3D Meshlike Polyacrylamide Hydrogel as a Novel Binder System via in situ Polymerization for High-Performance Si-Based Electrode

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Silicon has been considered as a promising anode material due to its high theoretical capacity (3579 mAh g$^{-1}$), however, it suffers from capacity degradation owing to the series of multiscale fractures in the electrode caused by the volume variation (=300%) during phase transitions. The molecular/structural design of polymeric binders has been pivotal in overcoming the challenges to improve the integrity of Si anode via strong interactions between active materials and binders. In this respect, the covalently crosslinked polyacrylamide (PAM) network, which effectively maintains its mechanical strength and shape, is introduced as a novel binder system for Si active materials. Unlike the thermal crosslinking, the abundant polar-functional groups, related to the strong interactions between Si and polymer, are not sacrificed in their network by virtue of the in situ polymerization. Through the PAM gel, the Si-based electrode exhibits a superior capacity of ≈1526 mAh g$^{-1}$ at an optimized crosslinker concentration after 500 cycles. In addition, the effect of the chemical/mechanical properties of PAM gel on the electrochemical properties of Si is adequately elucidated. The results will provide meaningful insight regarding the design of novel binders, especially in the application of the covalently crosslinked structure to Si-based electrodes.

1. Introduction

High-energy density with stable cycle-life performance is the prerequisite for Li-ion batteries to be universal power sources for future electronic devices as well as electric vehicles (EVs).[1] Application of Li-alloy-based materials having inherently high capacities is highly needed, therefore, the silicon is an attractive alternative to the graphite anode in conventional Li-ion batteries due to its high lithium storage capacity (nearly ten times higher than that of graphite).[2–4] However, Si-based electrodes are susceptible to the degradation of capacity, due to the built-up stresses from the inevitable lattice mismatches during a number of two-phase equilibriums. Namely, mechanical fractures on the level of particles, which occur by the volume change of Si (=300%) during lithiation/delithiation, lead to the mechanical failure of the electrode with the loss of conduction paths, and the formation of additional solid-electrolyte interface (SEI) layers on newly exposed surfaces.[5,6] In order to mitigate these problems, a lot of researches on modification of Si have been conducted in various ways: i) nanomorphological engineering of Si (e.g., nanoparticles, nanowires, hollow structures, porous structure, thin film, etc.)[7–12] and ii) fabrication of composite materials with carbon-based materials (disordered carbon, carbon nanotube, graphene, etc.).[13–18] Moreover, the modification of binder has been paid great attention since Si anode can be remarkably stabilized by changing only a small portion of the electrode without further modification of morphology and surface.

The polyvinylidene fluoride (PVDF) binder has been widely used in Li-ion batteries due to its electrochemical stability, reasonable binding capability, and facile absorption of the electrolyte. However, PVDF would be inappropriate for electrodes in which whole integrity of the electrode is to be maintained by strong interactions with active materials since good wettability of the PVDF binder with organic electrolytes accelerates the loss of their binder–Si adhesive interactions with unwanted side reactions.[19] Instead, so-called water-soluble binders have been regarded as an alternative binder system, owing to their various interactions with Si particles.[19–24] The well-known water-soluble binders, such as carboxymethylcellulose (CMC),[21,22] polyacrylic acid (PAA),[23] and alginate (Alg),[24] have shown great improvement on the electrochemical properties of
Si anodes. It has been accepted that the hydrogen bonding between functional groups of binder and hydroxyl groups (−OH) on the surface of Si (SiO2) and Cu foil (copper oxide) renders the binder reversible and strong binding on both Si particles and current collector, even after a number of cycles. The reversible bonding nature between polymer and Si can provide the electrode with self-healing effect. The researches on the self-healable polymers, which have the polymer network with supramolecular functionality via hydrogen bonding and metal–ligand coordination, showed the long-term electrochemical properties of nano/micrometer-sized Si, resulted from their automatic recovery of the electrode damage.25–28

It has also been suggested that the structural modification of multifunctional binders could enhance the interactions of polymer–polymer as an effective method for dissipating the mechanical stresses and confining the active materials in their carbon-chain network.29–36 For example, the hyperbranched-type binder (β-cyclodextrin), which can form multidimensional hydrogen bonding with Si particles, exhibited a remarkable improvement on cycling.31 The branched type polymer can effectively distribute the mechanical stresses at their attached points holding active materials during several electrochemical reactions. In addition, the network-polymeric binder (PAA-CMC),32 PAA-poly(vinyl alcohol) (PVA),33 and PVA-poly(ethylene imine) (PEI)34 obtained by thermal-crosslinking technique also showed greatly enhanced stability of Si electrode which is attributed to the higher mechanical strength of the gel binders, compared to that of the non-crosslinked polymers. Although the gel structure can effectively confine the active materials and maintain the integrity of electrode, the chemically crosslinked polymer cannot be easily applied to electrode fabrication as a binder. First of all, the slurry process is not feasible because almost solid-like characteristics of polymer after covalent crosslinking make slurry too viscous. Besides, the abundant functional groups of the polymer, which are directly related to the interactions between Si and polymer, are consumed via a condensation reaction when using thermal crosslinking. As a result, the polymer network is attached to the Si through strong covalent bonding, and it leads to the cleavage of the electrode during cycling, due to the loss of reversible bonding between the polymer and Si.27 Therefore, the interactions between Si and polymeric binder should be noncovalent bonding to reform the broken binding, and several functional groups are capable of such reversible bonding with active materials as hydrogen bonding (COOH−OH−Si) or ion–dipole interaction (COOLi−−OH−Si)2,20 in this respect, the new approach to covalent crosslinking without compromising the functional group of polymer is still prerequisite for designing more effective binder system.

In this work, the 3D meshlike polyacrylamide (PAM) gel was utilized as a polymeric network on the Si nanoparticles (Si NPs) with the functionalized carbon black (f-CB). The PAM hydrogel is a chemically crosslinked PAM network by crosslinker, maintaining its structure even under deformation. The polar amide groups (−CONH2), abundant in polyacrylamide chains, can interact with the hydroxyl group (−OH) on the Si surfaces (SiO2) via hydrogen bonding, and the mechanical property of gel structure was systematically controlled by crosslinker concentration. Finally, the covalently crosslinked polymer network was successfully applied as a binder in the entire electrode via in situ polymerization without loss of their functionality for superior capacity retention in the Si-based electrode.

2. Results and Discussion

2.1. Fabrication and Concept of PAM/Si/f-CB Composite Electrode

The composite electrodes are fabricated from an aqueous solution where the organic monomer, initiator, catalyst, Si, and carbon additives are all included. The resultant electrode is composed of Si NPs with f-CB particles, entangled by in situ PAM. As for the components, the Si NPs as active materials are of the crystalline phase, and the average particle size accounts for ≈50 nm (Figure S1a,b, Supporting Information). From the X-ray photoelectron spectroscopy (XPS) spectra of Si NPs (Figure S1c, Supporting Information), the peaks at 99.4 and 100.6 ev correspond to the binding energy of Si 2p1/2 and Si 2p3/2, respectively, and the peak at 103.3 eV originates from native SiO2 layer (Si−O−Si) on the surface.37 The Si NPs are generally terminated with the hydroxyl group (−OH) on their native oxide layer, resulting in a good dispersion in the aqueous solution, whereas the pristine carbon black (CB) particles are reluctant to be mixed with water due to its hydrophobicity. The CB particles are therefore acid-treated with a mixture of sulfuric/nitric acid to render the surface hydrophilic.38–40 Through the mild surface oxidation, the CB particles are functionalized to be miscible with water (shown in Figure S1d,e, Supporting Information), and both Si NPs and conductive additives (f-CB) can be uniformly dispersed in the monomer/crosslinker solution during synthesis of the composite electrode. As a result, the Si NPs and f-CB are well dispersed in the PAM/Si/f-CB electrodes at a micrometer scale (Figure S2, Supporting Information). From the transmission electron microscopy (TEM) image of the composite electrode (Figure S3, Supporting Information), the blurry layer on the surface is indicative of the remained PAM gel (yellow arrows). A series of procedures for the preparation of PAM/Si/f-CB electrode is provided in Figure 1a.

The fabrication of electrode via solution-based in situ polymerization, which was introduced to produce conducting-polymer-hydrogel binder system, is adequately applied to the synthesis of nonconductive PAM hydrogel.41–43 The concept of the synthesized PAM/Si/f-CB composite electrode is presented in Figure 1b. The 3D meshlike polymer structure, derived from the PAM hydrogel, builds the networks with Si NPs and f-CB, serving as a binder in the electrode. The PAM has a number of polar amide groups (−CONH2) in its monomer unit, and therefore, can form hydrogen bonds with the hydroxyl groups (−OH) on the Si NPs.44 The structure of the PAM network can systematically be tuned by controlling the degree of crosslinked sites (green dots) that interconnect the PAM backbone chains (gray lines).

2.2. Interactions of Polymer/Si and Mechanical Properties of PAM/Si/f-CB Electrode

Considering that the stability of Si-based electrode which is highly dependent upon the chemical interactions between the
Si NPs and neighboring polymer, Fourier-transform infrared (FTIR) spectroscopy was conducted to identify the interactions between Si NPs and PAM. The interaction between the polar amide group of the PAM gel and hydroxyl group of Si NPs is illustrated in Figure 2a, and the functional groups of the synthesized PAM and PAM/Si composites (0.0–1.0 mol% of crosslinker) are characterized in Figure 2b–d. From the PAM (dotted line) spectra, IR absorptions are observed at 3332, 3189, 1651, and 1600 cm$^{-1}$, corresponding to the N–H stretching, NH$_2$ in-plane rocking vibration, carbonyl stretching vibration (C=O), and N–H deformation vibration, respectively.[44–46] The successful polymerization of acrylamide with the crosslinker (0.0–1.0 mol%) is confirmed by comparing the spectra of commercial and synthesized PAM, as shown in Figure S1f (Supporting Information). The Si NPs (purple dashed line) show a broad peak around 3410 cm$^{-1}$, ascribed to the stretching of a hydroxyl group (–OH) with peaks for Si–O–Si asymmetric stretching (1073 cm$^{-1}$) and Si–OH stretching on the Si surface (968 cm$^{-1}$).[47,48] The intimate network of PAM and Si NPs is verified by matching the peaks of PAM/Si composites (solid lines) with those of Si NPs and PAM. It appears that the hydroxyl groups (–OH) on the surface of Si NPs form hydrogen bonding with amide groups (–CONH$_2$) since the hydrogen bonding would change the bond strength of both hydroxyl and amide groups. [49–52] In the magnified Figure 2c, the peaks assigned to the N–H vibration (≈1600 cm$^{-1}$) are slightly redshifted by ≈10 cm$^{-1}$, and the peak of C=O (1651 cm$^{-1}$) is blueshifted by ≈13 cm$^{-1}$. As mentioned before, the redshift of N–H bonding indicates that the –NH$_2$ groups participate in the hydrogen bonding with a hydroxyl group on the Si, and the blueshift of carbonyl group (C=O) can be attributed to the change of its own hydrogen bonding with the –NH$_2$ group in their polymer–polymer network. The small variation of –OH group (from 968 to 958 cm$^{-1}$) also confirms the presence of hydrogen bonding (Figure 2d).

The interactions between Si NPs and polar amide group (–CONH$_2$) of the PAM network can be possibly changed from hydrogen bonding to another type of interactions during the electrochemical reaction. From the previous report, Li$^+$ can change the carboxylic acid group (–COOH) of polyacrylic acid during lithiation (≈1.6 V vs Li/Li$^+$).[53] In addition, Manthiram's group reported that the carboxylate groups (–COO$^-$) in the lithium polyacrylate (LiPAA) actively participate in the chemical reactions of cathodes during cycling, by exchanging Li$^+$ ions with protons after several cycles.[54] In this respect, it is likely that the hydrogen bonding between Si and PAM gel can partially transform into the ion–dipole interactions having the similar supramolecular effects.

It is clear that the evolution of gel structure depends on the crosslinker concentration. As shown in Figure 3a, the hydrogel formation of PAM requires a threshold concentration of 0.5 mol% crosslinker. With the amount of crosslinker, the polymerized solution turns into a form of a solid-like hydrogel, which is attached to the wall of the vial afterward. On the other hand, less than 0.5 mol% of crosslinker is not enough for constructing a gel network, only to form small domains of hydrogel or remain sol phase in the aqueous solution. As expected, in the case of 0.0 mol% of crosslinker, the linear PAM polymer...
chains are dispersed in a solution. In order to verify the effect of crosslinked structure, the PAM/Si composites were analyzed by thermogravimetric analysis (TGA), and the remaining amount of polymer in the composites was detected (Figure S4a, Supporting Information). The leftover PAM dramatically increases once the crosslinker concentration is more than 0.5 mol%, the concentration of which satisfies the condition for the gel formation, as shown in Figure S4b (Supporting Information). However, PAM synthesized with 0.25 mol% crosslinker could be removed by a simple washing step. Furthermore, the adhesion of PAM/Si/f-CB composites on Cu foil was compared after tape peeling, as shown in Figure S4c (Supporting Information). After detaching the 3M-tape, the electrodes with a crosslinker concentration of 0.0 and 0.25 mol% show somewhat detached region, indicated as white arrows in the electrode. Therefore, the interactions of PAM and Si NPs (and f-CB) are closely related to the structure of polymer depending on the crosslinker concentration.

The mechanical properties of PAM/Si/f-CB composite electrodes were parameterized by nanoindentation. The typical load–displacement curves of PAM/Si/f-CB composite electrodes are shown in Figure 3b. The average elastic modulus and hardness of electrodes derived from the load–displacement curves are shown in Figure 3c with error bars. The non-crosslinked PAM/Si/f-CB electrode (0.0 mol%) exhibits the lowest level of hardness (24.7 MPa) and elastic modulus (0.94 GPa). The mechanical properties of crosslinker-added PAM/Si/f-CB electrodes are gradually increased depending on the concentration of crosslinker (Table S1, Supporting Information), due to the tough crosslinking of PAM network. The hardness of the electrode is the highest at 1.0 mol% of the crosslinker amount, while the elastic modulus of the electrode shows a slightly lower value than that of the electrode with 0.75 mol%, which can be resulted from the increased brittleness of highly crosslinked network at 1.0 mol%. The hardness and elastic modulus of binder are related to how strong the polymer network connects the Si NPs and f-CB absorbing the deformation energy during the volume changes by lithiation/delithiation. From the relationship between mechanical properties and sol-gel transition of PAM, the PAM network should be closely related to the mechanical properties of PAM/Si/f-CB electrodes during cycling.

2.3. Electrochemical Properties of PAM/Si/f-CB Electrode

The effect of gel network on the electrochemical properties of the electrodes was investigated via galvanostatic cycling in the voltage range of 0.01–1.2 V (vs Li/Li⁺). Figure 4a shows the first charge–discharge profiles of Si electrodes with PAM binder with different crosslinker concentrations (0.0–1.0 mol%). During the first lithiation, each discharge curve shows a plateau around 100 mV (vs Li/Li⁺), which is typically seen in the first cycle of the crystalline Si electrode, resulted from the two-phase reaction between crystalline Si and amorphous lithiated Si (LiₓSi). After the first lithiation, the amorphous Si phase is formed.
through the electrochemical solid-state amorphization.\textsuperscript{56,57} From the cyclic voltammetry (CV) curves of precycled PAM/Si/f-CB electrodes, all electrodes show the two cathodic peaks around 0.08 and 0.2 V and two anodic peaks around 0.37 and 0.5 V (vs Li/Li\textsuperscript{+}) (Figure S5, Supporting Information). The two anodic/cathodic peaks result from the two-phase reaction between amorphous Si and Li\textsubscript{x}Si in the PAM/Si/f-CB electrodes. The SEI layer formation, which generally occurs below \textapprox 1 V (vs Li/Li\textsuperscript{+}), begins from higher voltages (\textapprox 1.5 V vs Li/Li\textsuperscript{+}) due to the reduction of fluoroethylene carbonate (FEC) in the electrolyte.\textsuperscript{58} The average initial Coulombic efficiency (ICE) of all the PAM/Si/f-CB electrodes increased by the addition of crosslinker in their polymer network, as shown in Figure 4b. In this regard, it can be said that the crosslinked-binder structure can effectively hold both active materials and carbon additives with less amount of SEI layers.

The correlation between the concentration of crosslinker and stability of electrodes is reflected in the capacity retention of PAM/Si/f-CB electrodes, as shown in Figure 4c. The cyclability of electrode with non-crosslinked PAM (0.0 mol\%) is gradually decreased after \approx 80 cycles. On the contrary, the PAM/Si/f-CB electrodes with the crosslinker show the enhanced retention compared to that of the electrode with non-crosslinked structure. Moreover, for the capacity retention of the electrode with 0.75 mol\% of crosslinker, the cyclability is greatly improved with a discharge capacity of \approx 1526 mA\ h g\textsuperscript{−1} after 500 cycles, with \approx 60\% cycle retention. Meanwhile, the specific capacity of PAM/Si/f-CB electrode with 1.0 mol\% of crosslinker shows slightly lower capacity (1457 mA\ h g\textsuperscript{−1}) and cycle retention (\approx 53\%). It may result from the brittleness of highly crosslinked PAM, which can be largely deformed under large volume expansion during cycling. Therefore, it probably deteriorates the stability of the SEI layer of the electrode during several lithiation/delithiation processes. Figure S6 (Supporting Information) shows the Coulombic efficiency of PAM/Si/f-CB electrodes (0.0–1.0 mol\% of crosslinker) after precycling.

The effect of crosslinked-binder structure on the Si electrode is also reflected in the rate capability, as shown in Figure 4d. All of the electrodes are tolerable at a relatively high C rate (1 C = 3579 mA g\textsuperscript{−1}) with moderate capacity and cycle retention. However, in the case of the 0.0–0.5 mol\% of the crosslinker condition, the capacities of the electrodes amount to only half of their capacity (\approx 55\%) compared to those at 0.1 C. However, the capacities of the electrodes with 0.75 and 1.0 mol\% of crosslinker show high capacity of \approx 1800 mA\ h g\textsuperscript{−1} under 1 C, which is almost 85\% of capacity compared to that of the electrode at 0.1 C. Considering the remaining capacity at 0.2 C after 80th cycle, the capacity of the electrode with non-crosslinked PAM is gradually decreased. However, the retained capacities after high C rate test are linearly enhanced according to the crosslinker concentration in the electrodes. In agreement with the tendency of the cycle properties, the optimized gel structure of binder prevents the destruction of Si electrode and loss of electrochemical activity of Si.

The galvanostatic charge/discharge cycling, of which the maximum capacity of electrode was limited to 1200 mA\ h g\textsuperscript{−1}, was also conducted at 0.5 C to identify the cycle properties of the electrode under a less-volume-expansion (Figure 4e). It is clearly shown that the cycle retention of the PAM/Si/f-CB composite electrodes highly depends on the crosslinker concentration. First of all, the electrode with non-crosslinked PAM exhibits the poor cycle retention with a dramatic capacity loss after \approx 250 cycles. In the case of 0.25 and 0.5 mol\% of crosslinker, the electrodes start to degrade after \approx 350 cycles. From the capacity loss of electrodes with 0.25 and 0.5 mol\% of crosslinker, the electrode with 0.5 mol\% of crosslinker seems more stable than that of the electrode with 0.25 mol\%. Most of all, the composite electrode

![Figure 3. Synthesized PAM hydrogel and mechanical properties of the PAM/Si/f-CB electrodes with respect to the crosslinker concentration. a) Photo image showing the sol-gel transition of PAM. b) The load-displacement curves of PAM/Si/f-CB electrodes measured by nanoindentation. c) Hardnesses and elastic modulus obtained from (b).](image-url)
at optimum condition (0.75 mol%) maintains the capacity (1200 mAh g\(^{-1}\)) even after 1000 cycles. However, the capacity is rapidly decreased after 900 cycles with the highest crosslinker concentration (1.0 mol%). From the charge–discharge curves of limited-capacity assessment, the end potentials at the delithiation immediately reach a cutoff voltage (1.2 V vs Li/Li\(^{+}\)) in the case of 0.0–0.5 mol% of crosslinker concentration, as shown in Figure S6a–c (Supporting Information). For the electrodes with 0.75 and 1.0 mol% of crosslinker, it clearly shows that the end potentials for utilizing lithium (1200 mAh g\(^{-1}\)) are gradually increased during 70 h (≈50 cycles). In short, the proper amount of crosslinker is shown to be important even when the composite electrodes undergo less-volume expansion. To compare the electrochemical activity of Si in composite electrodes after 500 cycles, further cycling test was conducted after changing Li-metal counter electrode and electrolyte. The inset image in Figure 4f shows the deteriorated surface of Li-metal counter electrodes after 500 cycles. The PAM/Si/CB composite electrode (0.75 mol% of crosslinker) retains higher lithium extraction capacity of ≈1300 mAh g\(^{-1}\) than those of other electrodes for 50 cycles at 0.5 C. In this respect, the addition of adequate amount of crosslinker is important for the enhanced cycling performance of composite electrodes.

To compare the in situ polymerization method with the conventional electrode fabrication, we conducted the same electrochemical test using the electrode with commercial PAM and PVDF. The initial electrochemical behavior of electrodes with these linear polymers represents the typical lithiation/delithiation of crystalline Si anode at the first cycle, as shown in Figure S8a (Supporting Information). The initial Coulombic efficiencies of Si electrodes with PAM and PVDF binder are 78% and 81%, respectively. The higher ICE than that of the optimized PAM/Si/CB electrode (0.75 mol%) might result from the different structure of electrode. The conventionally fabricated electrode may induce a uniform polymer network in the electrode compared with the in situ polymerized electrode. The PVDF-based electrode shows huge capacity loss within ten cycles, and eventually died after 100 cycles (Figure S8b, Supporting Information). The electrode with commercial PAM binder exhibits enhanced electrochemical properties resulting from the robust hydrogen bonding of functional groups compared to that of the PVDF-based electrode. In general, the water-soluble binder, which has hydrophilic functional groups, can only absorb a small amount of organic electrolyte compared to that of PVDF binder.\[20–24\] Therefore, the maintenance of strong interactions between Si NPs (and CB) and PAM should be guaranteed under the electrolyte, preventing any side reactions between the electrode components and electrolyte. Although the functional groups of water-soluble binders can enhance the electrochemical properties of Si anode, the importance of binder structure should be highlighted, as seen from the cycle performance of PAM/Si/CB composite electrode with 0.75 mol% of crosslinker.

To confirm the effect of gel-polymer structure on the stability of electrodes, the surface morphologies of each PAM/Si/CB electrode before/after cycles were characterized by scanning electron microscopy (SEM) (Figure S9, Supporting Information).
In the case of the electrodes before cycling, all the electrodes exhibit porous morphology and smooth surface of both Si NPs and f-CB. In the photo images after 500 cycles, all the PAM/Si/f-CB electrodes are attached to the Cu foil after disassembly and washing with dimethyl carbonate (DMC) for several times. However, the PAM/Si/f-CB electrodes under a certain concentration of crosslinker (0.0–0.5 mol%) are covered with thick SEI layer on the surface of electrode and void space between Si NPs and f-CB (bottom SEM images of Figure S9, Supporting Information). On the contrary, the PAM/Si/f-CB electrodes with 0.75 and 1.0 mol% of crosslinker concentration show more rough and less aggregated structure with thin SEI layer. Therefore, it implies that the gel network ensures the stability of Si anode with less SEI layer formation after several electrochemical reactions.

In order to understand the relationship between the formation of a stable SEI layer and the structure of the binder, the thickness (or volume) change of the electrodes after precycling step was measured. We measured the thickness of the electrode with almost identical Si loading (≈0.6 mg cm\(^{-2}\)) in the electrode. Figure 5a is the SEM image for the thickness of pristine electrodes with different crosslinker contents. It is clearly shown that the morphologies of cycled electrodes are denser compared to that of the pristine electrode, as shown in Figure 5b. The thickness changes before/after precycling are plotted (Figure 5c) and the largest thickness change (≈12%) occurs in the electrode without crosslinker. In contrast, the expansion of electrode is hugely constrained when the concentration of crosslinker is increased (≈6% of thickness increase with 0.75 mol% crosslinker). The volume expansion of electrode after delithiation is related to the amount of SEI layer on the surface of composite electrodes. From the ICE of the first cycle of these electrodes, it can be said that the addition of crosslinker and the resulted gel structure in their polymer network can lead to the stable and less SEI layer formation. To summarize, the volume expansion of the Si electrode is facilely alleviated by tuning the binder structure through the proper crosslinking method.

The electrochemical impedance spectroscopy (EIS) analysis was conducted to identify the electrochemical properties of electrodes depending on the SEI layer, which resulted from the different amount of crosslinker. Figure S10 (Supporting Information) shows the impedance spectra of the PAM/Si/f-CB electrodes (0.0–1.0 mol% of crosslinker) after 500 cycles. The Nyquist plots of all the PAM/Si/f-CB electrodes show typical semicircles at high frequency, which represent the charge transfer resistance of electrode. The size of a semicircle of PAM/Si/f-CB electrode with 0.75 and 1.0 mol% of crosslinker is much smaller than that of the electrode with 0.0–0.5 mol% of crosslinker. This trend is consistent with the cycle retention of PAM/Si/f-CB electrode (Figure 4c), and it can be resulted from

![Figure 5](image-url)

**Figure 5.** Thickness variation of the PAM/Si/f-CB electrodes. a,b) Cross-sectional SEM images of the PAM/Si/f-CB electrodes before and after second delithiation, with a crosslinker concentration of 0.0, 0.25, 0.5, 0.75, or 1.0 mol%. c) The corresponding thickness variations estimated from the thickness of electrodes before/after second delithiation.
the sufficient integrity of electrode and minimized SEI layer on the electrode pores and surfaces.

3. Conclusions
In this research, 3D meshlike PAM gel, which is combined with both Si NPs and conductive additives (f-CB) via in situ polymerization, successfully served as a binder for nanosized Si active materials. The PAM gel, which forms the hydrogen bonding with Si NPs, guarantees the robust and stable integrity of the electrode during cycles. The mechanical property of the gel was carefully optimized by controlling the degree of crosslinking. Herein, PAM/Si/f-CB composite electrode (0.75 mol% of crosslinker) exhibited a superior capacity of \( \approx 1526 \text{ mAh g}^{-1} \) after 500 cycles at 0.2 C, which is much higher than that of Si anode using PVDF binder. Considering the great electrochemical properties of the electrode with crosslinked polymer, this straightforward crosslinking strategy is highly important to secure the mechanical stability of Si anode. We hope that this study of novel binder system can shed insights on designing the future polymer binders for more practical Si anode.

4. Experimental Section

Fabrication of PAM/Si/f-CB Electrode: Si NPs with an average particle size of \( \approx 50 \text{ nm} \) were purchased from Alfa Aesar. Monomer (acrylamide (C\(_2\)H\(_5\)NO)), crosslinker (N,N'-methylene bis(acrylamide) (C\(_7\)H\(_{12}\)N\(_2\)O\(_2\))), initiator (ammonium persulfate ((NH\(_4\))\(_2\)S\(_2\)O\(_8\))), and catalyst (tetramethylethylenediamine (C\(_6\)H\(_{16}\)N\(_2\))) were purchased from Sigma Aldrich for the synthesis of PAM hydrogel. CB was modified by well-known acid treatment using a mixture of sulfuric/nitric acid (2:3 vol. ratio). After the acid treatment, f-CB was washed using deionized (DI) water until neutralization (pH = 7), followed by vacuum drying at 90 °C for overnight. Commercial polymers (PAM ((C\(_3\)H\(_5\)NO\(_3\))\(_3\)) and PVDF ((C\(_2\)H\(_2\)F\(_2\))\(_n\))) were purchased from Sigma-Aldrich for conventional electrode fabrication.

To fabricate the polymer/nanoparticle composite electrodes, the in situ polymerization based on solution phase, which is designed to undergo concurrent polymerization of monomer/crosslinker with Si NPs and f-CB, and fabrication of electrode at the same time, was applied. We assumed that all molecules of monomer and crosslinker were almost consumed during polymerization. To enhance free-radical polymerization, the solvent was purged with N\(_2\) gas for 1 d to remove the residual oxygen in DI water. In the mixing step, both Si NPs and f-CB were evenly mixed with 0.8 mL of monomer solution (30 mg of acrylamide with 0.0–1.0 mol% of crosslinker). Next, 0.1 mL of catalyst solution was added in the nanoparticulate-monomer solution with 0.25 mol% of monomer. After the mixing step, 0.1 mL of initiator solution with 0.25 mol% of monomer was added and thoroughly mixed with stirring and sonication in an ice bath. The concentration and ratio of initiator/catalyst were optimized based on the condition for PAM hydrogel synthesis. After initiating polymerization, the aqueous solution containing Si NPs and f-CB was transformed into some viscous solution. Then the slurry was quickly bladed on Cu foil, and further polymerization of the slurry was conducted in the N\(_2\)-gas-filled oven at 35 °C for 1 d. After the complete polymerization, the electrodes were naturally dried under room temperature, followed by vacuum drying at 100 °C to remove the remaining water inside the electrode. The PAM/Si composites with the corresponding crosslinker concentration for FTIR measurement were synthesized with the same condition of electrode fabrication.

Materials Characterization: The morphologies of Si NPs, f-CB, and PAM/Si/f-CB electrodes before/after cycles were characterized using a field emission scanning electron microscope (FESEM, SIGMA: Carl Zeiss). The crystal structure of Si was examined by X-ray diffraction (XRD, D8 Advance: Bruker). In order to analyze the surface chemistry of Si NPs, XPS (AXIS-HSI: KRATOS) measurement was conducted. The chemical interactions between Si NPs and PAM were characterized using FTIR spectrometer (TENSOR27: Bruker). FTIR spectra were recorded with a spectral resolution of 4 cm\(^{-1}\) in the range of 400–4000 cm\(^{-1}\). For the TGA, PAM/Si composites were washed with DI water and centrifuged, followed by vacuum drying. TGA profiles were obtained using SDT-Q600 (TA Instrument) between 30 and 700 °C at a heating rate of 10 °C min\(^{-1}\) in the air. To characterize the mechanical properties of electrode, the nanoindentation technique was conducted by nanoindenter (Nano Indenter XP: MTS). The hardness and elastic modulus of the electrode were obtained from minimum five indentation points to ensure representativeness of the results. The maximum depth of indentation was controlled by 800 nm (below 10% of the electrode thickness) with different force to avoid any additional effect of the substrate (Cu foil).

Electrochemical Characterization: For the electrochemical characterization, all electrodes were tested in 2032 half-cell configuration with a Li metal as a counter electrode. It is assumed that the composition of each electrode was consisted of Si NPs, f-CB, and synthesized polymer (PAM) with a weight ratio of 6:2:2. Considering the amount of crosslinker, the difference between the weights of polymers in each electrode is negligible. The loading of active material (Si) in all electrodes was set to be similar for all electrodes (≈0.6 mg cm\(^{-2}\)) with the geometric area (1.54 cm\(^2\)). All electrodes were thoroughly dried under vacuum for 1 h before the cell assembly to remove residual water in the electrodes. 1 x of LiPF\(_6\) in ethylene carbonate (EC) and diethylene carbonate (DEC) (1:1 vol. ratio) with 10 wt% of fluoroethylene carbonate (FEC) was used as an electrolyte (Panax Etec). The electrodes were precycled at 0.05 C (\( = 179 \text{ mAh g}^{-1}\)) for two cycles to form a stable SEI layer at the initial stage, and then the assessments of cyclability were conducted at 0.2 C (\( \approx 716 \text{ mAh g}^{-1}\)) for 500 cycles using WBCS30005 tester (WonATech Co.). Also, the charge–discharge cycling performed with the limited capacity of 1200 mAh g\(^{-1}\) at 0.5 C. CV and EIS of electrodes were measured using a potentiostat (Zive MP1: WonATech Co.). The CV curves were obtained at various scan rates (0.01, 0.03, 0.05, and 0.07 mV s\(^{-1}\)) after precycling step. The EIS was conducted at the applied voltage at 0.37 V after 500 cycles, and the frequency range was from 10 mHz to 100 kHz with an AC amplitude of 5 mV.

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.

Keywords
binder, in situ polymerization, meshlike-polymer networks, Si anodes

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Supporting Information

3D Meshlike Polyacrylamide Hydrogel as A Novel Binder System via in situ Polymerization for High-Performance Si-Based Electrode

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Table S1. Values for the hardness and elastic modulus of PAM/Si/f-CB electrodes obtained from nanoindentation.

<table>
<thead>
<tr>
<th>Crosslinker Concentration (mol. %)</th>
<th>Hardness (MPa)</th>
<th>Elastic Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>24.7 ± 2.0</td>
<td>0.94 ± 0.07</td>
</tr>
<tr>
<td>0.25</td>
<td>27.6 ± 0.7</td>
<td>1.03 ± 0.05</td>
</tr>
<tr>
<td>0.5</td>
<td>29.8 ± 0.5</td>
<td>1.09 ± 0.02</td>
</tr>
<tr>
<td>0.75</td>
<td>39.9 ± 1.7</td>
<td>1.45 ± 0.12</td>
</tr>
<tr>
<td>1.0</td>
<td>40.0 ± 2.1</td>
<td>1.31 ± 0.11</td>
</tr>
</tbody>
</table>

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Figure S1. Materials characterization of the PAM/Si/f-CB electrode. (a) SEM image, (b) x-ray diffraction pattern, and (c) XPS Si 2p spectra of the Si nanoparticles. (d) SEM image of the functionalized carbon black (f-CB) and (e) photograph showing dispersion of the f-CB and that of non-functionalized carbon black in DI water. (f) FTIR spectra of commercial and synthesized PAM without crosslinker.
**Figure S2.** The optical images of PAM/Si/f-CB electrodes and PVDF-based electrode with photo images in the inset. (a) 0.0, (b) 0.25, (c) 0.5, (d) 0.75, and (e) 1.0 mol. % of crosslinker concentration, with (f) PVDF-based electrode.

To verify the dispersion of Si NPs and f-CB in the electrode, the PAM/Si/f-CB and PVDF-based electrode were observed by an optical microscope. Comparing the color of the electrodes in photo images, PAM/Si/f-CB electrodes show more dark green color than that of the PVDF-based electrode. Therefore, the carbon additives (f-CB) are well mixed and dispersed with Si NPs in the electrode.
Figure S3. TEM image of (a) bare Si nanoparticle (NP), (b) functionalized carbon black (f-CB), (c,d) PAM/Si/f-CB composite at 0.75 mol. % of crosslinker. Yellow arrows in (d) indicate the remained PAM gel after sample preparation.
Figure S4. (a) Thermogravimetric analysis (TGA) for detection of the leftover PAM in the composite after washing process. The gray line is TGA result of dried PAM-gel (1.0 mol. % of crosslinker concentration). (b) The remaining polymeric binder calculated from the TGA analysis. (c) Adhesion capabilities of PAM/Si/f-CB composite electrodes tested by attaching and detaching commercial 3M tape.
Figure S5. Cyclic voltammograms of PAM/Si/ν-CB electrodes at different scan rates (0.01, 0.03, 0.05, and 0.07 mV s\(^{-1}\)) in the voltage range of 0.01 - 1.2 V.
Figure S6. The Coulombic efficiency of PAM/Si/f-CB electrodes after precycling.
Figure S7. Galvanostatic charge/discharge curves of PAM/Si/f-CB electrodes for the crosslinker concentration of (a) 0.0, (b) 0.25, (c) 0.5, (d) 0.75, and (e) 1.0 mol. % in the cycle test with limited capacity (1200 mAh g$^{-1}$).
Figure S8. Comparison of electrochemical properties in Si electrode with commercial polymers (PAM and PVDF). (a) Galvanostatic charge/discharge profiles at 0.05 C (179 mA g$^{-1}$). (b) Capacity retention at 0.2 C (716 mA g$^{-1}$). All of the cells are cycled in the voltage range of 0.01 - 1.2 V.
Figure S9. Comparison of PAM/Si/CB electrodes before and after 500 cycles. The SEM images of PAM/Si/CB electrode for the crosslinker concentration of (a) 0.0, (b) 0.25, (c) 0.5, (d) 0.75, and (e) 1.0 mol. % with the morphological changes in the electrodes. The inset in the bottom images are photographs of the corresponding electrodes.
Figure S10. Nyquist plots of the PAM/Si/f-CB electrodes at 0.37 V after 500 cycles.