Effect of electrolyte additive on Si negative electrode prepared with polyimide binder

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Silicon (Si) has attracted attention as negative electrode material for lithium ion batteries because of its excellent lithium-ion storage capacity. However, the electrode structure significantly collapses due to volume expansion (max. 400%) and contraction of Si particles during charge and discharge. As a result, the capacity decreases rapidly with increasing cycle number.

In order to solve this problem, many researchers have modified the structure and composition of Si-based active materials and it has been reported that the use of nano-sized Si is effective to improve cycle stability. Previously, we successfully improved cycle stability of a Si electrode composed of conventional 4-5-μm Si particles (μm-Si) by applying polyimide (PI) as binder.[1)]

In this study, we have investigated the effect of electrolyte additive on our Si electrode with polyimide binder and tried to further improve the cycle stability of the Si negative electrode.

The Si electrode was prepared by the following steps: μm-Si, acetylene black (AB), and polyamic acid (PAA) as precursor of PI were mixed in a respective weight ratio of 75:10:15 with adequate amount of *N*-methyl-2-pyrrolidone (NMP), and the obtained slurry was cast onto a cupper-foil and dried at 80°C in a vacuum oven to remove NMP. Then the initial PAA was varied to PI via a dehydration condensation reaction at 300°C in a vacuum oven. In addition, the Si/C electrode composed of μm-Si, soft carbon (SC), AB, and PAA in a respective weight ratio of 50:25:10:15 was also prepared by the same procedure.

The test cells were assembled with the prepared electrodes, a lithium foil, and 1 M $LiPF_6$ binaly electrolyte composed of ethylene carbonate (EC) and dimethyl carbonate (DMC) by a volume ratio of 1:1. Vinylene carbonate (VC) and fluoro-ethylene carbonate (FEC) were mixed with the electrolyte as additives.

To evaluate the cycle stability, a constant-current charge-discharge test was carried out, and to investigate the properties of a solid-electrolyte interface (SEI) layer formed in various electrolytes, AC impedance analysis was performed.

Although the cycle stability of Si electrode improves in electrolytes containing both VC and FEC, we found that the properties of the SEI layer formed in various electrolytes are quite different. Fig. 1 shows the results of AC impedance measurement for the Si electrode in various electrolytes. At a discharge state in the 1st cycle, the magnitude of semicircles observed in higher frequency region, which seems to include the resistance of SEI layer, is almost same in any electrolytes. However, at a discharge state in the 10th cycle, the magnitude of the semicircles in higher frequency region does not change in the electrolyte without additives, increases with 3wt.% VC, and decreases with 3wt.% FEC. These results imply that the amount and thickness of SEI layer formed in the electrolyte containing VC increase with every cycle. Therefore, FEC should be better than VC as electrolyte additive to improve the cycle stability; a SEI layer formed in the electrolyte containing FEC may hardly inhibit the transportation of lithium ions even after repeated cycles.

Fig. 2 shows the cycle performance of Si/C electrodes in the electrolyte containing FEC. The discharge capacity begins to degrade significantly around at the 20th cycle in the electrolyte containing 3 wt.% FEC. This suggests that 3 wt.% FEC is not enough to maintain the stability of Si/C electrode during long-term cycling. When the collapse of electrode structure and the pulverization of silicon particles proceed with cycling and hence an increase in their surface area, 3 wt.% FEC may be insufficient to cover and protect newborn, increasing surface. Judging from the low impedance of SEI layer formed in the electrolyte containing FEC, however, we can still increase the FEC additive amount with keeping a low impedance: in fact, we succeeded in drastically improving the cycle stability of Si/C electrode composed of conventional 4-5 μm silicon particles with polyimide binder with increasing FEC amount: 10 wt.% (Fig. 2).

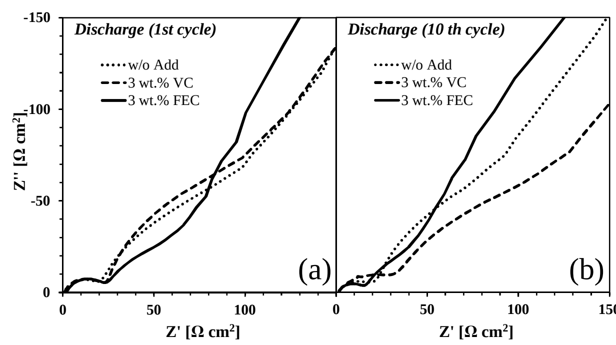

Fig. 1 AC impedance diagrams for Si negative electrode at discharge state in (a) 1st and (b) 10th cycles in the electrolytes without and with 3 wt.% of VC or FEC.

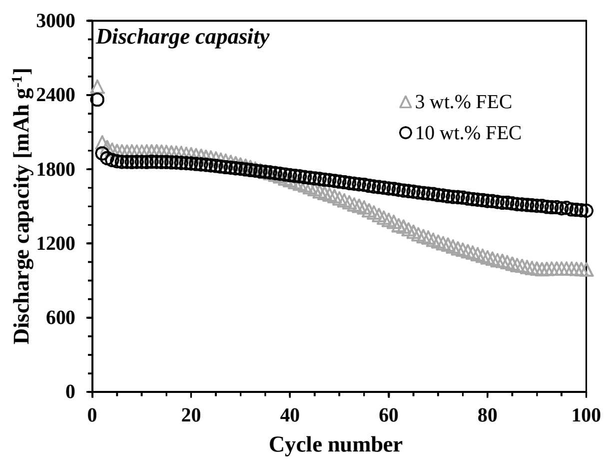

Fig. 2 Cycle performances of Si/C negative electrode in the electrolytes containing 3 or 10 wt.% of FEC.

Reference

1) S. Uchida, M. Mihashi M. Yamagata, and M. Ishikawa, *PRiME 2012*, Abstract, No. 903 (2012).

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