Effect of Electrolyte Additives on Non-Nano-Si Negative Electrodes Prepared with Polyimide Binder

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We investigated the effect of electrolyte additives on an untreated, conventional micro-sized (non-nano) Si electrode prepared with a polyimide (PI) binder (PI-Si electrode). Both additives, vinylenyl carbonate (VC) and fluoroethylene carbonate (FEC), improved the cycle stability of a PI-Si electrode half-cell. The solid-electrolyte interphase (SEI) formed by FEC includes a large amount of LiF and shows quite low resistance. This SEI effectively suppresses electrolyte decomposition, and an electrolyte containing VC mainly forms a SEI with organic components, and shows a smaller suppression effect on the electrolyte’s excessive decomposition. From the AC impedance measurement and SEM observation results, we found that the formation of a massive SEI prevents contacts among Si particles and increases the charge-transfer resistance of the PI-Si electrode. The applied FEC suppresses the revolution of this resistance, meaning that FEC functions as an electrolyte additive suitable for PI-Si electrodes. A PI, Si, and soft-carbon composite (PI-Si-SC) electrode half-cell shows excellent cycle stability and rate performance by an adjusted amount of FEC (10 wt%). A full-cell, which includes a LiNi0.5Mn1.5O4/O2 positive electrode, the PI-Si-SC negative electrode, and the electrolyte containing 10 wt% FEC, also exhibits quite good cycle stability.

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Since high energy-density Li-ion batteries (LIBs) are attractive in various fields, applications for them continue to expand. Advanced electric vehicles and power storage systems for renewable energy require the enhanced performance of LIBs with higher power, energy density, and more safety. The rapid development of such mobile electronic devices as smartphones, tablets, and thin laptops has also significantly increased power consumption, requiring higher capacity LIBs.

The energy density of LIBs has been greatly enhanced by improving electrode density and efficient packaging of each component into a cell. However, electrode active materials are basically unchanged from the beginning of LIB history; LiCoO2 and LiMn2O4 are used as a positive electrode, and graphite1 is generally applied to a negative electrode. To meet demands to further improve energy density, next-generation LIBs require enhanced capacity based on an active material. However, it is difficult to increase the weight-specific capacity of a positive electrode because such a “heavy” transition metal as a positive electrode material must increase the redox electrons and its redox potential.1-4 On the other hand, high-capacity negative electrodes are feasible since a new anode candidate is often composed of “light” elements like a graphite-based electrode. Silicon (Si) has quite a high theoretical Li-storage capacity (4,200 mAh g−1) that is approximately ten times as high as graphite (372 mAh g−1) and a relatively low average potential for alloying/de-alloying with Li ions (0.4 V vs. Li/Li+). Therefore Si has attracted much attention as a next-generation negative electrode material.

A crucial problem of Si negative electrodes for LIBs is the collapse of their electrode structure that occurs with large volume change8 at alloying/de-alloying with Li. The collapse of the electrode structure leads directly to the loss of electronic contacts, causing a rapid capacity loss with charge/discharge cycles.8-11 The application of nano-scale Si10 has been reported as an extremely effective method to solve this problem. For example, Si nano-wire material10 relaxes an internal electrode stress caused by volume expansion, and can prevent the collapse of electrode structure. In addition, the efficient electron conduction is ensured in a vertical direction. Si nano-particles/carbon composite also suppresses the loss of electric conduction in the electrode since the internal stress is relaxed by the Si nano-particles and the electric conductivity is enhanced by the applied carbon.14,15 However, since the preparation of nano-scale Si requires a very complex method, synthesizing a large amount of nano-scale Si is difficult due to practical industrial cost. Thus, the cycling degradation of Si negative electrodes must be suppressed by improving other electrode components or introducing a novel electrode design.

Previously, we reported that the cycle stability of a Si electrode composed of μm-order Si (μm-Si) particles is drastically improved by using polyimide (PI) as a binder.16 The PI binder suppressed the electrode structure’s collapse so that the discharge capacity of the μm-Si electrode that was prepared with the PI binder was maintained during 300 cycles under a condition where the charge capacity was limited to 800 mAh g−1. In that system, however, the pulverization of the Si particles themselves due to the stress caused by their volume change remains unsolved, which is another cause of the capacity degradation. The surface area of the Si particles increases significantly by pulverization, which leads to excessive electrolyte decomposition.17 Since the amount and the thickness of the solid-electrolyte interphase (SEI) increase, the electrode resistance also increases significantly.18 Since the pulverization of large-size Si particles such as μm-Si is essentially inevitable, electrolyte additives must be applied to form an effective SEI to suppress electrolyte decomposition.19 Vinylenyl carbonate (VC) and fluoroethylene carbonate (FEC) have already been reported to be effective to improve cycle stability of Si thin-film electrode.18,19 In this work, we investigated the effect of these electrolyte additives on μm-Si electrode prepared with a PI binder (PI-Si electrode). An effective electrolyte additive was also applied to the electrode from a μm-Si and soft carbon (SC) composite with a PI binder (PI-Si-SC electrode). We also improved the cycle stability of the PI-Si-SC electrode by optimizing the amount of electrolyte additive.

Experimental

The μm-Si electrode with polyimide (PI-Si electrode) was prepared in a dry room with a dew point of -55°C. The untreated μm-Si was mixed with acetylene black (AB, Denki kagaku kogyo Co., HS-100) and polyacrylic acid as a precursor of PI at a weight ratio of 75:10:15 with N-methyl-2-pyrrolidone (NMP, Kishida Chemical Co., 99.5%) as a solvent. The obtained slurry was cast onto a Cu-foil current collector and dried at 80°C for 2 h in a vacuum oven to remove the NMP. To change the polymeric acid into polyimide by dehydration condensation, the oven temperature was raised to 300°C and held for 10 min. After cooling to room temperature, the prepared electrode sheets were cut into 12-mm diameter disks for electrochemical measurements.

The μm-Si and SC composite electrode with the PI binder (PI-Si-SC electrode) was prepared in the same procedure. The μm-Si, AB,
SC, and polyamic acid were mixed at a weight ratio of 50:25:10:15. The mass loading of the active materials (Si or Si + SC) in the electrodes were approximately 2.0 mg cm$^{-2}$. The positive electrode for the full-cell test was prepared from LiNi$_{0.5}$Mn$_{0.5}$Co$_{0.5}$O$_2$, AB, and polyvinylidene fluoride (Kureha Co., #1100) at a weight ratio of 85:8:7.

We assembled the test cells for electrochemical measurements in an argon-filled glove box using a two-electrode-type cell (Hosen Co.). The negative electrode half-cells were assembled with the prepared PI-Si or PI-Si-SC electrodes, a Li foil (Honjo Metal Co.) with a 13-mm diameter disk, a 1 mol dm$^{-3}$ LiPF$_6$ in a 1:1 v/v mixture of ethylene carbonate (EC Kishida Chemical Co., LBG) and dimethyl carbonate (DMC, Kishida Chemical Co., LBG) without additive and with 3 wt% of VC (Kishida Chemical Co., LBG) or 3–10 wt% of FEC (Kishida Chemical Co., LBG), and highly porous polyolefin film coated with ceramic as a separator.

The charge and discharge cycle performance tests were carried out using a galvanostatic charge/discharge unit (Intex Co., BTS2004W). In this paper, we refer to the alloying process of Si with Li (i.e., the direction in which the cell voltage decreases) as the “charge” and the de-alloying process (i.e., the direction in which the cell voltage increases) as the “discharge”. Although in our previous report$^{16}$ the cycle performance tests were carried out under a condition where the charge capacity was limited, it was not limited in this paper because it is extremely difficult to limit only the charge capacity of a negative electrode in a full-cell. We measured the negative electrode half-cell in a voltage range of 1.500–0.005 V. The charging process proceeded to 0.005 V with a constant-current (C.C) mode and then proceeded with a constant-voltage (C.V) mode at 0.005 V until the current density decreased to 1/10 as much as the constant current in the C.C mode. The discharging process proceeded to 1.500 V with the C.C mode. The current densities at and after the initial cycle were 0.2 and 1.0–16.0 A g$^{-1}$. The full-cell was measured in a voltage range of 4.450–3.000 V, and the other conditions were the same as those of the half-cell.

The alternative current (AC) impedance spectra were measured using a frequency response analyzer (Solartron Analytical, 1255B). The cells were cycled until the preset cycle number and their voltages were relaxed for 10 h at an open-circuit condition for measurements in their steady state. All the measurements were carried out in a discharge state and the measurement frequency range was 100 kHz–10 mHz.

The surface morphologies of the Si electrodes were observed using a scanning electron microscope (SEM, Hitachi Co., SU-1500). The test cells were disassembled in an argon-filled glove box after relaxing the cell–voltage for 10 h at a discharge state of the 1st or 10th cycle. The electrodes removed from the cells were washed carefully in DMC and dried for 12 h in a vacuum state. The dried electrodes were stored in a sealed vial, and exposure to air was avoided as much as possible to prevent the transformation of the electrode surface morphology by oxidation until the observation.

We analyzed the chemical composition of the SEI on the electrode surface using an X-ray photoelectron spectroscope (XPS, JEOL Ltd., JPS-9010MC) with Mg K$\alpha$ radiation. The electrodes were removed from the test cells by the same procedure as the SEM observations after the 10th cycle. The dried electrodes were transferred from the glove box to the vacuum chamber of the XPS apparatus in an argon atmosphere using a transfer vessel to completely avoid changing the SEI’s chemical composition. The spectra derived from F 1s (676–696 eV), C 1s (274–294 eV), and O 1s (522–542 eV) were measured as a depth profile using argon etching treatment.

**Results and Discussion**

Figure 1 shows (a) the discharge capacity and (b) the cycle efficiency vs. cycle number of PI-Si electrode half-cells containing various electrolytes at current density of 1.0 A g$^{-1}$.

FEC further improved the cycle stability of the PI-Si electrode, especially the cycle efficiency. The cell’s cycle efficiency without additives is lower than that with them even in the early cycles, and begins to decrease rapidly around the 10th cycle. The cycle efficiency of the cell with VC also begins to decrease rapidly around the 35th cycle in contrast to that with FEC, which is always highest among the three cells.

Figure 2 shows the forepart of the discharge curves at the 1st and 50th cycles of the respective cells. The discharge curves start with initial polarization from 0.005 V. While discharging the Si electrodes, the crystalline and amorphous phases coexist in the lithiated Si, and the discharge potential for each phase is different.$^{20}$ Therefore, we cannot discuss complex cell resistance just using overall polarization between the charge and discharge. However, the initial polarization (or the initial voltage of discharge curves) should reflect an increase in the cell resistance. The initial polarization on discharging much increases during the 50 cycles for the cells without additives and with VC, while the initial polarization in the cell with FEC does not increase very much. The increase in the cell resistance seems related to the cycle efficiency, which is probably derived from the electrolyte decomposition affected by the electrolyte compositions.

To identify the origins of the increased cell resistance in detail, we measured the AC impedance of the PI-Si electrode half-cells with each electrolyte. Figure 3 shows the Nyquist plots at a discharge state of the 1st and 10th cycles. At least two semicircles (or arcs) are observed in all the profiles. The semicircle observed in the highest frequency increase very much. The increase in the cell resistance seems related with VC, while the initial polarization in the cell with FEC does not increase much during the 50 cycles for the cells without additives and with 3 wt% VC, while the initial polarization in the cell with FEC does not increase very much. The increase in the cell resistance seems related to the cycle efficiency, which is probably derived from the electrolyte decomposition affected by the electrolyte compositions.

Figure 1. Discharge capacity (a) and cycle efficiency (b) vs. cycle number of PI-Si electrode half-cells including various electrolytes at current density of 1.0 A g$^{-1}$.
region (the most left region) reflects the SEI resistance, and the larger semicircle (or arc) in the next highest frequency region (the right side next to the above region) includes a charge-transfer resistance. At a discharge state in the 1st cycle, the semicircle in the highest frequency region has almost the same magnitude in the three electrolytes. The other semicircle or arc next to the above semicircle in the cell containing FEC is obviously smaller than the other cells. After ten cycles, the magnitude of the semicircle in the highest frequency region respectively does not change, increases, and decreases in the electrolytes without additives, with 3 wt% VC, and with 3 wt% FEC. The other semicircle or arc becomes larger in the electrolytes without additives and with 3 wt% VC after ten cycles, but not in the electrolyte with FEC. The difference between the semicircles including the charge-transfer resistance will be discussed later with the SEM images of PI-Si electrodes after charge and discharge; here we only discuss the difference between the semicircles observed in the highest frequency region, derived from the SEI. The change of the resistance derived from SEI suggests that SEI’s amount and thickness formed by VC may increase during the ten cycles during which it was formed by FEC and became a desirable, lower resistance state.

These results suggest that the difference in the initial discharge voltage is affected by the SEI amount. We found that the FEC additive effectively improved the cycle stability of the PI-Si electrode and suppressed an increase in the SEI resistance. However, commercial Li-ion batteries are often stored at a charge state for a long period. The negative electrodes are always exposed to lower potential where electrolyte decomposition easily occurs. Therefore, we should also confirm the resistance derived from SEI when a PI-Si electrode half-cell is stored at a charge state.

Figure 4 shows the Nyquist plots after discharge at the 1st cycle followed by storage at a charge state for ten hours and without storage.
The cells were stored in open-circuit voltages of 50–70 mV. The resistance in the highest frequency region, derived from SEI, increases after storage at a charge state without additive and with VC, but it does not increase at all with FEC. The present results suggest that SEI formation progresses in electrolytes even during storage where pulverization of the Si particles by charge/discharge does not occur. Thus, we believe that the SEI which formed in the electrolytes with VC and without additives, does not suppress further SEI formation (i.e., excessive decomposition of the electrolytes). From the above results, using electrolyte additives is very effective to improve the cycle stability of the PI-Si electrode, especially the electrolyte containing FEC that greatly suppresses the electrolyte decomposition even in storage at a charge state.

Next, we observed the surface of the PI-Si electrodes after discharge to discuss their collapse mechanism. Figure 5 shows their SEM images after the 1st and 10th cycles. Very large cracks occurred in all the PI-Si electrodes after the 1st cycle, and the portions surrounded by these large cracks resemble an island, but the electronic contacts of the PI-Si electrodes are maintained because the pulverized Si particles that inflates the islands. Since a large amount of SEI prevents contact between the pulverized Si particles on an island and decreases the electric conductivity of the PI-Si electrodes, our consideration here corresponds well to the magnitude of the semicircles in the second higher frequency region in Fig. 3 (or Fig. 4). After ten cycles, the cracks width narrows and the shape of the islands slightly disintegrates with VC and without additives (Fig. 5d and 5b). In contrast, the islands with FEC maintain their original shape (Fig. 5f), although the cracks width narrows. From these changes in the electrodes structure, the decrease in the cracks width during the cycles may be attributed to repeated expansion and contraction, but we consider that the disintegration of islands shape is caused by the SEI growth due to the cycles. This result also correlates with the change of the semicircles in the second higher frequency region after ten cycles (Fig. 3). The electrolyte additives significantly affect the collapse mechanism of the Si electrode and the SEI formation. Therefore, the selection of electrolyte additives is as critical for the Si electrodes composed of μm-Si as the selection of binders.

We carried out an elemental analysis of the electrode surface to discuss the effect of electrolyte additives on the SEI components. Figure 6 shows the XPS spectra related to F 1s, C 1s, and O 1s of the PI-Si electrode surface after ten cycles. The number shown on the right side of Fig. 6a is the total time (seconds) for an Ar etching process, and the spectrum shown in the upper part indicates the information of a deeper position, which is the same in the other figures. The spectra observed in this study are slightly affected by being charged-up. Thus the assigned component and peak position may be slightly different from other literature values. Comparing Figs. 6a and 6b, a large amount of LiF exists on the surface of the PI-Si electrode that was cycled with FEC. One advantage of the FEC additive was reported; the SEI formed by FEC contains a relatively large amount of LiF and its resistance is fairly small. The effective component in our electrodes seems to be the same as LiF in the previous report. The peaks, which are assigned to C–O and C=O, are observed in the spectra related to C 1s (Figs. 6c and 6d) and O 1s (Figs. 6e and 6f), indicating that the organic components formed by the decomposition of electrolytes and their intensity on the PI-Si electrode cycled with VC exceeds that with FEC. Therefore, VC forms SEI mainly composed of organic components, which have a smaller effect on the suppression of the excessive decomposition of an electrolyte and lead to an increase in electrode resistance. At this point, there is a peak that has not been discussed yet between Li2O and C–O peaks in the O 1s spectra (Figs. 6e and 6f). This peak is observed only in a certain interior (indicated by the arrows in the Figs.) and not at the exterior surface. It is detected more strongly at the PI-Si electrode that was cycled with VC. At present, although we have not identified this peak completely, its position is very close to the peak position of SiO2. Therefore, we can suggest that this peak is attributed to oxidized silicon and the FEC additive has an inhibitory effect against the silicon oxidation associated with cycling.

Based on our present results, after concluding that FEC is more suitable than VC as an electrolyte additive for the PI-Si electrode, we applied FEC to the PI-Si-SC electrode to improve the cell performances even further. Figure 7 shows (a) the discharge capacity and (b) the cycle efficiency vs. the cycle number of the PI-Si-SC electrode half-cells with electrolytes containing 3 and 10 wt% FEC at a current density of 1.0 A g−1. The initial cycle efficiency improved to 82.45 % using a PI-Si-SC electrode (the initial cycle efficiency of the PI-Si electrode half-cell is 76.48%, which is not displayed in Fig. 1b). The electronic conductivity and the stress relaxation of the electrode seem to improve by mixing SC. The discharge capacity retention of the PI-Si-SC electrode half-cell with 3 wt% FEC at the 50th cycle relative with VC or without additives (Fig. 5c and 5a). The PI-Si electrodes should expand to the same extent in all the cells since the charge and discharge capacities are almost the same regardless of electrolyte composition. Nevertheless, the cracks width is different between the present electrodes, which indicates the difference in the density of the islands. The islands formed in the electrolyte with VC and without additives include a relatively large amount of SEI with pulverized Si particles that inflates the islands. Since a large amount of SEI prevents contact between the pulverized Si particles on an island and decreases the electric conductivity of the PI-Si electrodes, our consideration here corresponds well to the magnitude of the semicircles in the second higher frequency region in Fig. 3 (or Fig. 4). After ten cycles, the cracks width narrows and the shape of the islands slightly disintegrates with VC and without additives (Fig. 5d and 5b). In contrast, the islands with FEC maintain their original shape (Fig. 5f), although the cracks width narrows. From these changes in the electrodes structure, the decrease in the cracks width during the cycles may be attributed to repeated expansion and contraction, but we consider that the disintegration of islands shape is caused by the SEI growth due to the cycles. This result also correlates with the change of the semicircles in the second higher frequency region after ten cycles (Fig. 3). The electrolyte additives significantly affect the collapse mechanism of the Si electrode and the SEI formation. Therefore, the selection of electrolyte additives is as critical for the Si electrodes composed of μm-Si as the selection of binders.
to that at the 10th cycle slightly improved (80.53%) compared to the PI-Si electrode half-cell (77.53%); the improvement was less than we expected. Since the cycle efficiency of the PI-Si-SC electrode half-cell with 3 wt% FEC was also unstable like the PI-Si electrode half-cell, 3wt% FEC may be insufficient to protect an electrode surface whose area increases by the pulverization of Si particles. Thus we increased the amount of FEC to 10 wt% and drastically improved the capacity retention of the PI-Si-SC electrode half-cell at the 50th and 100th cycles: 91.44% and 78.74% (Fig. 7a). The efficiency was also stabilized (Fig. 7b). Although mixing SC reduced the electrode capacity, our PI-Si-SC electrode still has a high reversible capacity (1,900 mAh g$^{-1}$) and the mass loading of active materials (Si and SC) to the PI-Si-SC electrode is sufficient to accommodate the positive electrodes used in commercial Li-ion batteries.

Figure 8 shows the discharge capacity vs. the cycle number of the PI-Si-SC electrode half-cells with 10 wt% FEC at various discharge current densities (1.0–16.0 A g$^{-1}$). The charging process is based on a C.C-C.V mode regardless of the discharge current. Therefore, this measurement substantially exhibits a real discharge rate performance. The discharge capacity preserves high, stable values even when the current density increases to 4.0 A g$^{-1}$. At such high current densities as 8.0 and 16.0 A g$^{-1}$, the PI-Si-SC electrode half-cells with 10 wt% FEC still maintain a considerably high discharge capacity that exceeds 1,200 mAh g$^{-1}$ and seems stable even with repeated cycles, although the cycling tests were sometimes interrupted (Fig. 8) by short-circuit behavior at excessively high currents (8.0 and 16 A g$^{-1}$) for a half-cell with a Li-metal counter electrode.
Figure 7. Discharge capacity (a) and cycle efficiency (b) vs. cycle number of PI-Si-SC electrode half-cells at a current density of 1.0 A g\(^{-1}\) with 3 wt% and 10 wt% FEC.

We successfully and drastically improved the cycle stability of the negative electrode composed of non-nano, \(\mu\)m-Si particles by optimizing both the electrode and electrolyte components. To put the present results into a realistic cell system, we investigated the performance of a full-cell that includes a PI-Si-SC negative electrode and an electrolyte containing 10 wt% FEC. The positive electrode was mainly composed of \(\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2\) as an active material where the mass loading was approximately 14.5 mg cm\(^{-2}\). Regarding the negative electrode, the mass loading of the active material (Si + SC) was adjusted to approximately 1.3 mg cm\(^{-2}\), which is two-thirds of the PI-Si-SC electrode used in the half-cell, to balance a reversible capacity between the positive and negative electrodes. Figure 9 shows the charge/discharge capacities (corresponding to a vertical axis on the left side) and the cycle efficiency (the other vertical axis on the right side) vs. the cycle number of a \(\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2/\text{PI-Si-SC}\) cell containing 10 wt% FEC at approximately 2.0 A g\(^{-1}\) with respect to the Si and SC weight. The charge and discharge capacities of the \(\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2/\text{PI-Si-SC}\) cell decreased during the initial ten cycles and then leveled off around at least 90 cycles. The cycle efficiency maintains quite a high value exceeding 99.6% during the cycling except for the initial ten cycles. This result clearly substantiates that the present PI-Si-SC electrode with 10 wt% FEC electrolyte additive provides practical, excellent cycle stability for realistic full-cells.

**Conclusions**

Using such electrolyte additives as VC and FEC improves the cycle stability of Si electrode prepared with PI, but the SEIs formed by these additives have different characteristics. The SEI formed in the electrolyte containing VC is mainly composed of organic components and poorly suppresses the excessive decomposition of the electrolyte, which significantly increases the resistance derived from the SEI. In contrast, the SEI formed by FEC shows very low resistance and includes a large amount of LiF, which effectively suppresses the electrolyte decomposition. The Si electrode prepared with a PI binder can avoid fatal collapses by forming large cracks that resemble islands. In the SEM images, the amount of SEI formed with FEC is quite small and does not change the shape of the islands. Due to that effect, FEC is a better electrolyte additive than VC in terms of charge/discharge performance.

To further improve the cycle stability, we combined an electrolyte containing FEC with the PI-Si-SC electrode. Although the 3 wt% FEC is insufficient to obtain adequate cycle stability, the addition of 10 wt% FEC drastically improves the cycle stability, especially the rate capability of the PI-Si-SC electrode: more than 1,200 mAh g\(^{-1}\) at a high current density 16.0 A g\(^{-1}\). Moreover, the cycle stability does not degrade even at such a high current density. The \(\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2/\text{PI-Si-SC}\) full-cell containing 10 wt% FEC also shows excellent cycling stability during 100 cycles.
In this work, we obtained excellent cycle performance with a suitable binder like PI and with a suitable type and amount of electrolyte additive (10 wt% FEC), even though untreated, non-nano, μm-Si was used as an active material. We believe that the present work, which indicates the capability of large-sized Si particles, is a major step toward the practical application of Si negative electrodes.

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