Polyacrylate as Functional Binder for Silicon and Graphite Composite Electrode in Lithium-Ion Batteries

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Polyacrylates were applied as binder for the electrode of a particulate mixture of silicon, graphite, and Ketjen black for lithium-ion batteries. We found that poly(alkali acrylate) binder remarkably improved the electrochemical lithiation and delithiation performance of the silicon-graphite electrode compared to that of conventional binders. The polyacrylate coating on Si and graphite particles suppressed the electrode deterioration. When the electrode was prepared with 30 wt % poly(sodium acrylate) binder, the higher specific capacity and initial efficiency were obtained with much improved cycleability.

Key Words : Silicon, Polyacrylate, Binder, Lithium-ion Battery

1 Introduction

Since silicon undergoes electrochemical lithiation to form Si-Li alloys, silicon based materials are one of the potential candidates as negative electrode for lithium-ion batteries. When Si-Li alloys are electrochemically formed at Si electrode, the capacity is expected to be higher than that of the carbonaceous materials.¹⁾ However, the silicon electrode suffers from a large volume change during successive cycle, leading to cracking and pulverization of silicon,²⁾ which result in capacity fading. To solve this problem, nano-silicon,³⁾ carbon-coated silicon⁴⁾ and so on were previously reported. Furthermore, silicon thin films exhibited an excellent charge-discharge cycling behavior.^{5,6)} In recent years, the selection of polymeric binders is known to be important to improve the battery performance of particulate silicon. As previously reported,⁷⁻⁹⁾ sodium carboxymethyl cellulose (CMC-Na) is already known to be potential binder for silicon electrode.

We have investigated the surface passivation layer,¹⁰⁾ so-called SEI, and we proposed *functional binders*¹¹⁻¹³⁾ acting as the artificial SEI at graphite electrodes, such as poly(acrylic acid).¹²⁾ We pointed out that the polymer chain conformation of polyacrylate is important to modify the graphite surface¹³⁾ and that poly(lithium acrylate) (PAALi) and poly(sodium acrylate) (PAANa) binders enhance the rate performance of nitroxide radical polymer electrode in Li cells.¹⁴⁾ It is interesting that electrochemical performance of the Si and Sn based electrodes is also improved by polyacrylate binder as described by our group¹⁵⁾ and Dahn's group,¹⁶⁾ respectively. In this paper, we applied the poly(alkali acrylate)s as binder for the particulate silicon based negative electrode to improve the battery performance of lithium-ion batteries.

2 Experimental

Silicon (particle size is <100 nm Aldrich Co.), natural graphite (particle size is 3 μm , SEC Carbon Corp.), and

Fig. 1 Molecular structures of the polymeric binders.

Ketjen black (KB) (Lion Corp.) were used as received. Poly(vinylidene fluoride) (PVdF) (Polysciences, Inc.), CMCNa (Daicel Chemical Industries, Ltd.), and PAANa (Kishida Chemical Co., Ltd., polymerization degree: 22000-66000) were used as binders. The molecular structure of PAANa is shown and compared with PVdF in Fig. 1. Polyacrylates of lithium, sodium, and potassium salts were prepared as previously described¹³⁾ for comparison.

For electrode preparation, silicon, graphite, and KB were thoroughly mixed, and the binders were added to the particulate mixture to make the slurry by adding water and N-methylpyrrolidinon for polyacrylates and PVdF, respectively. The slurry was cast on Cu foil and dried at 150°C in vacuum, followed by roll pressing. The loading on Cu foil was *ca.* 1 mg cm⁻². The weight ratio of electrode mixture was adjusted as Si:graphite:KB:binder = 20:(70-*x*):10:*x* (wt %). The specific capacities are calculated on the basis of the weight of silicon and graphite. The coin-type cell was fabricated in Ar-filled glovebox and consisted of the prepared electrode, lithium foil electrode, and 1 mol dm⁻³ LiPF₆ ethylene carbonate/dimethyl carbonate (1:1 by volume) solution with separator. Electrochemical measurement of Li cells was carried out at room temperature around 25°C. Current reversal chronopotentiometry was successively carried out at a rate of -50 mA and 50 mA (g of silicon and graphite)⁻¹ in the potential region between 2.00 and 0.00 V except the initial electroreductive lithiation. The initial lithiation was done by the CC-CV mode, that is, a

constant current (CC) of -50 mA g^{-1} was applied until approaching 25 mV, and then the constant voltage (CV) of 25 mV was kept prior to delithiation. The total duration of CC-CV was fixed for 30 h to control the total capacity less than 1500 mAh g^{-1} . Laser Raman microscope (RAMANplus, Nanophoton Co., Japan, 532 nm laser radiation) was employed to observe electrode morphology and Raman spectra.

3 Results and Discussion

Generally, conventional PVdF binder is known to be crystalline polymer¹⁷⁾ and the polymeric molecular chains are bound into bundle (crystallized) during drying the slurry, so that the active material is not completely covered by PVdF. On the contrary, the whole active material is covered with amorphous poly(alkali acrylate) thin layer like glue as we previously described.^{12,13)} The polyacrylate layer on graphite electrode behaves as artificial solid-electrolyte interphase (SEI), as a result, lithium intercalation into the graphite in the propylene carbonate and organic ionic liquid media containing no film forming additives was attained by the polyacrylate.¹¹⁾

We applied PAANA as the binder for the mixture of silicon, graphite, and KB. In Fig. 2, the initial irreversible capacity between 1.0 and 0.5 V was clearly reduced by PAANA, which modifies the surface of the Si-based electrode including the SEI. The initial coulombic efficiencies were improved by adopting polyacrylate binder, i.e., 50, 65, 65, and 75 % for 10 % PVdF, CMCNa, and PAANA and 30 % PAANA electrodes, respectively, showing that the polyacrylate suppresses the electrolyte decomposition at the initial cycle not only for graphite¹²⁾ but also for Si-graphite electrode.

Figure 3 (upper) shows chronopotentiograms at the tenth cycle of the PVdF, CMCNa and PAANA electrodes. In all cases, the redox couple appears in the same voltage region between 0.8 and 0 V, which is typically observed for the mixed electrode of silicon and graphite,

Fig. 2 Initial current reversal chronopotentiograms of silicon-graphite electrodes prepared with (a) PVdF (10 wt %), (b) CMCNa (10 wt %), and (c) PAANA (30 wt %).

and the redox activity is due to the combination of lithium intercalation into graphite and Si-Li alloy formation. However, the specific capacity depends on the binders. The capacity was less than 400 and 800 mAh g^{-1} for PVdF and CMCNa, respectively. In contrast, the PAANA electrode exhibited the highest activity of approximately 1000 mAh g^{-1} . The similar electrochemical results were confirmed for the Si-graphite electrodes with poly(sodium acrylate), poly(lithium acrylate), and poly(potassium acrylate) binders. Since the theoretical limit of the lithium intercalation forming LiC_6 is as low as 372 mAh g^{-1} , the higher capacity for the PAANA resulted from the stable and reversible redox due to the lithiation of Si. From the potential variation during lithiation below 0.3 V in Fig. 3, the potential plateaux corresponding to staging Li intercalated graphite compounds¹⁸⁾ more clearly appear for the PVdF than the PAANA, suggesting that the electrochemical activity of Li-Si alloy is readily depressed during the initial ten cycles for PVdF.

Figure 3 (lower) shows the change in the reversible capacity of silicon-graphite mixture bound by three polymeric compounds. By comparing the 10 wt % binder electrodes for PVdF, CMCNa, and PAANA, the PAANA binder is the most suitable to retain the lithiation capacity. In case of PVdF, the capacity was drastically decreased during 10 cycles from 900 to 300 mAh g^{-1} . As

Fig. 3 (upper) Current reversal chronopotentiograms at the tenth cycle and (lower) variation in reversible oxidation capacities of silicon-graphite electrodes prepared with (a) 10 wt % PVdF and (b) 10 wt % CMCNa, and (c) 10 and (d) 30 wt % PAANA binder.

mentioned above, the activity at the 10th cycle is mainly due to lithium intercalation into graphite, indicating that the decrease in capacity is responsible for the silicon component. Such behavior of particulate Si is considered to be due to collapse of Si particle and fatigue of the composite electrode resulting from the large volume change by lithiation cycle. When CMCNa binder was used, the initial capacity was similar to that of PVdF and the better capacity retention was obtained, which should be due to the improved binding ability according to previous reports.^{8,9)} The gradual decrease of capacity

was observed for the CMCNa electrode, and its capacity was not remarkably different from that of PVdF after 30 cycles.

By adopting the polyacrylate binder, the cycle performance is improved as seen in Fig. 3. For 10 wt % PAA-Na, the capacity was approximately 1000 mAh g⁻¹ at the first cycle and reduced to 600 mAh g⁻¹ after thirty cycles. If graphite (60 %) is assumed to show 372 mAh (g of graphite)⁻¹, the specific capacity of silicon (20 %) in the PAA-Na electrode is calculated to be approximately 2880 mAh (g of silicon)⁻¹ at the first cycle. When the

Fig. 4 SEM images of the Si-graphite electrodes with 30 wt % PAANA binder (a)(b) before cycle and (c)(d) after 10 cycles; (a)(c) surface and (b)(d) cross sectional images. An image of 10 wt % PVdF electrode after 10 cycles is shown in (e) for comparison.

Fig. 5 (left) Superimposed images of optical and Raman microscopy, in which red, blue, and green portions correspond to appearance of Raman peaks of crystalline silicon, G-band of carbon, and D-band of carbon respectively, and (right) laser Raman spectra of selected points of Si-graphite electrodes with 10 wt % PVdF binder (a) before initial cycle and (b) after 10 cycles.

amount of PAANa increases to 30 wt %, the silicon based electrode demonstrated the reversible capacity of *ca.* 870 mAh g⁻¹ at the 30th cycle which corresponds to almost 90 % of the initial capacity. We confirmed that the increase of PVdF binder up to 30 wt % did not improve the electrode performance at all, suggesting the different functionality of PVdF and PAANa binder. The reversible capacity was much increased by increase in the silicon content in the PAANa electrode. Indeed, the PAANa strongly binds the particulate electrode materials and improves the adhesion strength onto Cu foil compared to the PVdF and CMCNa, and the adhesion strength increased with the increase in the amount of PAANa from 10 to 30 wt %, as confirmed by peel test.

We observed the morphological change of the electrodes by SEM. Figure 4 shows that the graphite particles, whose size is about approximately 3 μ m, are distinguishable at the surface of the pristine electrode and the thickness was about 10 μ m. The electrolyte decomposition during 10 cycles resulted in the deposition for the PAANa in Fig. 4 (c), but the larger amount of deposit covering the electrode surface is observed and the deposited layer is cracked for PVdF in Figure 4 (e). This should be one of origins of the severe deterioration for PVdF. From the cross sectional image, the electrode thickness of the PAANa hardly increased after tests, namely, there appears to be no apparent damage of the active material layer.

From Raman spectra, the crystalline Si remained after 10 cycles in case of PVdF, whereas crystalline Si disappeared for PAANa because of the amorphization of Si by lithiation and delithiation. In Fig. 5, laser Raman microscope observation proved that crystalline silicon partly distributed and remained after 10 cycles for PVdF, suggesting that a part of the crystalline silicon did not undergo lithiation due to electrical isolation. It is speculated that the lithiation of Si accompanied with severe electrolyte decomposition during the initial cycles leads to large volume expansion, resulting in partially electric isolation of silicon. It is in good agreement with the different electrochemical performances for PVdF and PAANa.

As described previously,^{12,13)} the uniform polyacrylate layer formed on graphite contributes the suppression of irreversible side reaction and desolvation of Li⁺ ions solvated with carbonate ester, so that highly reversible lithium intercalation. In this study, the graphite and Si particles are coated by polyacrylate which was evidenced by surface analyses. When silicon particles expand by electrochemical lithiation, the uniform polyacrylate coating should suppress the electrical isolation of silicon within the electrode. We believe that the polyacrylate suppresses the electrolyte decomposition not only on graphite but also on lithiated silicon surface,¹⁵⁾ which contributes to the higher initial efficiency as described in Fig. 2. It is likely that the chemical and physical crosslink of polyacrylate is developed because of its amorphous and dehydration nature. The complex effect-

tiveness of polyacrylate affected by molecular structure including crosslink, slurry structure, binding condition, adhesion state onto current collector, crystallinity, swelling with electrolyte etc. realized the improvement of particulate silicon based electrode. Further investigation is under progress to enhance the battery performance and understand the role of functional binders. The binder chemistry for lithium ion batteries has high potential to enhance the battery performance and to control interface structure including SEI.

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References

- 1) R. A. Sharma and R. N. Seefurth, *J. Electrochem. Soc.*, **123**, 1763 (1976).
- 2) M. Winter and J. O. Besenhard, *Electrochim. Acta*, **45**, 31 (1999).
- 3) H. Li, X. J. Huang, L. Q. Chen, Z. Wu, and Y. Liang, *Electrochem. Solid-State Lett.*, **2**, 547 (1999).
- 4) M. Yoshio, H. Wang, K. Fukuda, T. Umeno, N. Dimov, and Z. Ogumi, *J. Electrochem. Soc.*, **149**, 1598 (2002).
- 5) T. Takamura, S. Ohara, M. Uehara, J. Suzuki, and K. Sekine, *J. Power Sources*, **129**, 96 (2004).
- 6) S. Komaba, F. Mikami, T. Itabashi, M. Baba, T. Ueno, and N. Kumagai, *Bull. Chem. Soc. Jpn.*, **79**, 154 (2006).
- 7) L. B. Chen, X. H. Xie, J. Y. Xie, K. Wang, and J. Yang, *J. Appl. Electrochem.*, **36**, 1099 (2006).
- 8) J. Li, R. B. Lewis, and J. R. Dahn, *Electrochem. Solid-State Lett.*, **10**, A17 (2007).
- 9) N. S. Hochgatterer, M. R. Schweiger, S. Koller, P. R. Raimann, T. Wohrle, C. Wurm, and M. Winter, *Electrochem. Solid-State Lett.*, **11**, A76 (2008).
- 10) S. Komaba, T. Itabashi, T. Ohtsuka, H. Groult, N. Kumagai, B. Kaplan, and H. Yashiro, *J. Electrochem. Soc.*, **152**, A937 (2005).
- 11) S. Komaba, N. Yabuuchi, T. Ozeki, K. Okushi, H. Yui, K. Konno, Y. Katayama, and T. Miura, *J. Power Sources*, **195**, 6069 (2010).
- 12) S. Komaba, T. Ozeki, and K. Okushi, *J. Power Sources*, **189**, 197 (2009).
- 13) S. Komaba, K. Okushi, T. Ozeki, H. Yui, Y. Katayama, T. Miura, T. Saito, and H. Groult, *Electrochem. Solid-State Lett.*, **12**, A107 (2009).
- 14) S. Komaba, T. Tanaka, T. Ozeki, T. Taki, H. Watanabe, and H. Tachikawa, *J. Power Sources*, **195**, 6212 (2010).
- 15) T. Ozeki, K. Shimomura, S. Komaba, H. Yui, Y. Katayama, and T. Miura, *The 76th Annual Meeting of the Electrochemical Society of Japan, Abstr.*, 1P07, p.357 (2009) [in Japanese].
- 16) J. Li, D.-B. Le, P. P. Ferguson, and J. R. Dahn, *Electrochem. Acta*, **55**, 2991 (2010).
- 17) W. Ma, J. Zhang, and X. Wang, *J. Mater. Sci.*, **43**, 398 (2008).
- 18) S. Komaba, T. Itabashi, M. Watanabe, H. Groult, and N. Kumagai, *J. Electrochem. Soc.*, **154**, A322 (2007).