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Unraveling the effect of succinonitrile additive on cycling performance in cylindrical lithium-ion battery

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ABSTRACT

The effect of succinonitrile (SN) additive on cycle life at room temperature is performed with 18650 type cylindrical cell including $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$ and graphite. It is clearly investigated that the capacity degrades during cycling at room temperature with adding SN additive. In particular, the capacity of the cell with 1.5 wt % SN dramatically decreases from 60 cycles and by 45% of initial capacity after 100 cycles. Through analyzing cycled cells with different amount of SN additive using XRD and ICP-OES measurement, the amount of irreversible Li increases depending on the amount of SN additive and the number of cycling. The results of SEM and XPS measurement provide that the increased irreversible Li appears as a film-type reactant on the surface of anode electrode and it consists of components related with C-C, CO3, and Li. These analysis results verify that the SN additive affects generation of Li-carbonate species deposition and irreversible Li leads to a degradation of capacity.

1. Introduction

Recent studies of lithium-ion batteries are being actively carried out because of applications of mobile devices and electric vehicles. Many researchers and developers in the industries are exerting their efforts to improve the performance of lithium-ion batteries such as higher capacity, longer life, and higher level of safety. It is one of the most effective methods to develop functional electrolyte additive technology in order to address issues of poor lithium-ion batteries cell [1]. The electrolyte additives play various roles in lithium-ion batteries such as solid electrolyte interface (SEI) forming improver [2–7], cathode protection agent [8], $LiPF_6$ salt stabilizer [9], safety protection agent [10–12], lithium deposition improver [13], ionic salvation enhancer [14], Al corrosion inhibitor [15], and wetting agent [16].

The representative electrolyte additive with various functions is succinonitrile (SN, CN–[CH2]2–CN). The effect of SN additive in lithium-ion batteries was diversely studied by lots of researchers and developers to improve cell performances [17–20]. The outstanding effect of SN additive is that it improves thermal stability in lithium-ion batteries [17]. It was confirmed that SN additive plays a role in reducing gas emission at high temperature and increasing onset temperature of exothermic reactions. It also lowers exothermal heat into an electrolyte with graphite and Li_x-CoO_2, without damaging of cell performance such as cyclability and capacity in high temperature.

Various effects of SN additive were shown when it mixes with other electrolyte additives [18,19]. SN with lithium bioxalato borate (LiBOB) improves the electrochemical behavior with lower voltage cathode materials such as $LiFePO_4$, because it shows good thermal stability, high ionic conductivity, a wide electrochemical stability window, and good compatibility with lithium metal [18]. The incorporation of both SN and vinylene carbonate (VC) result in a significant decrease in impedance of anode electrode and dominant contribution to the impedance growth of pouch cells comes from the cathode electrode during cycling [19].

In another view, SN additive was studied about copper corrosion inhibition to protect lithium-ion batteries from over-discharge [20]. Their result is that the anodic Cu corrosion is suppressed until the voltage reaches to 4.5 V in the presence of SN additive. Because the corrosion inhibition is ascribed to the formation of an SN induced passive layer on a copper surface during the first cycling. And

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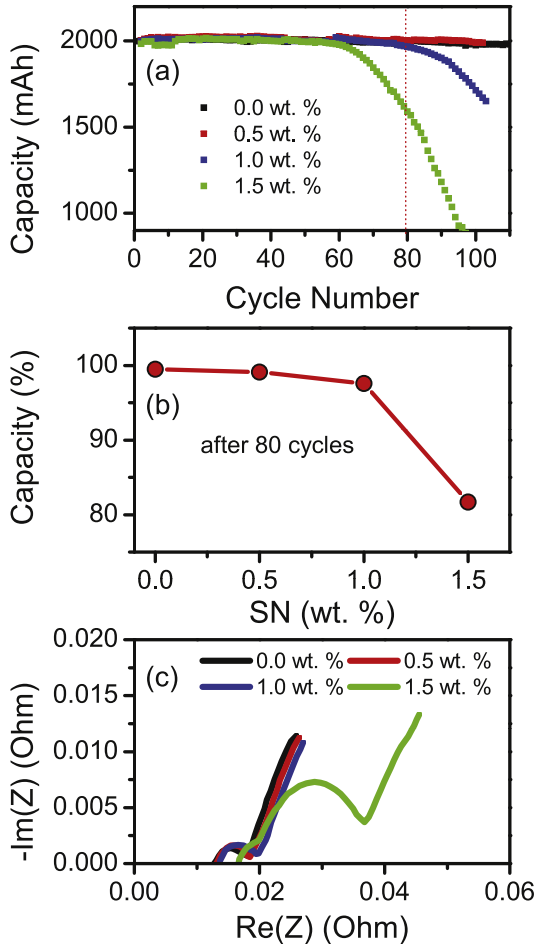

Fig. 1. The cycle dependence of different amounts of SN is shown in Fig. 1(a). Capacity of the cell with 1.5 wt % SN dramatically reduces. SN dependence of capacity after 80 cycles is shown in Fig. 1(b). Fig. 1(c) is the results of EIS measurement for cells after 80 cycles.

Raman spectroscopy and electrochemical quartz crystal microbalance measurements verified that the passive layer is composed mainly of $Cu(SN)_2PF_6$ units.

Fewer studies have been devoted to the effect of SN additive during cycling at room temperature, even though cycle life characteristic is an important key to improve the performance of lithium-ion battery cells. In this paper, we provide capacity changes of 18650 type cylindrical cell by the amount of SN additive during cycling at room temperature. Before disassembling cells, electrochemical impedance spectroscopy (EIS) is performed to evaluate at various levels of lithium ion intercalation. Moreover, we confirm various properties of $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$ and graphite in electrodes according to different capacities with analysis of disassembled cells using X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscope (SEM), and Inductively Coupled Plasma - Optical Emission Spectrometers (ICP-OES) measurement. $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$ is a more attractive cathode material in lithium-ion battery because of high capacity and inexpensive replacement of $LiCoO_2$ [21]. We provide clear understanding of the effect of SN additive in cathode and anode electrodes during cycling. In conclusion, we confirm the mechanism of capacity degradation by SN additive in 18650 type cylindrical cell.

2. Experimental

In this study, we used 18650 type cylindrical cells with capacity of 2.0 Ah. The cell is constructed as follows. The cathode electrode were made by coating a paste of $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$, carbon black, and polyvinylidene fluoride (PVDF) binder (96:2:2 (wt %)) on an aluminum foil. The anode electrode was deposited graphite and binder (98:2 (wt %)) on copper foil. The cathode and anode electrodes were separated by a porous polypropylene film. The electrolyte was used 1.15 M $LiPF_6$ solution in ethylene-carbonates (EC), ethylmethyl-carbonates (EMC), and dimethyl-carbonate (DMC) (2:2:6 (wt %)). And we added in cells four different amounts of SN additive that are 0, 0.5, 1.0, and 1.5 wt %. The cells were cycled at room temperature by constant current (1.0C) followed by constant voltage (4.2 V) protocol with 1/40C cutoff current. After taking a rest, cells were discharged to 2.5 V of the cutoff voltage with 1.0C with a current density of 2.18 mAh cm^{-2}. The electrochemical impedance was measured with a VMP3 (BioLogic) by applying frequency ranges from 0.1 MHz to 0.01 Hz. To confirm the change of cathode and anode electrodes in cells, we dismantled four cells after 80 cycles with different amounts of SN additive and three cells of 1.5 wt % SN with 100, 90, and 80% capacity in a glove box.

For investigating the difference of the atomic compositions of anode electrodes, we measured ICP-OES of ULTIMA2 (HORIBA JOBIN YVON). The measured cells were disassembled in an argon-filled glove box and anode electrodes washed with DMC and then

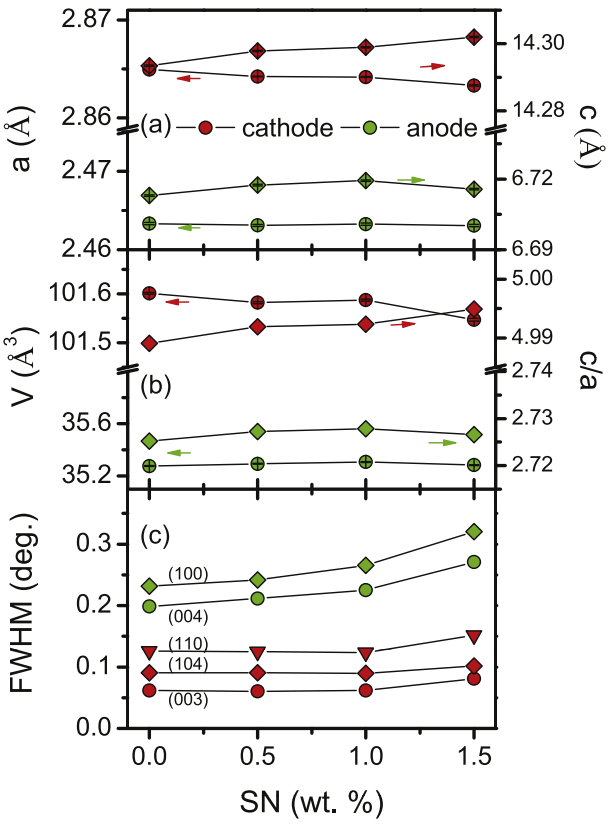

Fig. 2. The crystallographic properties of cathode and anode material due to SN additive are shown as red and green symbols. Fig. 2(a) is the dependence of SN additive for lattice constants for cathode and anode material. Unit-cell volume and *c/a* are show in Fig. 2(b). The widths of XRD peaks increase with increasing SN additive as shown in Fig. 2(c). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)