Effects of Adding HPC to Si-Alloy Anode Slurry of Lithium Secondary Battery

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Lithium secondary batteries are the power sources in electric cars and hybrid electric cars, and must have the characteristics of high power output, high capacity, high stability, and long life. Graphite is widely used as the anode material in lithium secondary batteries. However, it has a theoretical capacity of 372 mAh g⁻¹, which is much lower than that required by electric cars. Therefore, graphite must be replaced by new materials. One of the candidate materials presently being researched is high-capacity Si. Si has a large theoretical capacity of 4200 mAh g⁻¹. However, when lithium ions are inserted into Si-based materials, the volume of the latter expands by more than 300%, i.e., its capacity maintenance rate is low. Studies exploring methods for overcoming this drawback of Si have identified methods for controlling Si expansion by suppressing the generation of cracks by using Si nanowires, coating carbon and graphene on the Si to provide buffering and conductivity during expansion, or forming a matrix between Si and metal components such as Ni, Ti, and Fe. Most of these studies have focused on controlling expansion to improve the electrochemical characteristics by changing the Si itself. However, studies that overcame the disadvantages of Si by changing the rheology of the slurry when fabricating water-based electrodes are next to non-existent. When conventional graphite is used as an active material, fluorine-based poly(vinylidene fluoride) (PVDF) is used as a binder. However, the risk of self-heating (thermal runaway) occurs for PVDF because of the reaction of lithium metal and lithiated graphite (Li₄C₆). Further, when it is applied to a Si-based material, rather than graphite, there is a problem with adhesion, because the binder does not provide a buffering effect and the substance falls off as a result of expansion. Imide-based high-molecular-weight polyimide and polyamide imide (PAI) have been reported to be usable alternatives because they have adhesions superior to that of PVDF and buffering effects for expansion. However, to be used as a binder, they have to be hardened at high temperature. Moreover, the use of the organic solvent coagulation induced by the high polarity of water molecules, resulting in uneven distribution of the solidified electrode material and binder. Therefore, this study aims to investigate the effects of changing the slurry rheology in improving the characteristics by adding HPC, which can perform the roles of disperser and binder, when fabricating an electrode slurry using water as the solvent. The research steps involved analyzing changes in the following properties after the addition of HPC to the slurry when fabricating electrodes using a water-based binder in a Si alloy: viscosity, dispersibility of particles constituting the electrodes, electrode morphology, adhesiveness of pole plates, maintenance of charging/discharging capacity, and expansion behavior after charging at 0.1 C.

Experimental

To create the electrodes, the weight ratios of the active material:Ketjen black (ECP 600 JD, Ketjen black international company, Japan):PAI binder (30 wt% solution, water based, ZHAOYU, China) were set at 90:2:8, and for the active material, the Si alloy (∼5 μm, Si–Ti–Ni, MKE Electronics, Korea):graphite ratio was set at 65:35. As a solvent for producing the slurry, 45% deionized (DI) water was added to the electrode components and mixed. The PAI binder used for slurry production is a water-based binder with improved adhesion strength and a viscosity of 2300–3500 cps at 25 °C. The binder was diluted using deionized water, N-methyl-2-pyrrolidone, or dimethyl acetamide. HPC (M₉₀ ~80000, Sigma-Aldrich, USA) was produced as a 10 wt% solution in DI water, and 0.2–2.0 wt% was added to the electrode components (solids). The produced slurry was used for coating the Cu-foil current collector evenly (thickness 14 μm), using a doctor blade, followed by vacuum drying for 12 h at 110 °C to produce a sheet. The dried electrode underwent 24-h aging in a vacuum chamber of the glove box prior to the production of the cell.

To evaluate the slurry quality, we examined the particle size distribution, viscosity, and dispersion stability, according to the addition of HPC. The particle size distribution was measured with a particle size analyzer (LS230, Beckman Coulter, USA) after adding 0.7 wt% HPC and solvent to Ketjen black and mixing them in a paste mixer.
Figure 1. Relative viscosity as a function of shear rate for slurry with different HPC addition.

at 1,500 rpm. The viscosity was measured using a viscometer (DV-II+ Pro, Brookfield, USA) as the shear rate (0–250 s⁻¹) increased. For dispersion stability evaluation, the time-dependent changes in the slurry backscattering were assessed using TURBISCAN (Turbiscan Lab Expert, Formulaction, France). In addition, for evaluation of the adhesiveness of the electrodes, the relative adhesiveness was assessed using a tape, by comparing the degree of smearing on the tape.

The electrochemical characteristics were measured in the voltage range 0.01–1.5 V vs Li/Li⁺, with a current density of 5 mAh cm⁻², using a 2032 coin cell in an Ar atmosphere in a glove box, and designing the theoretical capacity to be 650–700 mAh g⁻¹. We used lithium metal as the counter electrode, and 1 M LiPF₆ in EC+DEC+FEC (ethylene carbonate:diethyl carbonate:fluoroethylene carbonate) as the electrolyte at ratios of 5:70:25 v/v. The expansion in electrode thickness was calculated as (after charging electrode thickness – before charging electrode thickness) ÷ before charging electrode thickness × 100 by measuring the cross-sectional thickness of the electrode that was charged at 0.5 mAh cm⁻². Electrochemical impedance spectra were measured in the frequency range 0.01–100 kHz at a scanning speed of 10 mV s⁻¹.

Results and Discussion

Figure 1 shows the viscosity changes with varying shear rates; as the shear rate increased, the viscosity tended to decrease. To determine the degree to which the viscosity decrease and the dispersion are interrelated, the dependence of the dispersion stability of the anode slurry on the addition of HPC was assessed using TURBISCAN. The results are shown in Fig. 2. As a result of measuring the slurry dispersion every 4 h for 15 days, it was found that the backscattering values were not uniform for different heights and decreased over time at the top part of slurry, to which HPC was not added. However, the values were uniform in the slurry mixed with 0.7 wt% HPC. In other words, the particles in the slurry without HPC grew over time as a result of coagulation, and the specific surface area became smaller. Thus, coagulation at the top layer and precipitation at the bottom layer reduced backscattering between the light and particles. From these results, it could be inferred that the addition of HPC was conducive to homogeneous dispersion of the particles of Ketjen black, and lowered the gravity between the particles, thus increasing the viscosity.

Fig. 3 shows surface images of electrode sheets with and without HPC, observed using scanning electron microscopy (SEM). In the case of addition of 0.7 wt% HPC, the electrode surface structure was dense and the particles were regularly distributed, but in the absence of HPC, the structure was porous and the particles coagulated. Furthermore, cracks were observed around the coagulated particles.

Figure 2. Backscattering profile of slurry measured for 15 days: (a) without HPC and (b) with HPC 0.7 wt%.

Figure 3. SEM images of electrode surface with different HPC contents: (a) without HPC and (b) with HPC 0.7 wt%.

This phenomenon may be ascribed to the irregularity of the electrode surface as a result of particle coagulation in an aqueous environment and changes in the evaporation speed of the solvent during drying. This leads to cracks forming and an irregular electrode surface, thus impairing the electrode performance.

To check how the adhesiveness changes when HPC is added, a taping test was conducted, in which a tape was affixed to the electrode surface and then removed, as shown in Fig. 4. When HPC was not
The initial charge/discharge capacity increased to 946/809 mAh g\(^{-1}\) of adding HPC to the slurry on the charge/discharge characteristics. Initial charge/discharge measurements performed to check the effects up to 0.7 wt% of HPC; beyond that point, the capacity tended to decrease. This HPC-mediated increase in the adhesive strength of the electrode is assumed to be attributable to the homogeneous distribution of the binder as a result of the increased specific surface of the particles. Moreover, a different study, in which HPC was used as the binder, confirmed the role of HPC as a binder with excellent adhesive strength.\(^{27}\) Fig. 5 shows the results of initial charge/discharge measurements performed to check the effects of adding HPC to the slurry on the charge/discharge characteristics. The initial charge/discharge capacity increased to 946/809 mAh g\(^{-1}\), up to 0.7 wt% of HPC; beyond that point, the capacity tended to decrease, even to below 882/758 mAh g\(^{-1}\), the baseline charge/discharge capacity before adding HPC. The increase in the initial discharge capacity induced by the addition of HPC is ascribable to the effect of uniform dispersion. In general, attraction forces are exerted between particles via van der Waals attractive force. Colloidal particles that undergo Brownian motion approach and collide with one another, thereby forming coagulates held together by van der Waals attractive forces in the absence of factors that may inhibit the inter-particle approaches, which destroys the dispersion stability. On a related note, stable colloidal stability can be maintained by forming factors that can suppress coagulation.

Coagulation can be suppressed by two methods: steric stabilization and electrostatic stabilization. An HPC disperser is a polymer that improves inter-particle coagulation via steric stabilization. HPC adhered to the particle interface can suppress inter-particle coagulation at shorter distances than electrostatic stabilization. Moreover, HPC has an additional advantage in that it can be used as both a water-based and non-water-based disperser. As such, uniform dispersion can be ensured by adding HPC, which adsorbs to particle interfaces and thus suppresses inter-particle coagulation. The conductivity of electrodes is enhanced, especially through homogeneous distribution of Ketjen black, which is assumed to be responsible for the increase in the initial charge/discharge capacity. In contrast, there was no significant HPC-content-dependent difference in the initial efficiency, which ranged between 85.4 and 86.0%. This can be explained by the fact that the increase in the initial charge capacity, induced by the enhanced conductivity, was offset by the discharge in proportion to the charge owing to the HPC-mediated uniform dispersion of Ketjen black. If a different active material had been used when fabricating the electrodes, a different initial capacity would have been obtained.\(^{28}\)

When PAI was used as the binder in the water-based slurry, the dependence of the cycling characteristics (up to 50 cycles) on the amount of HPC added was investigated; the results are shown in Fig. 6. The cycling characteristics improved as the amount of HPC increased. In particular, when 0.7 wt% HPC was added, the capacity maintenance rate was boosted to its maximum value of 50 cycles. Such an improvement in the cycling characteristics may be attributable to the improved adhesiveness and homogeneous dispersion of HPC, as confirmed above (Figs. 3 and 4).\(^{17}\) Figure 7 shows the dependence of impedance on the amount of HPC added; the results prove that the addition of HPC increases the initial charge/discharge capacity and cycling characteristics. Until the mixed amount of HPC reached 1.0 wt%, the polarization resistance decreased below the level before the addition of HPC. In particular, when 0.7 wt% HPC was added, the lowest polarization resistance was obtained. However, when 1.0 wt% or more was added, the resistance increased again. These results may be explained by mitigation of the problem of coagulation of Ketjen black through the addition of HPC, along with the increased specific surface area, thus improving the conductivity through homogeneous distribution on the Si-alloy particles. Furthermore, the decreasing polarization resistance indicates that up to a certain amount of HPC addition, the particles and binder are evenly distributed, but beyond that critical point, the heterogeneity is increased again because of a bridging phenomenon, in which a chain is formed at the tail end of the polymer.\(^{29}\)

To evaluate the expansion of Si-alloy electrodes with different amounts of added HPC, the cross-sectional thicknesses of the
electrodes before and after charging/discharging were observed in SEM images, and the results are shown in Fig. 8. The measurements were performed with the current density set at 0.1 C. When the electrode thicknesses were checked, it was found that in the case of no added HPC, the thickness expanded by 63.9% (charge capacity 892.5 mAh g\(^{-1}\)), but in the case of 0.7 wt% HPC (charge capacity 938.2 mAh g\(^{-1}\)), it expanded by 29.7%. In brief, when HPC 0.7 wt% was added, the charge capacity value was large, but the expansion rate decreased. Therefore, if HPC is added, the expansion decreases because HPC is adsorbed on the particle surfaces and acts as a buffer when the Si alloy expands. Additionally, the homogeneous distribution of the binder as a result of HPC-mediated inhibition of coagulation of the electrode material led to the improvement in adhesive strength. This is assumed to have controlled the charge-dependent volume expansion of the electrode. However, the images in Fig. 8 confirm the HPC-mediated decrease in the volume expansion of the electrode and increase in surface roughness. This is attributable to the heterogeneous adhesive strength between binder and particles under the HPC-non-added condition and the ensuing linear volume expansion of the particles. Under the HPC-added condition, in contrast, the homogeneous adhesive strength between binder and particles results in the binder filling the gaps among the expanded particles more tightly, thus resulting in the decrease in the total volume expansion of the electrode, but an increase in surface roughness. Figure 9 shows the electrode surfaces with and without HPC addition, observed using SEM after 50 cycles. In the case of no added HPC, cracks formed between the particles because of volume expansion, and the fine particles fell off the electrode surface. In contrast, when 0.7 wt% HPC was added, no cracking occurred and the electrode surfaces prior to charge/discharge were unchanged.

When HPC is added to a slurry composed of a Si alloy, graphite, Ketjen black, a PAI binder, and DI water as the solvent, the electrochemical performance of the anode is improved. To observe which solidified particles’ coagulation is controlled by the addition of HPC, each type of solidified particle was dispersed in solvents with and without HPC, and their particle size distribution were measured. The Si-alloy and graphite particles showed little difference in particle size or size distribution, regardless of whether or not HPC was added, but in the case of Ketjen black, large differences in the particle size and size distribution appeared, as shown in Fig. 10. These results suggest that the addition of HPC increases the specific surface area by dispersing Ketjen black. Therefore, the electrochemical characteristics were improved because Ketjen black was evenly dispersed on the surface of the Si alloy and the conductivity was improved.

Conclusions

A water-based slurry was produced using a Si alloy, graphite, Ketjen black, a PAI binder, and DI water, and we checked the effect of the added amount of HPC on the rheology and dispersion characteristics of the slurry, expansion of the electrode, adhesiveness to pole plates, and electrochemical characteristics. The addition of HPC resulted in reduced viscosity and excellent dispersion in the slurry, and improved the adhesiveness of the electrode and pole plates. In the battery, the initial capacity, polarization resistance, and cycling performance were improved. Furthermore, the expansion in thickness was reduced. This was because adsorption of HPC on the particle surfaces of the Si alloy and Ketjen black hindered coagulation, because of steric

Figure 7. Electrochemical impedance spectra of Si-alloy anodes with different HPC contents.

Figure 8. Cross-sectional SEM images of anodes without HPC (a and c) and with HPC 0.7 wt% (b and d); (a and b) as-prepared electrodes and (c and d) after charging at 0.1 C.

Figure 9. SEM images of electrode surfaces after 50 cycles: (a) without HPC and (b) with HPC 0.7 wt%.

Figure 10. Particle size distribution of Ketjen black with/without HPC.
hindrance, and, at the same time, acted as a binder. In conclusion, the dispersion improvement provided by HPC addition can be applied in electrode materials for lithium secondary batteries that use conductive nanoparticles.

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References