Electrochemical lithiation has been extensively studied and discussed for application in lithium-ion batteries. Generally, active materials with higher-capacity lithiation suffers from repeated volume change during lithiation/delithiation especially in lithium silicide system. Si-based electrodes demonstrate high-capacity lithiation, however, capacity fade inevitably arises from the huge volume change. The lithiation of Si-based electrodes is improved by binder selection, e.g. carboxymethylcellulose, polyimide, polyacrylate, compared to conventional fluorinated binders. Poly(acrylic acid) (PAH), commodity chemicals used in industry, improves mechanical stability of composite electrodes against the volume change. Because poly(acrylic acid) is weak polyacid, its conformation in water is modulated by neutralization with alkali hydroxides, which is capable to adjust the slurry rheology and leads to better electrode performance. The capacity retention of the Si-based composite was highly improved with 80% neutralized polyacrylate binders because of self-forming porous structure of the composite. Furthermore, PAH binders with cross-linkage between two carboxylic groups with polycarbodiimide efficiently improved the lithiation performance of Si. The cross-linkage proceeded in organic solvent during slurry process. In this study, we prepare a new water-soluble cross-linked binder, synthesized by copolymerization of acrylic acid with coexistence of crosslinker, diallyl ether, and demonstrate the battery performance of silicon-graphite electrodes with the copolymers.

Experimental

Cross-linked poly(acrylic acid) was synthesized by copolymerization of acrylic acid with different amount of diallyl ether as a crosslinker, H2C=CH-CH2-(O-CH2-CH2)n-O-CH2-CH2=CH2 (n = 1 ~ 4) as shown in Fig. 1a. Acrylic acid monomers were polymerized with different amounts of the crosslinker, 0, 0.007, 0.07, 0.14, and 0.7 mol% and the obtained polymers are hereafter denoted as PAH, 1CLPAH, 10CLPAH, 20CLPAH, and 100CLPAH, respectively. The polymers were dissolved in water to prepare 1 wt% binder solution, and further neutralized by dropping 1 mol dm$^{-3}$ NaOH (titration up to pH 6.7) to convert 80% of –COOH into –COONa, and they are similarly denoted as PAH0.2Na0.8, 1CLPAH0.2Na0.8, 10CLPAH0.2Na0.8, 20CLPAH0.2Na0.8, and 100CLPAH0.2Na0.8. Viscosity measurement of the 1 wt% binder aqueous solution was conducted by a rotational viscometer (HAAKE MARS III, Thermo Scientific Inc.) at 20$^\circ$C. All the chemicals for binder synthesis were commercially available from Wako Pure Chemical Industries, Ltd.

Details of electrode preparation and cell assembly were described in our previous paper. Silicon (particle size < 100 nm), graphite (particle size 3 μm), and acetylene black (AB) were mixed thoroughly. The copolymer solution and adequate amount of distilled water were added to the mixture to prepare slurry for electrodes. Reagent grade poly(vinylecylene fluoride) (PVdF) binder was used for comparison. The slurry was cast onto copper foil and dried under vacuum, followed by roll press. The weight ratio of Si:graphite:AB:binder was 3:5:1:1. The sample loading was adjusted within 0.6 ~ 1.0 mg cm$^{-2}$. For cycle tests, the initial lithiation (reduction) was carried out at constant current of –50 mA g$^{-1}$ until reaching 0.00 V. Following oxidative delithiation was done at +50 mA g$^{-1}$ up to 2.0 V. From the second cycle, the current density increased to 100 mA g$^{-1}$. The gravimetric capacity was calculated based on the weight of silicon and graphite. For cross sectional observation by scanning electron microscopy (SEM, S-4800, Hitachi), the electrodes before electrochemical tests were dry-etched by argon-ion milling under inert atmosphere (IM-4000, Hitachi).

Results and Discussion

Figures 1a/1b show the copolymerization reaction and molecular structures/conformations of each polyacrylate prepared by adjusting the cross-linking degree and neutralization. Generally, vinyl groups of acrylic acid polymerize in liquid phase with the aid of a radical initiator and/or catalyst to form poly(acrylic acid). As the polymerization proceeds with coexistence of allyl compounds, (acrylic acid)-based heteropolymers is prepared via copolymerization of the vinyl and allyl groups. The small amount of diallyl monomers is added into the polymerization medium containing the initiators. This copolymerization method is advantageous to control the cross-linking degree by changing a crosslinker and its amount. In this study, we select the diallyl ethers as a crosslinker with consideration of the solubility in water and lithium ion conductivity of polymerized ethylene oxide. As drawn in Figure 1b, the 10CLPAH is designed to possess more conformational freedom than the 1CLPAH because of the high fraction of allyl groups in the copolymer.
Fluid viscosity of 1 wt% polymer solution was examined using a rotational viscometer. Figures 1c/1d show shear stress vs. shear rate plots, in which (shear stress)/(shear rate) equals viscosity. Generally, linear/non-linear relation of the plots corresponds to Newtonian/Non-
Newtonian fluid, respectively. In case of linear plots as shown in Figures 1c/1d, the lower slopes in plots indicate the higher viscosity, due to gelation with exceedingly cross-linking network. The 80%
neutralization degree, which was due to the preformed SEI of polyacrylate coating,10 resulting in the higher reversibility of about 77%. The irreversible reaction is observed for PVdF and is suppressed by PAH and 10CLPAH binders. The 20CLPAH0.2Na0.8 binder greatly suppressed the irreversible electrolyte decomposition, which is due to the preformed SEI of polyacrylate coating,10 resulting in the higher reversibility of about 77%.

The polymers are used as binders for the silicon/graphite electrodes. Figures 2a/2b represent the optical photos of surface and cross-sectional SEM images of the prepared composite electrode, respectively. The PAH electrode is not uniform in millimeter and micrometer scale. From comparison between PAH and 10CLPAH, the cross-linked polyacrylate is efficient in uniform dispersion with less cracks in the composite. The neutralization of 10CLPAH further improves the uniformity in millimeter scale. These differences relate to the rheological property including the viscosity as already described. Note that the self-forming porous structure is observed for 10CLPAH0.2Na0.8, which is due to the sol-gel transition during slurry drying as we previously reported.5 Furthermore, the porous and homogeneous composite is also observed in 20CLPAH0.2Na0.8. Consequently, the moderate chemical/physical cross-linkage and suit-
ability neutralization degree are able to design rheology of slurry and porosity/dispersion of the composite.6 We believe that this fact is of great advantage for polymer industry because they are controllable factors by conventional and low cost processing.

The electrochemical lithiation/delithiation cycle is examined for the different binder electrodes as presented in Figure 3. These electrodes show high redox-capacity in the potential region below 1.0 V as seen in Figure 3a because of reversible lithium intercalation into graphite and the formation of lithium-silicide.4 The higher delithia-
tion capacity is demonstrated with the cross-linked and neutralized polymers than those of PAH and PVdF. It is well-known that the solid electrolyte interphase (SEI) is formed by electrolyte decomposition during the first electroreduction around 0.8 V.4 Figure 3b represents differential curves of the first lithiation to compare the SEI formation process. Clearly, the irreversible reaction is observed for PVdF and is suppressed by PAH and 10CLPAH binders. The 20CLPAH0.2Na0.8 binder greatly suppressed the irreversible electrolyte decomposition, which is due to the preformed SEI of polyacrylate coating,10 resulting in the higher reversibility of about 77%

Figure 3c shows cycle performance of the Si/graphite electrode with cross-linked polyacrylic acids. Although almost the same capacity is obtained during the initial cycles, the capacity retention is clearly enhanced by cross-linkage. Moreover, the retention depends on the

Figure 1. (a) Copolymerization of acrylic acid and diallyl ether as a crosslinker. (b) schematic drawing of polymer conformation of PAH, 1CLPAH, 10CLPAH, and 10CLPAH0.2Na0.8 dissolved in water, (c) relation between shear stress and shear rate of acidic polymer solutions (1 wt%), and (d) relation between shear stress and shear rate of 80% neutralized polymer solutions (1 wt%).
amount of added cross-linkers, which agrees with the previous result of the polycarbodiimide cross-linkage. As a result, the moderate cross-linkage attains the better capacity retention, and 10CLPAH is the most optimum binder among them. Figure 3d further compares the cyclability with the NaOH-neutralized binders. The capacity retention is totally improved by neutralization, identical to our previous result. Namely, the best capacity retention was achieved by 20CLPAH0.2Na0.8. The moderate cross-linkage and partial neutralization of polyacrylate synergically affect the highly reversible lithiation for silicon.

Figure 4a shows the change in Coulombic efficiency during first ten cycles for the Si-graphite electrodes with the different binders. Similarly to the results of capacity retention, the efficiency is improved by the moderate cross-linkage and further increased by the

![Figure 2](image)

**Figure 2.** (a) Optical microscope images and (b) cross-sectional SEM images of pristine electrodes with different binders.

![Figure 3](image)

**Figure 3.** (a) Initial charge/discharge curves, (b) their differential curves, and (c, d) capacity retention.
neutralization as shown with 20CLPAH$_{0.2}$Na$_{0.8}$. It is thought that the surface modification with amorphous polyacrylate thin coating on the Si/graphite particles contributes efficient SEI passivation. The most efficient coating is achieved by the network structure of the cross-linked sodium polyacrylate.

Since lithium silicide is severely reactive leading to self-delithiation accompanied with electrolyte decomposition, self-delithiation rates in 12th cycle after ten days storage at room temperature for the fully lithiated electrodes were examined with different binders. The capacity retention was 84.7, 88.7, 90.7, and 92.3% for PAH, 1CLPAH, 10CLPAH, and 20CLPAH$_{0.2}$Na$_{0.8}$, respectively. As a result, the self-delithiation is the most efficiently suppressed in the 20CLPAH$_{0.2}$Na$_{0.8}$ electrode. A 90-degree peel test was conducted to estimate adhesion strength of the composite layer, because the electrochemical cyclability is known to be correlated to the mechanical durability of silicon-based electrodes. The peel test reveals that the adhesion strength increases twice by moderate cross-link and does further 1.5 times by the neutralization. That is, the peeling tension estimated becomes three times from PAH to 20CLPAH$_{0.2}$Na$_{0.8}$. These results are consistent with the electrochemical performance.

The 20CLPAH$_{0.2}$Na$_{0.8}$ electrode was tested under the same condition, except the limited voltage between 0.0 and 1.0 V that is advantageous for cycle stability, to confirm the dual additive effect of 1 vol% fluoroethylene carbonate (FEC) and 1 vol% vinylene carbonate (VC). As shown in Figure 4b, the capacity retention is remarkably enhanced by the additives; the higher capacity more than 1000 mAh g$^{-1}$ over 50 cycles by the effects merged with the binder and additive as SEI-improver while the capacity is slowly declined during 50 cycles in additive-free electrolyte. Figure 4c confirms the rate capability for the 20CLPAH$_{0.2}$Na$_{0.8}$ electrode with 1 vol% FEC and 1 vol% VC. The test was performed by changing only delithiation current up to 1000 mA g$^{-1}$. Almost no capacity degradation was observed even at the higher current with acceptable capacity retention.

Figure 4d summarizes proposed improvement mechanisms related to the size of materials with our new binder. Considering the C-C bond length and polymerization degree of 20CLPAH$_{0.2}$Na$_{0.8}$, we assume that the 600 nm polymer chains cover and form networks on the Si, graphite, and AB composite. The polymer possesses the stretched conformation and is cross-linked by the covalent and hydrogen bonding. Thus, the network polymer much efficiently modifies the surface of particles, leading to the suppression of irreversible capacity and self-delithiation. Furthermore, the covalent network strengthens the mechanical durability of the composite to avoid electrical isolation and collapse of the Si particles embedded in the composite.

Conclusions

The lithiation reversibility and cyclability of silicon/graphite composites are improved by the binder development of neutralized and cross-linked polyacrylate. The improvement is attributed to homogeneous dispersion and suitable rheology for slurry, resulting in proper
porosity, uniform polyacrylate coating, and high mechanical strength of composites. The acrylate-based copolymers have high potential as functional binders for silicon-graphite composite electrodes in practical application.

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References

1. M. N. Obrovac and V. L. Chevrier, Chemical Reviews, 114, 11444 (2014).
2. N. S. Hochgatterer, M. R. Schweiger, S. Koller, P. R. Raimann, T. Wöhrle, C. Wurm, and M. Winter, Electrochemical and Solid-State Letters, 11, A76 (2008).
3. A. Magasinski, B. Zdyrko, I. Kovalenko, B. Hertzberg, R. Burtovyy, C. F. Huebner, T. F. Fuller, I. Luzinov, and G. Yushin, ACS Applied Materials & Interfaces, 2, 3004 (2010).
4. S. Komaba, T. Ozeki, N. Yabuuchi, and K. Shimomura, Electrochemistry, 79, 6 (2011).
5. Z.-J. Han, N. Yabuuchi, K. Shimomura, M. Murase, H. Yui, and S. Komaba, Energy & Environmental Science, 5, 9014 (2012).
6. Z.-J. Han, K. Yamagawa, N. Yabuuchi, J.-Y. Son, Y.-T. Cui, H. Oji, A. Kogure, T. Harada, S. Ishikawa, Y. Aoki, and S. Komaba, Physical Chemistry Chemical Physics, 17, 3783 (2015).
7. Z.-J. Han, N. Yabuuchi, S. Hashimoto, T. Sasaki, and S. Komaba, ECS Electrochemistry Letters, 2, A17 (2013).
8. Shinichi Komaba, Naoki Yabuuchi, Zhen-Ji Han, Takeo Sasaki, Shota Hashimoto, Kuniaki Okamoto, and Tsuneaki Maesawa, International patent, WO/2014/0065407, (2014).
9. K. M. Raju, M. P. Raju, and Y. M. Mohan, Polymer International, 52, 768 (2003).
10. S. Komaba, N. Yabuuchi, T. Ozeki, K. Okushi, H. Yui, K. Konno, Y. Katayama, and T. Miura, Journal of Power Sources, 195, 6069 (2010).
11. B. Key, R. Bhattacharyya, M. Morcrette, V. Szénic, J.-M. Tarascon, and C. P. Grey, Journal of the American Chemical Society, 131, 9239 (2009).
12. M. Murase, N. Yabuuchi, Z.-J. Han, J. Y. Son, Y.-T. Cui, H. Oji, and S. Komaba, ChemSusChem, 5, 2307 (2012).
13. T. Yim, S. J. Choi, Y. N. Jo, T.-H. Kim, K. J. Kim, G. Jeong, and Y.-J. Kim, Electrochimica Acta, 136, 112 (2014).
14. H. Li, X. Huang, L. Chen, Z. Wu, and Y. Liang, Electrochemical and Solid-State Letters, 2, 547 (1999).
15. M. Gautier, D. Mazouzi, D. Reyter, B. Lestriez, P. Moreau, D. Guyomard, and L. Roue, Energy & Environmental Science, 6, 2145 (2013).