copper(II) bromide, tris[2-(dimethylamino)ethyl] amine (Me₆-Tren), 6-aminohexanoic acid, *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDC), 4-(dimethylamino)pyridine

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Figure 4. High-mass-loading BBP cathodes. a) SEM images (cross-sectional view) of the BBP cathodes with different thicknesses, that is, different areal mass loadings. b) Charge/discharge profiles (expressed as the areal capacities of the BBP cathodes) and c) specific gravimetric capacity (based on the weight of the NCM811 particles) of the BBP cathodes as a function of areal mass loading at a charge/discharge current density of 0.1C/0.1C. d) Cycling performance of the BBP cathodes as a function of areal mass loading at a charge/discharge current density of 0.2C/0.2C at a voltage range of 3.0–4.2 V. e) Comparison of areal capacity (plotted as a function of areal mass loading) between the BBP cathode (this study) and previously reported cathodes containing various binders (more details on the references are listed in Table S2 in the Supporting Information).

(DMAP), pyridine, hydrochloric acid (HCl), trifluoroacetic acid (TFA), HPLC grade and anhydrous grade dichloromethane (DCM), tetrahydrofuran (THF), methanol (MeOH), and toluene were purchased from Sigma-Aldrich. *Cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride and 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-Hydroxy TEMPO) were purchased from TCI chemicals. [(H₂IMes) (PCy₃) (Cl)₂Ru = CHPh] Grubbs 2nd generation catalyst was purchased from AK Scientific. [(H₂IMes) (Pyr)₂(Cl)₂Ru = CHPh], **G3**, was prepared according to literature procedure.^[56,57]

Polymer Characterization: ¹H NMR spectra were recorded with a Bruker 500 MHz FT-NMR spectrometer using CDCl₃ as the solvent. The molecular weight (M_n) and molecular weight dispersity (D) were measured by GPC using THF as an eluent, and carried out using a system equipped with a Waters 1515 pump, a Wyatt Optilab T-rEX differential refractive index detector, and a WYATT DAWN HELEOS 8+ Angle light scattering system. The instrument was operated at a flow rate of 0.5 mL min⁻¹ at 40 °C.

Synthesis of Norbornene Carboxylic Acid Imide (NB-COOH): Cis-5norbornene-exo-2,3-dicarboxylic anhydride (1.0 eq., 10 g, 60.9 mmol), 6-aminohexanoic acid (1.0 eq., 8 g, 60.9 mmol), trimethylamine (0.1 eq., 0.062 g, 0.609 mmol), and toluene (100 mL) were added and mixed in a round-bottom flask (250 mL) with a stirring bar and reflux condenser (Scheme 1b). The mixture was heated at 110 °C and reflux overnight, cooled to room temperature, and the toluene was removed by a rotary evaporator under reduced pressure. The remaining product was redissolved in dichloromethane, washed with water (3×), washed with brine (3×), and the organic phase was dried over magnesium sulfate. The solvent was removed in vacuo to yield norbornene carboxylic acid imide as a white or slightly off white solid (95% yield).

¹H NMR (500 MHz, CDCl₃) δ (ppm) 6.22 (t, J = 1.8 Hz, 2H), 3.43–3.38 (m, 2H), 3.21 (p, J = 1.7 Hz, 2H), 2.61 (d, J = 1.4 Hz, 2H), 2.28 (t, J = 7.4 Hz, 2H), 1.59 (p, J = 7.5 Hz, 2H), 1.51 (ddt, J = 8.9, 7.5, 3.7 Hz, 2H), 1.45 (dp, J = 9.9, 1.6 Hz, 1H), 1.32–1.25 (m, 2H), 1.15 (dd, J = 9.7, 1.6 Hz, 1H).

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Synthesis of exo-Norbornenyl-Functionalized Nitroxide Radical (NB-NRC): To a round-bottom flask, exo-norbornene carboxylic acid imide (1.0 eq., 5 g, 18 mmol), 4-Hydroxy Tempo (1.1 eq., 3.45 g, 20.0 mmol), EDC (1.2 eq., 4.14 g, 21.5 mmol), and DMAP (0.2 eq., 0.43 g, 3.52 mmol) were added, followed by 50 mL anhydrous DCM (Scheme 1b). The mixture was deoxygenated by purging with argon for 30 min and was conducted at room temperature overnight. The reaction mixture was washed with water (3×), washed with brine (3×), and the organic phase was dried over magnesium sulfate. The organic phase was concentrated via a rotary evaporator under reduced pressure and the remaining residual was purified by silica gel chromatography (ethyl acetate/hexane, 2:1 v/v) to obtain the product the product as a reddish orange solid (80% yield).

¹H NMR (500 MHz, CDCl₃) δ (ppm) 6.18 (s, 2H), 4.99–4.91 (m, 1H), 3.39–3.33 (m, 2H), 3.17 (s, 2H), 2.57 (s, 2H), 2.16 (t, J = 7.5 Hz, 2H), 1.88–1.77 (m, 2H), 1.59–1.39 (m, 7H), 1.25–1.19 (m, 2H), 1.16 (s, 6H), 1.13 (s, 6H), 1.10 (s, 1H).

¹H NMR (500 MHz, CDCl₃) δ (ppm) 6.49 (s, 2H), 4.32 (q, *J* = 6.8 Hz, 1H), 3.68 (s, 2H), 3.48 (s, 2H), 2.88 (s, 2H), 2.61–1.37 (m, 16H).

Synthesis of PtBA: The polymerization of PtBA was conducted under general Cu(0)-mediated ATRP conditions (Scheme 1b). To a 100 mL Schlenk tube, the initiator methyl 2-bromopropionate, CuBr2, and Me_6Tren at a ratio of [I]:[CuBr₂]:[Me₆Tren] = 1:0.05:0.1 and tBA monomer were added with acetone as the solvent. The solution was degassed by three freeze-pump-thaw cycles. During the final cycle, the Schlenk tube was filled with argon and a stirring bar with the preactivated copper wire (5 cm) was guickly added to the frozen reaction mixture. The Schlenk tube was sealed, evacuated, and backfilled with argon three times. The polymerization was initiated by placing the flask in a preset oil bath at 50 °C and allowed to reach >90% conversion. The polymerization was quenched by soaking the flask in liquid nitrogen and exposing the reaction mixture to air. The mixture was diluted with DCM and filtered through neutral alumina column to remove the copper catalyst. The diluted mixture was concentrated via a rotary evaporator under reduced pressure. Finally, the product was precipitated in cold methanol/water (5:5 v/v) and dried in vacuo.

Synthesis of Norbornene-Functionalized Macromonomers (NB-PtBA): A 50 mL round-bottom flask was charged with PtBA-Br, *exo*-norbornenyl-functionalized nitroxide radical, CuBr, and Me₆Tren at a ratio of [PtBA]:[NB-TEMPO]:[CuBr₂]:[Me₆Tren] = 1:1.0:1.1:1.1 and toluene/DMSO (5:5 v/v) (Scheme 1b). The solution was deoxygenated by purging with argon for 30 min and was conducted at room temperature for 2 h in argon-filled glovebox. The mixture was diluted with DCM and filtered through neutral alumina column to remove the copper catalyst. The diluted mixture was concentrated via a rotary evaporator under reduced pressure. The remaining residual was diluted with acetone, transferred to a dialysis tube, and stirred against acetone to remove the unreacted NB-TEMPO. After dialysis, the solvent was removed and dried in vacuo (100% yield).

NB-PtBA (1 *kDa*): ¹H NMR (500 MHz, CDCl₃) δ (ppm) 6.27–6.25 (m, 2H), 4.94 (dq, J = 10.9, 5.6, 4.2 Hz, 1H), 3.63 (d, J = 3.0 Hz, 3H), 3.43 (t, J = 7.4 Hz, 2H), 3.25 (t, J = 2.0 Hz, 2H), 2.65 (s, 2H), 2.27–2.16 (m, 9H), 1.61–1.07 (m, 147H).

NB-PtBA (7 *kDa*): ¹H NMR (500 MHz, CDCl₃) δ (ppm) 6.27 (d, J = 2.0 Hz, 2H), 3.64 (d, J = 2.2 Hz, 3H), 3.46–3.42 (m, 2H), 3.26 (s, 2H), 2.94 (s, 1H), 2.87 (s, 1H), 2.32–2.14 (m, 76H), 1.42 (s, 710H).

Synthesis of PNB-g-PtBA via ROMP: NB-PtBA was added to a glass vial A and anhydrous DCM was added ([NB-PtBA] = 0.05 M) in a glove box at room temperature (Scheme 1b). G3 was added to the separate vial B and dissolved in DCM ([G3] = 0.005 M). G3 solution was injected into the vial A using a gas-tight syringe ([NB-PtBA]/[G3] = target DP) to initiate ROMP of NB-PtBA. After 1 h, vial A was removed from the glove box, and the polymerization was quenched with excess of ethyl vinyl ether. The PNB-g-PtBA BBP was precipitated into cold methanol and dried in vacuo.

Hydrolysis of PNB-g-PtBA to PNB-g-PAA BBPs: In a glass vial equipped with a stirring bar, PNB-g-PAA was dissolved in DCM. Excess of TFA was added to the solution and the mixture was stirred at ambient temperature. The hydrolysis reaction of the *tert*-butyl groups on the PtBA was left to proceed for 24 h. The reaction mixture was filtered with filter paper and washed with excess of DCM and dried in vacuo. The resulting BBP, PNB-g-PAA, was collected as white or slightly yellow solid.

Structural/Physicochemical Characterization of BBP Binders: The electrochemical stability window of the BBP binder was investigated using LSV performed on a working electrode (stainless-steel) and a counter/ reference electrode composed (Li metal), and the LSV measurements were performed with a scan rate of 1.0 mV s^{-1} . The adhesion strength between the binder films and the Al current collectors was measured by a universal testing machine (DA-01, Petrol LAB) at a peel speed of 300 mm min $^{-1}$. For the electrolyte swelling test, the binder films were immersed in the liquid electrolyte at 60 °C and their volume change was measured before/after the electrolyte immersion. To quantitatively estimate the TM ion-chelating capability of the BBP binder, manganese perchlorate solution (10×10^{-3} M Mn(ClO₄)₂-containing 1 M LiPF₆ in EC/DEC = 1/1 (v/v)) was prepared as a model solution. After being soaked in the solution for 2 h at room temperature, the samples were washed with a dimethyl carbonate (DMC) solvent, and then, the amount of the captured Mn²⁺ was estimated by ICP-MS (ELAN DRC-2, Perkin Elmer) analysis. To characterize the dispersion state of the cathode components in the NMP suspension, the mixture suspension was centrifuged (Combi-514R, Hanil Science Medical) for 30 min at 2000 rpm to obtain supernatants and then, UV-vis spectroscopy (Agilent, Cary 5000) was conducted. The dispersion state of cathode slurries was also analyzed by fluorescent confocal images using a multiphoton confocal microscope (LSM 780 NLO, Carl Zeiss).

Structural/Physicochemical Characterization of NCM811 Cathodes with BBP Binders: The surface and cross-sectional morphologies of the NCM811 cathodes were investigated using field emission secondary electron microscopy (FE-SEM, S-4800, Hitachi) and energy-dispersive X-ray spectroscopy (EDS, JSM 6400, JEOL). The electrical resistivity and contact resistance of the NCM811 cathodes were measured using and electrode measurement system (RM2610, Hioki). The ICP-MS (ELAN DRC-2, Perkin Elmer) analysis was conducted to quantitatively estimate the metal (Ni, Co, and Mn) deposited on the Li metal anode after the cycling test. The interfacial exothermic reaction occurring between the charged NCM811 and liquid electrolyte was examined using DSC (Q200, TA), in which the cells were charged to 4.2 V at a current density of 0.1C and then disassembled in a glove box to obtain the charged electrode.

Electrochemical Characterization of NCM811 Cathodes with BBP Binders: The NCM811 cathodes with the BBP binders (i.e., BBP cathodes) were fabricated by casting NMP solvent-based slurry composed of 97 wt% of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811, LG chem.), 2 wt% of carbon black (Super C65), and 1 wt% of BBP binder. The casted electrode slurry was vacuumdried at 120 °C for 12 h and followed by roll-pressing to be compactified. The PVdF cathodes with the same compositions were fabricated using the same method. The electrode density of both cathodes were \approx 3.5 g cc⁻¹. The electrochemical performance of the BBP cathode was characterized using 2032-type coin cells (BBP cathode/polyethylene separator (thickness = 20 μ m, Toray-Tonen)/Li metal anode (200 μ m)). A liquid electrolyte of 1 M LiPF₆ in EC/EMC = 3/7 (w/w) with 10 wt% FEC and 2 wt% VC additives were used. The cell was assembled in an argon-filled glove box. The cell performance was investigated using a cycler test (PNE solution) under various charge/discharge conditions. The GITT profiles and AC impedance of the cells were obtained using a potentiostat/ galvanostat (VSP classic, Bio-Logic). The diffusion coefficients of Li ion in the electrode were obtained from the GITT results. The diffusion coefficients were calculated using the following equation

$$D = \frac{4}{\pi \Delta \tau} \left(\frac{m_{\rm B} V_{\rm M}}{M_{\rm B} S} \right) \left(\frac{\Delta E_{\rm S}}{\Delta E_{\tau}} \right)^2 \tag{2}$$

where $m_{\rm B}$ is assigned to mass of the NCM811, $M_{\rm B}$ to the molar mass of NCM811 (97.28 g mol⁻¹), $V_{\rm M}$ is the molar volume of NCM811

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(20.53 cm³ mol⁻¹), and S is the area of the electrode (1.13 cm²). τ represents the duration of current pulse time. ΔE_s represents voltage change during the single GITT step and ΔE_{τ} represents overall cell voltage change during the constant current step.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

amphiphilicity, bottlebrush polymers, cathode binders, high-massloading cathodes, lithium-ion batteries

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