Thermally Cross-Linkable Diamino-Polyethylene Glycol Additive with Polymeric Binder for Stable Cyclability of Silicon Nanoparticle Based Negative Electrodes in Lithium Ion Batteries

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ABSTRACT

We developed a new type of additive with poly(acrylic acid) (PAA) for stable cycling retention of silicon anodes. Diamino-Polyethylene Glycol (diamino-PEG) is used as a thermally curable additive with PAA polymeric binder for silicon nanoparticle based negative electrodes. Amino groups of the diamino-PEG form amide bonds with carboxylic acid groups of the PAA binder, which gives strong binding force even under high humidity. The highly cross linked amide bonds between diamino-PEG and PAA binder in silicon nanoparticle based negative electrodes leads to reduced electrical contact loss of silicon particles during electrochemical reaction. It also supports stable cycling performance and enhances specific capacity compared to the case of using only a silicon anode PAA binder.

KEYWORDS: Additives, Binders, Cross-Linking, Lithium Ion Batteries, Silicon.

Silicon (Si) has received substantial interest due to the extremely high theoretical specific capacity of 3579 mAh g⁻¹ for Li₁₅Si₄ with 280% volumetric expansion.¹ However, volume expansion and contraction inevitably occur during lithium ion insertion and extraction into Si particles.² After long cycling retention, mechanical instability arises from cracking and pulverization of Si particles, resulting in loss of electrical contact in Si composite negative electrodes.³,⁶

Continuous contraction and expansion of Si particles finally leads to pulverization of the particles after long cycle retention.⁵,⁶ Many research groups are exerting extensive efforts to minimize extreme contraction and expansion of Si particles during charging and discharging of Si anodes. Using Si nanoparticles below 150 nm is an innovative method to reduce pulverization of Si particles during the alloying reaction.⁷ However, excessive Solid Electrolyte Interphase (SEI) film formation and the loss of electrical contact among Si nanoparticles in electrodes are critical obstacles.⁸ In order to solve these problems a variety of nano-structured Si electrodes and void spaced Si anodes with carbon coating have been introduced.⁴–¹¹ These approaches for Si anodes are still too complicated for use in mass production. Another approach is improving binders for Si anodes.¹²–¹⁵ Although alginic acid based binders present an excellent opportunity for Si anode application, they may cause decomposition of carbonate based electrolytes. Thermally cured poly(acrylic acid) (PAA) and carboxymethylcellulose (CMC) based polymeric binder greatly improves cycle retention compared to a PAA binder in Si negative electrodes.¹⁶ The condensation reaction (dehydration) of PAA and CMC to trigger the formation of a highly cross linked polymeric binder is extremely simple. To maximize the functions of the polymeric binder for Si anodes a binder having fine-tuned electronic property was introduced. To tailor the structure with controlled electronic property, carbonyl (C=O) groups were functionalized in the binder and methyl benzoic ester (MB, –PhCOOCH₃) groups were functionalized to enhance the binder’s adhesion to Si particles. Recently, mussel inspired adhesive binders have been introduced.¹⁴ The catechol groups of dopamine from the mussel presented strong adhesion properties and alginate
strengthened the adhesion force. These polymeric binders with improved adhesive strengths need to be improved to prevent the loss of electrical contact in Si anodes during charging and discharging.

Herein, we presented a simple method to avoid Si particles loss in the electrodes during the electrochemical reaction by using a thermally cross-linkable additive to form a highly cross linked polymeric binder network in Si negative electrodes. The thermally cross-linked PAA and additive improved the specific capacity and provided stable cycle retention in Si anodes. Carboxylic groups of the PAA polymeric binder form a thermally cross-linked anhydride structure by a dehydration reaction at high temperature for the Si anodes, which contributes to suppression of the volume expansion of Si particles during the charging/discharging process. The carboxylic groups form Si–O links (covalent ester bonds) with Si–OH groups on the surface of the Si particles, leading to partial adhesion between the polymeric binders and Si particles.

We present a simple methodology to introduce a new additive to form a highly cross-linked polymer based on PAA and crosslinking agents such as hexamethylene diamine, 1,12-diaminododecane, and 4,7,10-trioxa-1,13-tridecanediamine. The new additives build amide bonds between the carboxylic acid groups of PAA and the amino groups of additives at high temperature (150°C) for 4 hr. We investigated the Fourier transform infrared (FT-IR) spectra to detect the formation of amide bonds in the specimens composed of reagents (40 mg PAA and 5 mol% additives) which were thermally cured in a vacuum oven condition at 150°C for 4 hr. As seen in Figure 1, carboxylic acid groups and OH groups of PAA were originally detected at 1715 cm⁻¹ with a strong single peak and at 2400~3200 cm⁻¹ with a broad peak, respectively. After thermal curing between PAA and diamino-polyethylene glycol (PEG) at 150°C for 4 hr under a vacuum condition, new weak peaks were formed at 1590 and 1690~1700 cm⁻¹ in accordance with the amide bond. A different broad peak was also confirmed at 3100~3400 cm⁻¹; this new broad peak was slightly weak and differently positioned compared with the OH groups of PAA. A new weak peak was also detected at 1620 cm⁻¹ in accordance with primary amines from residual diamino-PEG; excessive 5 mol% diamino-PEG and other additives remained after thermal curing.

Galvanostatic cycling tests were performed from 0.0 to 2.5 V versus Li/Li⁺ with a 2016 coin type half cell. Figure 2(a) shows the cycling performance of the Si nanoparticles with PAA binder and additives at 0.1 C. These four additives are different in chain length and polarity. Diamino-PEG and diamino-PEG 600 are hydrophilic, but hexamethylene diamine and 1,12-diaminododecane are hydrophobic. Compared with other additives, diamino-PEG showed a superior capacity. Long chain additives (diamino-PEG 600, 1,12-diaminododecane) ended up with the poor results on cyclic capacities of silicon electrode in comparison with short chain additives (diamino-PEG, hexamethylene diamine) due to the increased resistance. Moreover, it appeared that short chain hydrophobic additive (hexamethylene diamine) had an insignificant effect on cyclic capacities of silicon electrode because it was difficult to blend in DI water which was solvent of PAA binder. Therefore, it was difficult to make a homogeneous slurry (silicon, conductive carbon black, PAA binder and additive), thus hydrophobic additive effect to local electrode was indistinctive. Using short chain hydrophilic additive (diamino-PEG) resulted in the improved cyclic capacities of the silicon electrode.

We also experimentally determined the optimal amount of diamino-PEG, which was up to 1 mol% of diamino-PEG with 40 mg of PAA on the basis of the feeding ratio (active material:Super P:Binder = 6:2:2 weight ratio) to fabricate Si negative electrodes. A small quantity of diamino-PEG (0.5 mol%) had an inconspicuous effect on cyclic capacities of silicon electrode and a relatively large quantity of diamino-PEG (3 mol%) had backfired on cyclic capacities of silicon electrode.

Fig. 1. FT-IR spectra of thermally cured with PAA, c-CLR-PAA reagents at 150 °C for 4 hr under a vacuum condition (5 mol% diamino-PEG was used for detection) and chemical structures of additives.
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As seen in Figure 2(b), the initial Coulombic efficiency (ICE) of the highly cross-linked agent (diamino-PEG) and PAA (c-CLR-PAA) in the Si anodes was 82.5%; this was relatively higher than the case of Si anodes (78.7%) having only PAA. The initial charge capacity was 3345 mAh g$^{-1}$ in the case of electrode using c-CLR-PAA polymeric binders and 3141 mAh g$^{-1}$ for the case of Si anode using only PAA polymeric binder, respectively. According to these results, we confirmed that c-CLR-PAA in Si anodes not only enhances the ICE, but also contributes to high capacity. c-CLR-PAA forms a stable Si anode composite and controls volume expansion. First lithiation/delithiation capacities were 3141 mAh g$^{-1}$ and 2473 mAh g$^{-1}$ for Si anode containing only PAA, and 3345 mAh g$^{-1}$ and 2760 mAh g$^{-1}$ for Si anodes having c-CLR-PAA.

In order to identify the formation of stable Si anode composites, we conducted a long cycle retention test over 100 cycles. As seen in Figure 3, c-CLR-PAA used in Si anodes led superior capacity over 2500 mAh g$^{-1}$ after 7th cycle and the capacity maintained until 35th cycle. Gradual capacity fading subsequently occurred from 36th cycle. On the other hand, PAA used in Si anodes brought typical cycle retention results. c-CLR-PAA in Si anodes resulted in higher Coulombic Efficiency (CE) of 98.78% than PAA in Si anodes (97.06%) (see Fig. 4). These results verified that a highly cross linked polymeric network was developed by diamino-PEG with PAA under the thermal curing conditions. This led to rigidity that controlled the volume expansion of Si anodes and finally minimized electrical contact loss in the Si anodes.$^{16,17}$

Figure 5 shows the rate performance of Si anodes using c-CLR-PAA and PAA, respectively. In the case of electrode using PAA only, the Si anodes showed rapid capacity fading until 4th cycle at a 0.5 C-rate, and had relatively stable delithiation capacity until a 3 C-rate. At a high rate condition of 5 C-rate, the electrodes using PAA binder showed rapid capacity fading. At a continuous low rate condition of 0.1 C-rate, they exhibited delithiation capacity higher than 1600 mAh g$^{-1}$. Electrodes using c-CLR-PAA showed slightly gradual capacity fading from a 0.5 C-rate to a 5 C-rate and high delithiation capacity higher than 2600 mAh g$^{-1}$ at a 0.1 C-rate. These results indicated that Si anodes with c-CLR-PAA had a stable performance even after high rate performances.

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Fig. 2. (a) Discharge capacity versus cycle number for the silicon composite electrodes with various additives at a current density of a 0.1 C rate. (b) Initial charge–discharge profiles of Si anode composites thermally cured with PAA, c-CLR-PAA binder at 0.1 C-rate between 0.0 and 2.0 V versus Li/Li$^+$. As seen in Figure 2(b), the initial Coulombic efficiency (ICE) of the highly cross-linked agent (diamino-PEG) and PAA (c-CLR-PAA) in the Si anodes was 82.5%; this was relatively higher than the case of Si anodes (78.7%) having only PAA. The initial charge capacity was 3345 mAh g$^{-1}$ in the case of electrode using c-CLR-PAA polymeric binders and 3141 mAh g$^{-1}$ for the case of Si anode using only PAA polymeric binder, respectively. According to these results, we confirmed that c-CLR-PAA in Si anodes not only enhances the ICE, but also contributes to high capacity. c-CLR-PAA forms a stable Si anode composite and controls volume expansion. First lithiation/delithiation capacities were 3141 mAh g$^{-1}$ and 2473 mAh g$^{-1}$ for Si anode containing only PAA, and 3345 mAh g$^{-1}$ and 2760 mAh g$^{-1}$ for Si anodes having c-CLR-PAA.

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Fig. 3. Li extraction capacity versus cycle number for the silicon composite electrodes at a current density of a 0.1 C rate.
Impedance test results presented in Figure 6 showed that the Si anodes with c-CLR-PAA had high initial resistance until the 30th cycle, however, resumed to show stable resistance, compared with the case of Si anodes using PAA. The high initial resistance results appear to be inevitable for c-CLR-PAA in Si anodes because the highly cross-linked polymeric binder would likely interrupt the initial lithium ion migration.

In addition, we investigated the morphology change of Si anodes with PAA and c-CLR-PAA before and after 100 cycles, through scanning electron microscope (SEM). After the 100th cycle retention test, the case of using only PAA in the electrodes displayed numerous cracks all over the surfaces. In contrast, the electrodes that used c-CLR-PAA had small amounts of cracks on the surfaces. The highly cross-linked polymeric binder by diamino-PEG with PAA after thermal curing effectively reduced volume expansion and loss of electrical contact in the Si anodes.

In conclusion, we successfully introduced a thermally cross-linkable additive with PAA in Si negative electrodes by forming amide bonds between carboxylic groups of PAA and amide groups of diamino-PEG, which induced a highly cross-linked polymeric binder network in the Si anodes. We investigated the amide bonds formation by FT-IR and confirmed that microscale cracks formed in the Si electrodes incorporating 1 mol% diamino-PEG after 100 cycles by SEM images, compared with the case of using PAA only. The Si anode with 1 mol% diamino-PEG and PAA showed enhanced cycle retention with high specific capacity. We presented a facile method to obtain high specific capacity and stable cycle retention by using a small amount of cross-linkable agent as an additive with PAA in Si anodes. We also confirmed stable and high capacity at a high C-rate (5 C-rate with a high reversible capacity of 2400 mAh g$^{-1}$).

1. EXPERIMENTAL SECTION

1.1. Fabrication of c-CLR-PAA Si Anode and Electrochemical Measurements

Si nanoparticles (≤100 nm) and Poly (acrylic acid) (PAA) (Mw of 250,000, Diamino-Poly(Ethylene Glycol) (Diamino-PEG; 4, 7, 10-trioxa-1, 13-tridecanediamine (97%)) were purchased from Sigma-Aldrich. Galvanostatic cycling tests were performed from 0.0 to 2.5 V versus Li/Li$^+$ with a 2016 coin half cell type using a Wonatech 3000 battery measurement tester. The electrolyte consisted of 1.3 M LiPF$_6$ salt in a solution of ethylene carbonate (EC) and diethyl carbonate (DEC) (3:7, v/v), 3 wt% fluoroethylene carbonate (FEC, Soulbrain CO. Ltd.) A Celgard 2502 membrane was used as a separator. To fabricate c-CLR-PAA (cross-linked Cross Linking Reagent (1 mol% diamino-PEG) and Poly(acrylic acid)) of the Si anode, Si active materials and Super PAA polymeric binder were mixed in a 6:2:2 weight ratio by a thinky mixer. 1 mol% diamino-PEG was then carefully added dropwise, and the slurry solution was subsequently mixed again. For an impedance test the evaluated frequency range was from 50 kHz to 100 mHz under an ac stimulus with 10 mV amplitude and no applied voltage bias.

1.2. Characterization

The scanning electron microscopy (SEM) images were taken with an S-4800 field emission scanning electron microscope.
microscope (15 kV, Hitachi, Japan). FT-IR spectra were investigated by Varian 640 FT-IR spectrometer.

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References and Notes