

# Effect of Film-forming Additive on Electrochemical Performance of Silicon Negative-Electrode in Lithium-Ion Batteries

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Received: 17 July 2015 / Accepted: 2 September 2015 / Published: 30 September 2015

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Effect of film-forming additives, such as vinylene carbonate (VC) and fluoroethylene carbonate (FEC), on electrochemical performance of Si negative-electrode in lithium-ion batteries was investigated using a thick-film prepared by gas-deposition without any binder and conductive additive. In VC-containing electrolyte, Si electrode exhibited better cycle performance with a discharge capacity of 1000 mA h g<sup>-1</sup> beyond 750th cycles at a constant charge capacity of 1000 mA h g<sup>-1</sup>. In FEC-containing electrolyte, in addition, Si electrode showed good rate performance with a discharge capacity of 2000 mA h g<sup>-1</sup> even at a high current rate of 10 C. When the current rate was returned to an initial low current rate of 0.4 C, more than 90% of initial discharge capacity was maintained. Film-forming additives relatively suppressed change in the surface morphology of Si thick-film electrode after charge-discharge cycling; disintegration of Si electrode was prevented by the additives.

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**Keywords:** Lithium-Ion Battery, Silicon Negative-Electrode, Film-Forming Additive, Vinylene Carbonate, Fluoroethylene Carbonate

## 1. INTRODUCTION

Lithium-ion batteries (LIBs) have been utilized as power sources of electric vehicle and hybrid electric vehicle in recent years due to their high energy density compared to other rechargeable systems [1]. The energy density of commercially available LIBs using graphite negative-electrode is insufficient to meet the growing energy demand. On the other hand, Si is a strong candidate for active material of negative-electrode in next-generation LIBs because of its high theoretical value of 3580

mA h g<sup>-1</sup> (Li<sub>15</sub>Si<sub>4</sub>) compared to currently used graphite (372 mA h g<sup>-1</sup>) [2,3]. Si undergoes significant volume expansion and contraction during alloying (charging) and dealloying (discharging) reactions with Li, respectively. The volumetric change ratio per Si atom from Si to Li<sub>15</sub>Si<sub>4</sub> corresponds to 380%, which results in a generation of high stresses and large strains in the active materials [4]. The strains accumulated by repeating charge-discharge cycle cause a disintegration of Si electrode, leading to a rapid capacity fading and poor cycle performance. In addition, Si has disadvantages of a low electrical conductivity and a low diffusion coefficient of Li<sup>+</sup> in it ( $D_{\text{Li}^+}$  : 10<sup>-14</sup> to 10<sup>-12</sup> cm<sup>2</sup> s<sup>-1</sup>) [5,6]. For these reasons, a practical application of Si electrodes has been hindered.

Because an electrolyte solution is one of the key components determining battery performance, it is very important to select optimized electrolyte solution for each Si-based electrode [7-10]. It has been reported that film-forming additives, such as vinylene carbonate (VC) [11-13], fluoroethylene carbonate (FEC) [10,14-17], succinic anhydride [18], and tris(pentafluorophenyl) borane [19], improve the electrochemical performances of Si-based electrode. A surface film would be formed on the negative-electrode through reductive decomposition of the additives in an initial stage of charging. This surface film should reasonably avoid stress accumulation in localized regions, which suppresses the severe disintegration of the Si-based electrode that leads to rapid capacity fading. However, the effects of film-forming additives on Si itself of active material are unclear; Si-based negative-electrode containing binder and conductive additive have been used in most of the previous studies.

In the present study, we investigated the effects of film-forming additives of VC and FEC on the electrochemical performances and the disintegration of Si negative-electrode through the use of thick-film prepared by gas-deposition (GD) without any binder and conductive additive [10,20]. The mechanism of GD method has been described in our previous reports [21-24].

## 2. EXPERIMENTAL

In the preparation of GD-film electrode, Si powder (Wako Pure Chemical Industries, Ltd. 99.9%) that passed through a sieve (less than 26 μm) was used as active material. A current collector of Cu foil substrate with 20 μm in thickness was set at a distance of 10 mm from nozzle in a vacuum chamber with a guide tube [21-24]. The nozzle with 0.8 mm in diameter was connected at the end of guide tube. An argon carrier gas with a purity of 99.99% was set under a differential pressure of 7.0 x 10<sup>5</sup> Pa. After the chamber was evacuated to a base pressure of several ten Pa, an aerosol consisting of the carrier gas and the active material powder of Si was generated in the guide tube, and instantly gushed from the nozzle to the Cu substrate. The weight and the thickness of the deposited active material on the substrate were estimated to be 20-29 μg and ca. 2 μm, respectively [8].

We assembled 2032-type coin cells consisted of the obtained GD-film electrode as working electrode, Li foil (Rare Metallic, 99.9%, thickness: 1.0 mm) as counter electrode, electrolyte solution, and glass-based separator. The electrolyte solutions used were 1 M lithium bis(trifluoromethanesulfonyl)amide (LiTFSa) dissolved in propylene carbonate (PC; C<sub>4</sub>H<sub>6</sub>O<sub>3</sub>, Kishida Chemical Co., Ltd.), either alone or containing 5 vol.% of VC (C<sub>3</sub>H<sub>2</sub>O<sub>3</sub>, Kishida Chemical Co., Ltd.) or FEC (C<sub>3</sub>H<sub>3</sub>FO<sub>3</sub>, Kanto Denka Kogyo Co., Ltd.). The preparation of the electrolyte solution and the

cell assembly were carried out in Ar-filled glove box (Miwa MFG, DBO-2.5LNKP-TS) with a dew point below  $-100^{\circ}\text{C}$  and oxygen content below 1 ppm. Charge-discharge tests were carried out using an electrochemical measurement system (HJ-1001 SM8A, Hokuto Denko Co., Ltd. or BS2506, KEISOKUKI) in the potential range between 0.005 and 2.000 V vs.  $\text{Li}^+/\text{Li}$  at 303 K under a constant current density of  $3.0 \text{ A g}^{-1}$  (0.83 C). The rate capability was evaluated at various current rates from 0.4 to 10 C (1.4 to  $36 \text{ A g}^{-1}$ ). The surface morphology of the Si negative-electrode before and after charge-discharge cycling was observed using field-emission scanning electron microscopy (FE-SEM, JSM-6701F; JEOL Co., Ltd.).

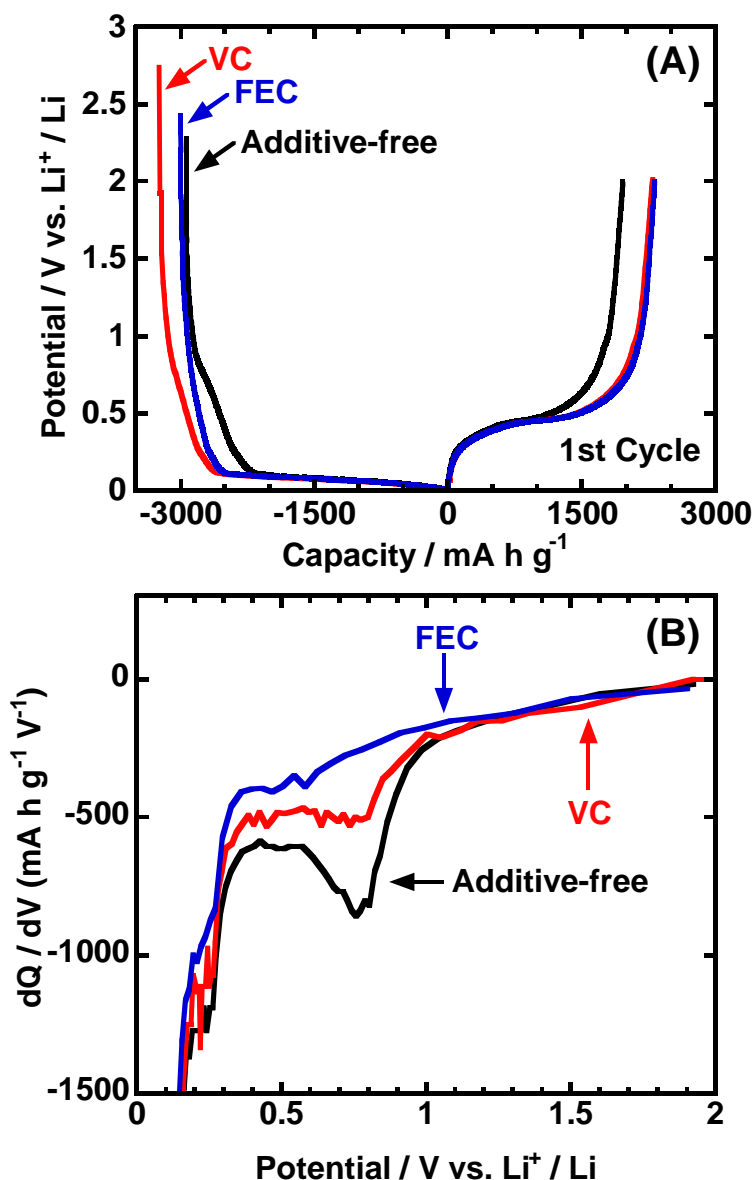
### 3. RESULTS AND DISCUSSION

Figures 1A and 1B show the first charge-discharge (Li insertion-extraction) curves of Si thick-film electrodes in LiTFSA-based electrolyte solutions, and the expansion of its differential capacity curves in negative direction, respectively. As shown in Figure 1A, potential plateaus were observed at around 0.1 and 0.4 V vs.  $\text{Li}^+/\text{Li}$  on charge and discharge curves in all electrolyte solutions, respectively. These potential plateaus are attributed to the alloying and dealloying reactions of Si with Li [25,26]. In Figure 1B, a peak was observed at around 0.8 V in additive-free electrolyte, which assigned to the reductive decomposition of the electrolyte solution containing LiTFSA and PC. This peak, on the other hand, became smaller in VC-containing electrolyte, and disappeared in FEC-containing one. It has been reported that VC and FEC are reductively decomposed at higher potentials of 1.0-1.1 V to form surface films on Si electrode [11].

Although the fractional peaks which assigned to reductive decomposition of VC and FEC did not appear in Figure 1B, surface films ought to form on Si electrode at the potentials between 1.0 and 1.1 V. On the basis of these results, it is considered that the VC- and FEC-derived surface films are electrical insulating, leading to the suppression of the reductive decomposition of the electrolyte. In addition, the suppressive effect of FEC is stronger than that of VC.

Figure 2 shows dependence of discharge capacities on cycle numbers for Si thick-film electrodes in 1 M LiTFSA/PC with 5 vol.% of VC, and FEC. For comparison, a cycle performance with additive-free electrolyte solution is also plotted in this Figure. The Si electrode in additive-free electrolyte showed rapid decay of discharge capacity until 100th cycle, resulting in a very poor cycle performance. As noted above, Si volume significantly changes during alloying/dealloying reactions with Li, and the expansion ratio of the specific volume from Si to  $\text{Si}_{15}\text{Li}_4$  reaches approximately 380% [4]. So, this capacity fading is arising from change in the Si volume, which cause exfoliation of active material layer from the current collector and/or pulverization of Si particle. In VC-containing electrolyte, on the other hand, the Si electrode showed better cycle performance; over  $500 \text{ mA h g}^{-1}$  of the discharge capacity was maintained even after 1000th cycle. As for FEC-containing electrolyte, the discharge capacity was about  $350 \text{ mA h g}^{-1}$  at 1000th cycle. Therefore, it was revealed that the film-forming additives of VC and FEC significantly improve the cycle performance of Si electrode.

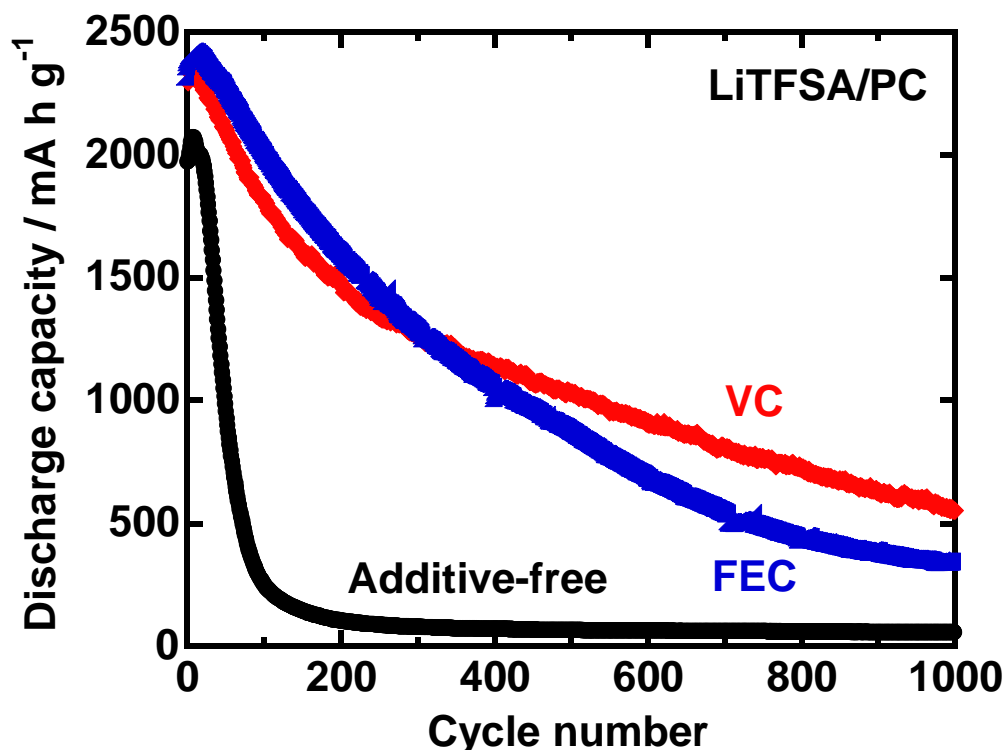
To clarify changes in the surface morphology of Si thick-film electrode during charge-discharge cycles, FE-SEM observation was performed. Figure 3 shows FE-SEM images of Si electrode surface before and after 100th cycles in the electrolytes with and without additives.



**Figure 1.** (A) First charge-discharge curves of Si thick-film electrodes in 1 M LiTFSA/PC with and without 5 vol.% additives, and (B) expansion of its differential capacity curves in the negative direction.

The as prepared Si electrode exhibited a comparatively smooth surface, as shown in Figure 3A. In Figure 3B, we can clearly confirm the disintegration of Si electrode in the electrolyte with no additives related to rapid capacity fading; dead Si seems to be removed. In addition, it is obvious that the regions where the disintegration occurred were localized. After cycling in VC- and FEC-containing electrolytes (Figures 3C and 3D), on the other hand, the disintegration of the Si electrode was relatively suppressed, even though an exfoliation of Si and a formation of cracks were observed. The exfoliation was uniformly occurred over the entire electrode compared to that in the electrolyte without

additives. Based on these results, VC- and FEC-derived surface films should have mechanical properties to relax high stresses and large strains in the active materials, leading to prevent the disintegration of Si negative-electrode. In addition, we have reported the similar morphological changes in ionic liquid electrolytes [8,9]; the film-forming additives in organic solvent prevent Si electrode from the disintegration, as is the case with ionic liquid electrolytes.

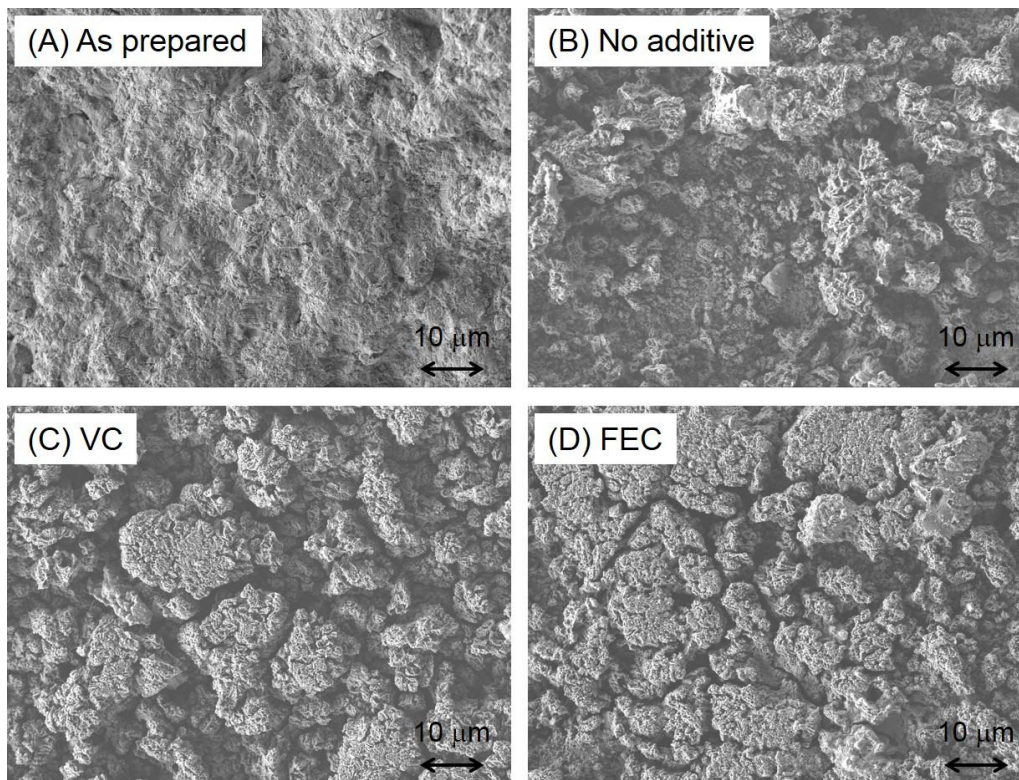


**Figure 2.** Cycling performance of Si thick-film electrodes in 1 M LiTfSA/PC with and without 5 vol.% additives.

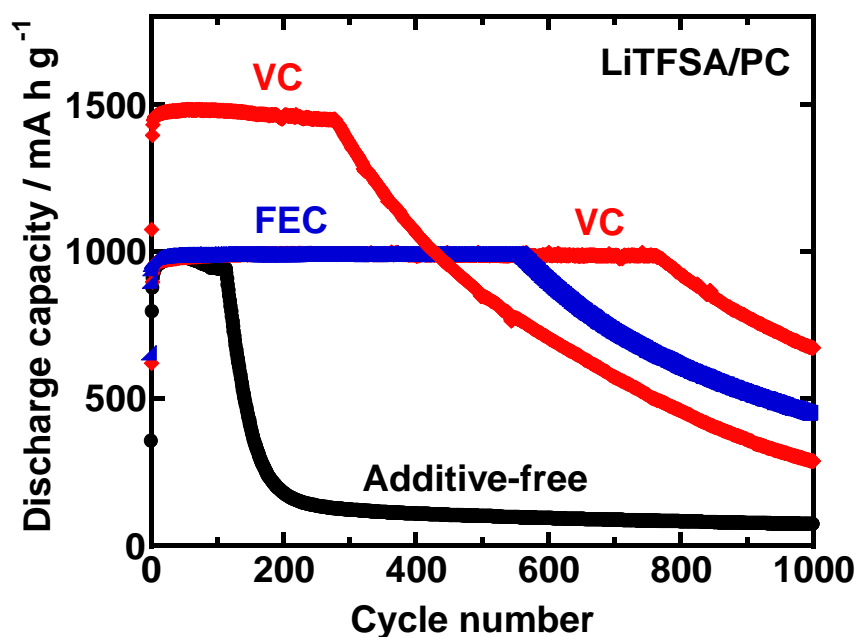
While the cycle performance of Si electrode was improved using film-forming additives, capacity fading could not be prevented completely. In order to suppress a little exfoliation of active material and formation of crack during charge-discharge reactions, the amount of Li insertion into Si was controlled. Figure 4 shows dependence of discharge capacities on cycle numbers for Si thick-film electrodes in 1 M LiTfSA/PC with and without 5 vol.% film-forming additives at constant charge capacities of 1000 or 1500 mA h g<sup>-1</sup>. Cycle performance of Si negative-electrode was improved even in the additive-free electrolyte solution; a discharge capacity of 1000 mA h g<sup>-1</sup> was maintained over 110th cycle, which indicates that the limitation of charge capacity is very effective for an improvement of the cycle performance. Additional increase in durability, however, is demand for the application of LIBs.

A discharge capacity of 1000 mA h g<sup>-1</sup> was maintained until 760th and 560th cycles in the electrolyte solutions containing VC and FEC, respectively. In addition, the discharge capacities were 670 and 450 mA h g<sup>-1</sup> even at 1000th cycle in VC- and FEC-containing electrolytes, respectively. These results indicate that the Si electrode in additive-containing electrolytes show better cycling

performance, and that VC improves the durability of Si negative-electrode compared to FEC. It is considered that VC-derived surface film has mechanical properties suitable for relaxation of the stress from Si compared to FEC-derived one, and that disintegration of Si electrode is suppressed in the electrolyte containing VC.

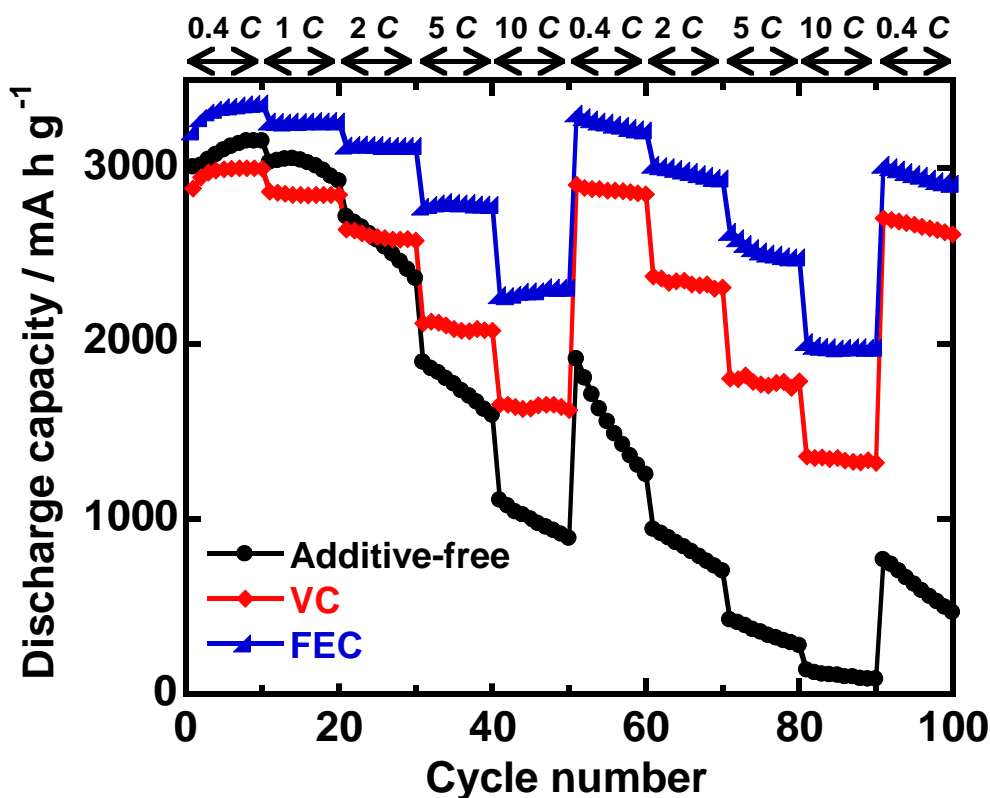


**Figure 3.** FE-SEM images of Si thick-film electrodes (A) as prepared and after 100th charge-discharge cycles in 1 M LiTFSA/PC with (B) no additive, (C) 5 vol.% VC, and (D) 5 vol.% FEC.



**Figure 4.** Dependence of discharge capacities on cycle numbers for Si electrodes 1 M LiTFSA/PC with and without 5 vol.% additives at constant charge capacities of 1000 or 1500 mA h g<sup>-1</sup>.

The difference in the mechanical properties would be attributed to the chemical structure of these additives; VC has a carbon-carbon double bond, and therefore would be reductively electropolymerized, in addition to ring-opening polymerization, whereas FEC has no double bond [27,28]. In order to understand the effect of a fixed Li-insertion level on cycle performance of Si negative-electrode, a cycle performance with VC-containing electrolyte at constant charge capacities of 1500 mA h g<sup>-1</sup> is also plotted in Figure 4. The discharge capacity of 1500 mA h g<sup>-1</sup> was maintained until 280th cycle, and it was 290 mA h g<sup>-1</sup> at 1000th cycle, as shown in Figure 4. On the basis of these results, it was revealed that an appropriate value of charge capacity is very important in order to obtain good cycle performance.



**Figure 5.** Rate performance of Si thick-film electrodes in 1 M LiTFS/PC with and without 5 vol.% additives at various current rates from 0.4 to 10 C.

Figure 5 shows rate performance of Si thick-film electrodes at various current rates from 0.4 to 10 C (1.4 to 36 A g<sup>-1</sup>). The Si electrode in the additive-free electrolyte showed a rapid decay of the discharge capacity at high current rate of 10 C; the discharge capacity was about 890 and 80 mA h g<sup>-1</sup> at 50 and 90th cycles, respectively. When the current rate was returned to the initial value of 0.4 C, the discharge capacity was about 470 mA h g<sup>-1</sup> at 100th cycle which is less than one-sixth of initial value of 3000 mA h g<sup>-1</sup>. This poor rate capability is attributed to disintegration of Si electrode due to the large volume change during alloying/dealloying reactions with Li. On the other hand, the Si electrode in VC- and FEC-containing electrolytes achieved a comparatively high discharge capacity of ca. 1300 and 2000 mA h g<sup>-1</sup> even at a high current rate of 10 C (90th cycle), respectively. When the current rate

was returned to 0.4 C, more than 90% of initial discharge capacity was maintained. Consequently, film-forming additives should enable rapid charge-discharge of Si electrode.

Nakai *et al.* have previously reported that FEC-derived surface film protected against not only the decomposition of the electrolyte solution, but also oxidation of the Si negative-electrode [29]. Based on their result, surface of Si electrode was oxidized in the electrolyte solution without FEC after charge-discharge cycles, and then Si oxide was formed. On the other hand, oxidation of Si did not proceed in FEC-containing electrolyte. Consequently, it is considered that better rate performance with FEC is attributed to improvement of Si utilization rate due to non-oxidation of Si.

#### 4. CONCLUSION

We investigated the effect of film-forming additives of VC and FEC on the electrochemical performance of Si negative-electrode prepared by GD method. Si electrode in VC-containing electrolyte exhibited good cycle performance with the discharge capacity of 1000 mA h g<sup>-1</sup> beyond 750th cycles at a constant charge capacity of 1000 mA h g<sup>-1</sup>. In FEC-containing electrolyte, in addition, the discharge capacity of 2000 mA h g<sup>-1</sup> was obtained even at a high current rate of 10 C. VC- and FEC-derived surface films are electrical insulating, which leads to the suppression of the additional reductive decomposition of the electrolyte. Changes in the surface morphology of Si thick-film electrode in VC- or FEC-containing electrolytes were suppressed compared to those without film-forming additives. Based on our results, it was revealed that VC and FEC effectively improve the electrochemical performances of Si negative-electrode in LIBs.

#### ACKNOWLEDGEMENTS

This work was supported by Japan Society for Promotion of Science (JSPS) KAKENHI, Grant-in-Aid for Scientific Research B (Grant Number 24350094).

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