Effect of Temperature on Negative Electrode Performance of Si Leaf Powder®

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Li-Si alloy negative electrodes have attracted much attention for high-energy density lithium-ion batteries because of their high theoretical capacity (ca. 4200 mAh g^{-1}) [1]. However, poor cycleability is a serious problem for practical use. The poor capacity retention is ascribed to a large volume change during the charge/discharge cycling, which leads to particle fracture and electrochemical pulverization [2]. We have reported that the use of Si thin flakes, (i.e. Si Leaf Powder® (Si-LP), Oike & Co., Ltd.), is very effective to improve the cycleability by relaxization of the stress due to the volume change [3-7]. In this study, we investigated the properies of Si Leaf Powder® as a negative electrode for Li-ion batteries at elevated temperatures, and discussed the effect of the addition of vinylene carbonate (VC) on the cycleability of Si-LP at elevated temperatures.

The test electrodes were fabricated by coating slurry on Cu foil as a current collector. The slurry was prepared by mixing 83.3 wt.% Si-LP powder (thickness: 100 nm), 5.6 wt.% Ketjen Black (KB) as a conductive agent and 11.1 wt.% carboxymethyl cellulose sodium (NaCMC) salt as a binder. Charge-discharge characteristics were evaluated by constant current-constant voltage (CC-CV) charge/ discharge tests with a coin-type cell. The counter electrode was Li foil. The electrolyte solution was 1.0 M $LiPF_6$ dissolved in EC+DEC (1:1 by volume). Temperature of measurement is 30, 45, and 60°C.

The charge and discharge curves of Si-LP at 30°C without VC and at 60°C with and without VC (10 wt.%) are shown in Fig. 1. At 30°C, the charge/discharge characteristics are typical of amorphous Si, where the discharge curve starts at ca. 0.25 V and the potential increased monotonously without a clear plateau. At 60°C, the curves are similar to those obtained at 30°C; however, a plateau appeared at ca. 0.5 V after the 30th cycle, which showed the formation of a crystalline $Li_{15}Si_4$ phase at low potentials (>0.03 V *vs.* Li/Li^+) [8]. This indicates that the formation of the crystalline phase is accelerated at elevated temperatures. The addition of 10 wt.% VC suppressed the formation of the crystalline phase even at 60°C (Fig 1(c)).

Table 1 summarizes the initial discharge capacities and coulombic efficiencies. The addition of VC did not affect the coulombic efficiency at 30°C; however, it significantly decreases the coulombic efficiency at 60°C. This is due to a high irreversible capacity in the first cycle as shown in Fig. 1(c). This fact clearly shows that the decomposition of VC was promoted at 60C in the first cycle and thick SEI film was formed. Fig. 2 shows the cycleability of Si-LPs with and without VC. The discharge capacity at 60°C without VC dropped significantly after the 20th cycle, where the plateau at 0.5 V appeared on the discharge curve in Fig. 1(b). On the other hand, the addition of VC gave a superior cycleability to Si-LP at 60°C. The capacity retention was 81% after 50 cycles, which was higher than that at 30°C without VC. It is considered that the SEI formed by decomposition of VC has a role in suppressing the crystallization at 60°C, though the detailed mechanism is not clear at present.

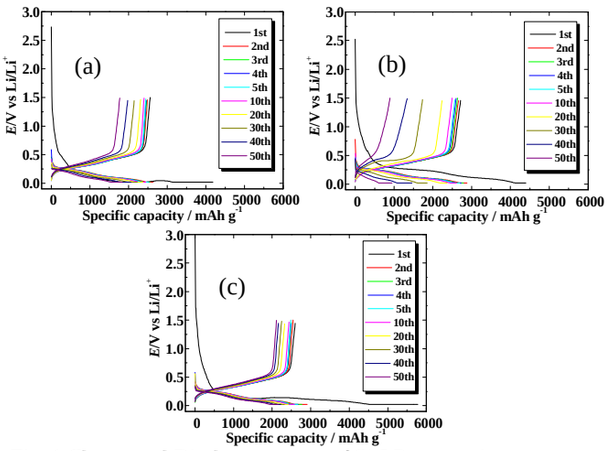

Fig. 1 Charge and Discharge curves of Si-LP composite electrodes in 1 M $LiPF_6$/EC+DEC(1:1) at (a)30°C, (b)60°C, and (c)60°C with VC 10wt.%. Potential range: 0.02-1.5 V *vs.* Li/Li^+.

Table 1. Initial discharge capacity and coulombic efficiency of Si-LP composite electrodes at 30°C and 60°C with and without VC 10 wt.%. Potential range: 0.02-1.5 V *vs.* Li/Li^+.

	Without VC		With VC 10 wt.%	
Temperature / °C	Initial Discharge capacity /mAh g^{-1}	Initial coulombic efficiency / %	Initial Discharge capacity /mAh g^{-1}	Initial coulombic efficiency / %
30	2559	61	2778	64
60	2773	62	2609	45

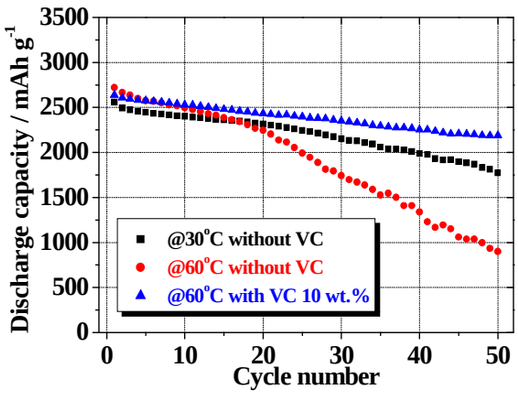

Fig. 2 Cycleability of Si-LPs composite electrode in 1 M $LiPF_6$/EC+DEC(1:1) at 30°C, 60°C, and 60°C with VC 10wt.%. Potential range: 0.02-1.5 V *vs.* Li/Li^+.

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