1. Introduction

As practical energy storage devices, lithium (Li) ion batteries (LIBs) have been essential to almost all portable electronic devices, electric vehicles (EVs), and stationary energy storage systems. Launched in 1991, LIBs are superior in their high energy density, high operating voltage, and limited self-discharging, as compared to the other secondary batteries.1–3 Their performances have steadily increased over time to enable valuable products and services, e.g., longer driving distances and faster charging for EVs or carrying heavier packages for drone deliveries.4–6 The energy density of the existing commercial LIBs has increased to ≈4 X of the initially introduced LIBs. It was recently reported that the theoretical limit in the existing chemical systems, based on the combination of a graphite anode and an Li metal oxide or phosphate cathode, may soon be reached.7 To surpass this existing energy density limit, there have been investigations using inherently higher capacity materials for both cathodes and anodes.8–10

Silicon (Si) is one of the most attractive active materials for LIB anodes, as it has extremely high gravimetric capacity (3579 mA h g−1 at room temperature, if lithiated to Li15Si4), a low discharge voltage (the average delithiation voltage is around 0.4 V vs Li/Li+), the second most abundant element on earth, and environmentally benign.11,12 However, practical usage of Si anodes has not yet been widely commercialized due to its poor capacity retention. It has been attributed to the enormous volume change (300–400%) after lithiation and delithiation cycles, resulting in three failure mechanisms: (i) mechanical fracture such as cracking and pulverization which causes electrical isolation within particles, (ii) loss of interparticle electrical contact due to expansion and contraction, and (iii) repeated side reactions

A self-healing polymer (SHP) with abundant hydrogen bonds, appropriate viscoelasticity, and stretchability is a promising binder to improve cycle performance of Si microparticle anodes in lithium (Li) ion batteries. Besides high capacity and long cycle life, efficient rate performance is strongly desirable for practical Si anode implementation. Here, polyethylene glycol (PEG) groups are incorporated into the SHP, facilitating Li ionic conduction within the binder. The concept of the SHP-PEG binder involves improving the interface between Si microparticles and electrolytes after cycling based on the combination of self-healing ability and fast Li ionic conduction. Through the systematic study of mixing PEG Mw and ratio, the polymeric binder combining SHP and PEG with Mw 750 in an optimal ratio of 60:40 (mol%) achieves a high discharging capacity of ≈2600 mA h g−1, reasonable rate performance especially when >1C and maintains 80% of their initial capacity even after ≈150 cycles at 0.5C. The described concept for the polymeric binder, embedding both self-healing ability and high Li ionic conductivity, should be equally useful for next generation batteries utilizing high capacity materials which suffer from huge volume change during cycling.
with electrolytes because of the unstable interface between Si particles and electrolytes. These three modes of failure lead to rapid fading capacity of Si anodes by losing active materials, consuming huge amount of Li ions and electrolytes and increasing internal resistance.\[9,12\]

To solve the critical issues for practical Si anode implementation, researchers have been developing various Si nano materials such as nanowires\[13–15\], core–shell structures\[16–18\], nanoparticles coated by graphene\[19–21\], and nanosheets\[22,23\] which can resist mechanical degradation both at the particle and electrode levels. Such nanostructured Si electrodes have been shown to improve cycle performance significantly. However, Si nanomaterials are usually synthesized by complex and multistep processes to achieve specific structures, resulting in high material costs and lower scalability for their industrial applications. Also, the high surface area of Si nanomaterials usually causes low initial coulomb efficiency due to high consumption of electrolytes during initial liithiation.\[24,25\] On the other hand, Si micросized particles (microparticles) are readily commercially available at low cost due to their simple preparation processes. They also show high initial coulomb efficiency because of relatively low surface area compared to nanoparticles.\[24,25\] However, bare Si microparticles suffer from drastic capacity fading after only ten or less cycles because of the significant fracture and particle detachment in the electrodes.\[26,27\]

To overcome this challenge, we hypothesized that a properly selected polymeric binder could serve to maintain the integrity of Si electrodes after their huge volume fluctuations. To date, besides conventional polyvinylidene difluoride (PVdF) and carboxymethyl cellulose (CMC),\[28,29\] various new polymer binders have also been reported, e.g., cross-linked polymers,\[30,31\] a alginate binder,\[32\] a catechol-conjugated polymer,\[33\] natural gum\[34,35\] and conductive polymers.\[36–38\] These binders have all been shown to improve the cycle life of Si nanoparticle electrodes. However, due to their poor mechanical stretchability and relatively weak interaction with Si particles, these binders could not provide stable electrode operation for Si microparticles, especially when they are subjected to large stress generation and serious pulverization due to their huge volume changes.

Figure 1. a) Schematic chemical structure of the SHP-PEG binder. b) Schematic illustration of the Si microparticle electrode with SHP-PEG binder. i) Self-healing based on dynamic hydrogen bonding close to a crack caused after cycling. ii) Li ion conduction facilitated by PEG groups.
A self-healing polymer (SHP) with abundant hydrogen bonds, appropriate viscoelasticity, and stretchability is an attractive candidate to improve the cycle performance of Si microparticles. Since they can strongly interact with Si particles through their hydrogen bonds to maintain the integrity of the electrodes and, subsequently, recover themselves after generating cracks on Si surface during cycling. This results in retention of electrical contact with the electrodes and suppresses side reactions with electrolytes at freshly exposed electrode surfaces from cracks. In addition, practical rate performance (>0.5C) related to fast charging and high power density is strongly desirable for eventually introducing Si microparticle electrodes with low cost and high reproducibility for next generation batteries. Previous strategies to enhance rate performance included the improvement of the electron and Li ion transport at the electrode surface and in its bulk. To achieve practical Si microparticle-based electrodes, we reasoned that improving Li ion transport by utilizing functional binders (thereby eliminating costly complex nanostructured Si materials) is essential to achieve their good rate performance.

Here, we describe a new polymeric binder which incorporates polyethylene glycol (PEG) groups into the SHP, for Si microparticle-based electrodes that affords high capacity, long cycle, and improved rate performance. The concept of SHP-PEG binder involves improving the interface between Si microparticles and electrolytes after cycling based on the combination of self-healing ability and fast Li ionic conduction. Through autonomous and spontaneous self-healing and high ionic conductivity by SHP-PEG binder, the Si microparticle electrodes are able to still maintain electric conduction after numerous cycling, suppress side reaction with electrolytes and, finally, showed higher rate performance than the previous SHP binder by facilitating Li ion charge transfer between Si particles and electrolytes. These attributes are effective and promising to afford the ideal interface between Si particles and electrolytes, hence further increase our understanding of polymer binder design for the next-generation Si microparticle anode electrodes.

### 2. Results and Discussion

Figure 1 illustrates the chemical structure of the supramolecular SHP-PEG binder, which consists of fatty oligomers, urea groups, and PEG groups. To impart Si microparticles with desired parameters such as high capacity, long life cycle, and good rate performance, our design strategy of the polymer binder has two important aspects (Figure 1b): First, it has self-healing ability based on dynamic hydrogen bonding, enabling cracks to spontaneously heal if Si’s volume changes.

**Table 1. Synthesized binders and their structural characterization.**

<table>
<thead>
<tr>
<th>Binder</th>
<th>PEG $M_w$</th>
<th>Ratio$^a$ (PEG%$^b$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHP</td>
<td>–</td>
<td>5:0 (0)</td>
</tr>
<tr>
<td>SHP-PEG750(40)</td>
<td>750</td>
<td>5:2 (40)</td>
</tr>
<tr>
<td>SHP-PEG750(100)</td>
<td>750</td>
<td>5:5 (100)</td>
</tr>
<tr>
<td>SHP-PEG2000(40)</td>
<td>2000</td>
<td>5:2 (40)</td>
</tr>
<tr>
<td>SHP-PEG2000(100)</td>
<td>2000</td>
<td>5:5 (100)</td>
</tr>
</tbody>
</table>

$^a$The ratio between the number of urea and PEG groups determined by the feeding ratio; $^b$PEG mol% of total of urea and PEG groups determined by the feeding ratio.

Figure 2. DSC curves of the binders at different PEG $M_w$ and ratio SHP to PEG.

Figure 3. Rheological results of a) frequency sweep at 1% strain of these binders and b) storage modulus ($G'$) and loss modulus ($G''$) at 0.1 Hz of these binders.
caused by the repeated charging and discharging processes (Figure 1b-i). The hydrogen bonds should also promote good adhesion between Si microparticles due to the interaction with hydroxyl groups on Si surface.\cite{39} Second, polyether units are introduced to the SHP to facilitate Li ion conduction within the binder (Figure 1b-ii). Specifically, we decided to use PEG, and it refers to the polyethylene oxide (PEO) with a molecular weight below 20 000 g mol\(^{-1}\). PEO is a well-known material for solid polymer electrolytes, which can effectively transfer Li ion because its lone-pair electrons on the oxygen can coordinate and assist Li ion transport in the matrix.\cite{48,49} Recently, studies have indicated the possibility of PEO modified binders for both anodes and cathodes to decrease their ionic resistance.\cite{50-53} Also, PEO is a semicrystalline polymer that might decrease the polymer network dynamics.\cite{49} Hence, we introduced PEG units of two molecular weights and each at two ratios in hope to alleviate their crystallinity, such as to maintain their self-healing ability and improve ionically conductive properties (Table 1).

Figure 4. Optical microscope images of a) SHP, b) SHP-PEG750(40), c) SHP-PEG750(100), d) SHP-PEG2000(40) and e) SHP-PEG2000(100) before and after scratching. The arrows indicate.

Figure 5. Peel test comparison of the Si micrometer particle electrode with each binder.
We first used differential scanning calorimetry (DSC) to characterize the polymer’s crystallinity. In contrary to SHP (which shows only glass transition temperature), all PEG modified polymers showed distinct melting points (Figure 2). The melting temperatures are influenced by PEG $M_w$ and ratio. Higher PEG $M_w$ and ratio have collectively increased their melting points, which indicate that their crystallinity was increased due to aggregation of PEG groups. It is essential for us to adjust the appropriate incorporation of binders to the Si electrodes to optimize the balance between crystalline and amorphous structures. The self-healing ability is driven by the dynamic reassociation of hydrogen bonds. The amorphous phases of the binders allow the polymer chains to rearrange and, thus, to subsequently heal any formed cracks autonomously. Furthermore, its crystalline phases are able to effectively contribute toward the polymer’s mechanical property, which hence maintains the Si electrode structure despite its large fluctuation processes.

To identify the mechanical properties of these binders, the rheology experiment was performed at room temperature using frequency sweep. As shown Figure 3a,b, when higher PEG $M_w$ is used or when all of the polymer chains are end functionalized with PEG, the storage modulus ($G'$) was increased much more than the loss modulus ($G''$) at low frequencies. The results indicate that modified PEG groups tend to result in the mechanical transition from viscoelastic materials to crystalline solid materials that behave linearly in the timescales that were tested. The observation also corresponds well to the data of DSC, which indicate that higher PEG $M_w$ and ratio show higher melting temperatures influenced by their crystalline phases.

For self-healing ability test, each binder film was first scratched by a razor blade, then left to self-heal at room temperature (Figure 4). SHP and SHP-PEG750(40) both showed significant self-healing ability at room temperature, even though the size of scratches is on the order of hundreds of micrometers. The inflicted wound was healed after $\approx 3$ h, indicating that the presence of crystalline PEG domains did not interrupt the dynamic hydrogen bonding formation and property. We observed that other films with higher PEG $M_w$ and ratio could not effectively heal their damages at room temperature even after 24 h. The above observation corresponds well with the degree of crystallinity observed for these polymers.

Adhesive strength is an important factor to maintain Si electrode structures and electrical contact between Si microparticles after cycling. The common “peel test” was performed to evaluate these binders’ adhesive properties.[37,43] In this test, the interface between Si microparticles was peeled off, which the collected data then reflects the adhesion between the Si particles. Our obtained results (Figure 5) showed that SHP has the strongest adhesive property toward Si particles. As for PEG modified binders, higher PEG $M_w$ and ratio tend to result in lower adhesion strength toward Si particles, although they all showed much better adhesion than the conventional PVdF binder. The relatively low adhesive properties could be caused by two reasons. First, decreasing the number of urea groups due to embedding much more PEG groups prevent from hydrogen bonding interaction between urea of the compounds and Si–OH groups on
Si. Second, their higher crystallinity (Figure 2) causes lack of the anchor effect to contact with Si effectively.

To evaluate their adhesive tolerance in electrolytes, Fourier transform infrared (FTIR) spectrum was collected for each electrode, after being soaked in ethylene carbonate/diethyl carbonate (EC/DEC, 1/1 v/v), for two weeks and then cleaned to remove completely EC/DEC on the electrode. As shown in Figure 6a, all electrodes after the above test have characteristic peaks from the polymers, i.e., peaks at 3250, 1550, and 1650 cm\(^{-1}\) corresponding to the N-H stretching, bending and C=O stretching band respectively.[42] This result suggests that all binders can stay on Si surfaces after soaking in electrolytes. We think the strong adhesion between Si-OH on the Si surface and binder molecules is built based on the hydrogen bonding interaction which is reported in many other binder studies including CMC, alginate.[29,32]

Li ionic conductivity of each binder film was tested to confirm the effect of modified PEG groups. The tests were performed via electrochemical impedance spectroscopy (EIS) measurements with two stainless steel blocking electrodes. Regarding the procedure of the test cell, first the binder film with electrolytes consisted of 1 m LiPF\(_6\) and EC:DEC (1/1 = v/v) was prepared and then it was sandwiched between two stainless steel electrodes in a dry glove box filled with Ar. The impedance spectrum was used to calculate the Li ionic conductivity by the high frequency intercept of \(Z'\) which was related to the bulk resistance.[42,43] The result showed that all PEG modified films facilitate Li ionic conductivity better than SHP (Figure 7). The improvement is attributed to the incorporation of PEG groups which are known to be good polymer electrolytes.[51] Although the binders with higher \(M_w\) PEG groups have increased crystallinity, they showed higher Li ionic conductivity. The PEG ratio did not seem to influence their Li ionic conductivity. This may depend on the connectivity between PEG domains and trade off in conductivity due to increased crystallinity.

To verify the effect of these binders for electrochemical performances, we proceed to prepare coin cells of the Si electrode with each binder (SHP, SHP-PEG750(40) and SHP-PEG2000(40)) and carbon black (CB). In general, electrochemical stability of a binder is required because it has to tolerate reductive reaction around 0–1.5 V versus Li/Li\(^+\). In order to characterize the electrochemical stability of these binders, cyclic voltammetry (CV) measurements were subsequently performed at a scan rate of 0.1 mV s\(^{-1}\) over the potential range of 0.01–1.5 V versus Li/Li\(^+\). As shown in Figure 8, all Si electrodes with the binders and CB show similar electrochemical profiles which have typical lithiation and delithiation peaks of

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**Figure 8.** CV measurements of Si/binder/CB (black line) and binder/CB without Si (red line). a) SHP. b) SHP-PEG750(40). c) SHP-PEG2000(40).

**Figure 9.** Voltage profiles of the Si electrode with each binder at the first cycle.

**Figure 10.** EIS measurements of the Si electrode with each binder after two activation cycles.
Si comparable to previous studies.\[39,41\] For comparison, the CV profiles of all electrodes without Si exhibited current densities that are roughly two orders of magnitude lower than the electrodes with Si, indicating that these binders have reasonable electrochemical stability for Li ion battery anodes.

The electrochemical cycling test was evaluated using galvanostatic cycling from 0.01 to 1 V versus Li/Li\(^+\) at several current densities. In this study, C-rate is defined as 1C = 3579 mA g\(^{-1}\) which is the theoretical specific capacity of Si at room temperature.\[11,43\]

All Si electrodes with SHP, SHP-PEG750(40) and SHP-PEG2000(40) reached initial delithiation capacity of ≈2600 mA h g\(^{-1}\) at a current density of 0.05C, contrary to the Si electrode with PVdF, which showed negligible capacity. Voltage profiles indicated that these binders enable Si to charge and discharge due to their adhesion with Si surface and Li ionic conductivity at the interface between Si surface and electrolytes (Figure 9). In terms of initial coulombic efficiency (CE), it was measured at ≈83%, which was higher than common Si nanostructured electrodes. The initial coulombic efficiency is important because it directly influences the full cell capacity. Si nanostructured electrodes have impressive advances for the cycle performance, but they generally tend to consume lots of electrolytes to form solid electrolyte interphases (SEI) at the first cycle due to their large surface area, which causes low initial coulomb efficiency. These binders enable the use of Si microparticle, which is advantageous in terms of low manufacturing cost and in suppressing side reactions with electrolytes to afford higher coulomb efficiency at first cycle.

To evaluate the effect of PEG groups for the charge transfer resistance \(R_{ct}\) between Si particles and electrolytes, EIS studies were performed in the frequency range of 1 MHz to 0.1 Hz after two activation cycles at 0.05C. It is established that the semicircle in the EIS profile corresponds to the \(R_{ct}\) at the interface between electrodes and electrolytes. In general, the behavior of \(R_{ct}\) is influenced by both electronic and ionic resistance because charge transfer reaction is required to bring electron and Li-ion to the interface reaction sites.\[52\] For quantitative comparison of each \(R_{ct}\), the equivalent circuit shown on the lower right corner in Figure 10 was used to fit the collected experimental EIS data. \(R_1\) stands for the ohmic resistance of the electrolyte and electrode \(R_s\), \(R_2\) is for the \(R_{ct}\) constant phase element is the double-layer capacitance, \(W_1\) represents the diffusion-controlled Warburg impedance.\[54,55\]

As shown Figure 10 and Table 2, the Si electrode with SHP-PEG750(40) noticeably improved its \(R_{ct}\) by ≈2X as compared to the Si electrode with SHP. This result indicates that PEG groups can indeed help decrease \(R_{ct}\) at the interfaces between Si particles and electrolytes, most likely due to effective Li ion pathways of PEG groups. Interestingly, the Si electrode with SHP-PEG750(40) shows better \(R_{ct}\) than the Si electrode with SHP-PEG2000(40) in spite of the fact that SHP-PEG2000(40) binder was found a higher Li ionic conductivity as shown Figure 7. As mentioned, \(R_{ct}\) is influenced by both ionic and electronic resistance. In our case, SHP-PEG750(40) can maintain the Si electrode structure even after cycling likely because of its better adhesive property with Si surfaces, which thus contributes to building good electronic networks between Si particles and preventing the portions of Si particles from being electronic inactive (Figure 5). This assumption also corresponds to the data of initial delithiation capacity in which the electrode with SHP-PEG750(40) shows higher capacity than the electrode with SHP-PEG2000(20) as shown in Figure 9.

X-ray photoelectron spectroscopy (XPS) is used to characterize the composition of each electrode’s surface (C 1s, O 1s, and F 1s) after first cycling process as shown in Figure 11. Characteristic peaks of C–C (284 eV), C–H (285 eV), C–O

![Figure 11](image URL) XPS spectra of C, O, and F 1s peaks of i) Si/SHP/CB, ii) Si/SHP-PEG750(40)/CB, and iii) Si/SHP-PEG2000(40)/CB after first cycling at C/20.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>(R_1) [Ω]</th>
<th>(R_{ct}) [Ω]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/SHP/CB</td>
<td>6.5 (±0.8)</td>
<td>71.0 (±8.8)</td>
</tr>
<tr>
<td>Si/SHP-PEG750(40)/CB</td>
<td>6.4 (±0.8)</td>
<td>35.0 (±0.8)</td>
</tr>
<tr>
<td>Si/SHP-PEG2000(40)/CB</td>
<td>5.2 (±0.7)</td>
<td>49.7 (±2.3)</td>
</tr>
</tbody>
</table>

Table 2. Equivalent circuit parameters obtained from fitting the experimental EIS spectra.
(286.5 eV), and carbonate (290.5 eV) are observed.\textsuperscript{[56,57]} In specific, Si/SHP-PEG750(40)/CB had the peak of C–O attributed to PEG groups, indicating that SHP-PEG750(40) can remain stably on the electrode surface after cycling and contribute to effective Li ion pathways. On the other hand, Si/SHP-PEG2000(40) showed a dominant peak of C–C, which was attributed to CB. This observation suggests SHP-PEG2000(40) does not exist on the electrode surface homogeneously, most likely due to inability to maintain good contact to Si. We hypothesized that the higher crystallinity of SHP-PEG2000(40) adversely prevents effective contact with Si surface, resulting in its inhomogeneity. Hence, the lower adhesion with Si surface results in it “peeling off” from the Si surface after cycling. Next, the peaks at O 1s and F 1s which correspond to SEI composition showed similar profiles, indicating that the difference among these electrodes depends on if PEG units are in contact with the Si surface. Our collected XPS data thus provide evidence consistent with the observation of SHP-PEG750(40) having a lower $R_{ct}$ than SHP-PEG2000(40).

Once the effect of modified PEG groups is verified, the rate performance of the Si electrodes with these binders was tested. In this measurement after two activation cycles at 0.05C, the cells were tested at 0.1C, 0.5C, 1C, and 2C every two cycles. As shown in Figure 12, Si/SHP-PEG750(40)/CB exhibits higher specific capacity, especially when >1C. This electrode achieved ≈1400 mA h g\textsuperscript{−1} at 1C and ≈900 mA h g\textsuperscript{−1} at 2C, which is more than twice higher than conventional graphite anodes (the theoretical capacity 372 mA h g\textsuperscript{−1}). These results correspond to the EIS data (Figure 10), which indicates that the improvement of rate performance depends on whether a lower $R_{ct}$ is achieved between Si particles and electrolytes. Furthermore, our collected voltage profile also supports the notion that the SHP-PEG750(40)-fabricated electrode mitigated the issue of overpotential as compared to other electrodes (Figure 13). Previous studies have suggested that by using active nanomaterials for the rate performance (because of their larger surface area) led to increase reaction sites and short diffusion pathway in their bulk.\textsuperscript{[44–47]} However, Si nanomaterials usually tend to suffer from relatively low initial coulombic efficiency and high manufacturing cost. Our strategy using functional binders to improve $R_{ct}$ between electrodes and electrolytes is thus attractive for practical application.

Finally, we evaluated cycle performances for these Si electrodes at 0.5C, which is a relatively higher rate than previous studies for SHP based binders(0.1C and 0.05C).\textsuperscript{[39,41–43]} As shown in Figure 14, the Si electrodes with SHP and SHP-PEG750(40) both showed better cycle performances. They can maintain ≈1300 mA h g\textsuperscript{−1}, 80% of their initial capacity even after ≈150 cycles at 0.5C. In contrast, the electrode with SHP-PEG2000(40) showed a lower cycle performance, as it can maintain only 80% of its capacity after ≈50 cycles. These results indicate that both SHP and SHP-PEG750(40) are effective to maintain their electrically electrode structures after cycling, both of which have stronger adhesion between Si particles than SHP-PEG2000(40) and spontaneous healing of the cracks by the dynamic urea hydrogen bonding (Figures 4 and 5). Furthermore, cross-sectional scanning electron microscope (SEM) images after 150 cycles (Figure 15) showed that both Si/SHP/CB and Si/SHP-PEG750(40)/CB are able to maintain the electrode structures, allowing each Si particle to effectively charge and discharge after long cycling. However, Si/SHP-PEG2000(40)/CB suffers from “electrical disconnection” from each particle. From the SEM images after cycling, we did observe significant structural degradation of the Si/SHP-PEG2000(40)/CB layer leading to their reduced adhesion and lack of self-healing ability, resulting in its capacity decay.

Figure 12. Rate performances of the Si electrode with each binder.

Figure 13. Voltage profiles of a) Si/SHP/CB, b) Si/SHP-PEG750(40)/CB, c) Si/SHP-PEG2000(40)/CB at charging/discharging rate of 0.1C, 0.5C, 1C, and 2C.
As for coulombic efficiency during cycling, SHP-PEG750(40) showed a 99.2% average after five cycles. We hypothesized that the coulombic efficiency of SHP-PEG750(40) is derived from a balanced $R_{ct}$ and strong adhesion with Si surfaces by modified PEG750, which suppresses side reactions with electrolytes.

3. Conclusion

We have successfully prepared a polymeric binder, incorporating both self-healing ability and improved Li ionic conductivity, to afford Si microparticle anode electrodes that are of high capacity, long cycle with efficient rate performance. The urea’s hydrogen bonds within our polymeric binder enabled both effective adhesion to Si surface and self-healing of generated cracks after cycling. Hence, the electrode structures can be mechanically and electrically maintained even after severe pulverization of the Si microparticles after cycling. The polymer’s PEG side groups can alleviate the charge transfer resistance between Si particles and electrolytes, as they can facilitate Li ionic conduction to enable good rate performance. We also observed that while the modified PEG groups are useful, they tend to increase crystallinity that adversely affects its adhesion to Si, hence ruining its self-healing ability when excess amount is incorporated. Through systematic investigation of mixing $M_w$ and ratio, the polymeric binder combining SHP and PEG750 in an optimal ratio of 60:40 (mol%) affords the best and well-balanced battery performances, including high capacity, long cycle stability, and reasonable rate performance. Our described concept for the polymeric binder, embedding both self-healing ability and high Li ionic conductivity, should be equally effective for other high capacity materials which suffer from huge volume change after cycling.

4. Experimental Section

Synthesis of Materials: All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. SHP precursor is a mixture (2.673 mmol amine groups/1 g polymer) which was synthesized according to a reported method.\textsuperscript{[39]} PEG-C6-isocyanate (NCO) polymers were prepared by using a literature procedure.\textsuperscript{[58]}

Synthesis of 40% PEG-Functionalized Self-Healing Polymers: In a 250 mL three-neck flask were added SHP precursor (2.0 g, 5.35 mmol amine groups) and 100 mL of dry dichloromethane and stirred to totally dissolve. Then the mixture was cooled to 0 °C by an ice bath and PEG750-C6-NCO (1.92 g, 2.14 mmol) was added into the system. After completion, remove an ice bath and return to room temperature to stir for 3 h. Subsequently, ethyl isocyanate (0.23 g, 3.21 mmol) was added by a syringe dropwise to react with the residual amine.

Figure 14. Cycle performances and coulombic efficiency of the Si electrode with each binder.

Figure 15. Cross-sectional SEM images of a) Si/SHP/CB, b) Si/SHP-PEG750(40)/CB, and c) Si/SHP-PEG2000(40)/CB after 150 cycles.
groups. After stirring for additional 3 h, remove the solvent under vacuum and bake the product in vacuum oven under 80 °C to give SHP-PEG750(40) in a quantitative yield. The same procedure was used to obtain SHP-PEG2000(40) in a quantitative yield. As shown by NMR (Figures S2 and S3, Supporting Information), all the primary amine groups were converted into urea.

Synthesis of 100% PEG-Functionalized Self-Healing Polymers: In a 250 mL three-neck flask was added SHP precursor (1.0 g, 2.67 mmol amine groups) and 100 mL of dry dichloromethane and stirred to totally dissolve. Then the mixture was cooled to 0 °C by an ice bath and PEG750-C6-NCO (2.40 g, 2.67 mmol) was added into the system. After completion, remove an ice bath and return to room temperature to stir the mixture for 3 h. Finally, remove the solvent under vacuum and bake the product in vacuum oven under 80 °C to give SHP-PEG750(100) in a quantitative yield. The same procedure was used to obtain SHP-PEG2000(100) in a quantitative yield. As shown by NMR (Figures S4 and S5, Supporting Information), all the primary amine groups were converted into urea.

Analysis and Characterization: NMR (1H) was recorded on a Varian Mercury 400 NMR spectrometer at room temperature. DSC measurement was performed by a DSC-Q2000 (TA Instruments) from −70 to 150 °C with a heating and cooling speed of 10 °C/min. Rheology measurement was done using a stress-controlled rheometer (TA Instruments Model AR-G2) with a parallel plate geometry for the top plate and a temperature controlled Peltier plate at 25 °C for the bottom plate. The gap height was 1 mm. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA-dtA851 analyzer (Switzerland) from 25 to 300 °C with a heating rate of 10 °C/min. Adhesion test of an Si electrode was performed on an Instron 5365. For the preparation of the electrode, Si particles (D50:0.8 μm, Fuzhou Hokin Chemical Technology Co.) and a synthesized binder were dispersed in ethanol by a planetary mixer. Then the dispersion was coated on a copper foil (Fukuda) and dried at room temperature to get the test sample (5 cm long by 2 cm wide). The copper side of the electrode was fixed to a glass substrate and the adhesive side of the Scotch magic tape (3 M) was applied on the surface of the electrode. The tape was peeled off at a rate of 20 cm min⁻¹. FTIR spectrum was acquired by a Nicolet iS50 FT/IR Spectrometer equipped with a diamond attenuated total reflectance (ATR). To confirm that the binder remained on Si surface in electrolytes, experiment was performed after soaking the electrode (prepared by the same way of adhesion test in EC/DEC (1/1 = v/v)) for 2 weeks. SEM images were taken from an FEI XL30 Sirion electron microscope with field emission gun (FEG) source. XPS spectra were measured with a PH 5000VersaProbe system with an Al Kα radiation (1486 eV) source.

Electrochemical Characterization: The synthesized binder was dissolved in chloroform and then added CB (Tritmag) by a planetary mixer (binder:CB = 20:3 w/w). The suspension was dropcasted on a glass substrate and dried overnight to get a binder/CB composite film. Si particles (D50:0.8 μm, Fuzhou Hokin Chemical Technology Co.) were dispersed in ethanol (200 mg mL⁻¹) and coated on a 1 cm copper foil (Fukuda) and dried at room temperature then pressed by a calendar press. The prepared binder/CB film coated by a razor blade on the Si-only electrode was heated at 100 °C on a hot plate as previously reported [39,41]. The prepared electrode was dried overnight at 40 °C in a vacuum oven. The weight ratio was Si/binder/CB = 65/30/5. Si loading of the electrode was 0.5–0.7 mg cm⁻².

2032 stainless-steel Coin cells were assembled by Si/binder/ CB working electrode, separator (Celgard 2400), and lithium metal (1 cm² disc) counter electrodes inside an Ar glovebox. The electrolyte for all tests was 1 M LiPF₆ in ethylene carbonate/diethylcarbonate/fluoroethylene carbonate (EC/DEC/ECF, 1/1/0.1 = v/v/v).

An ABT 2000 testing station (Arbin Instruments) was used for galvanostatic charge/discharge cycling. Charge/discharge rates were calculated based on Si theoretical capacity at room temperature (3579 mA h g⁻¹). All the coin cells were cycled at a rate of 0.05C in the first two cycles for activation. The CE (%) was calculated as (C_{charge}/C_{discharge}) × 100, where C_{charge} and C_{discharge} were the capacity of the anodes for lithiation and delithiation.

EIS tests and CV were performed by a VMP3 potentiostat (Bio-Logic).

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.

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