

Short communication

Improvement of 12 V overcharge behavior of LiCoO₂ cathode material by LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ addition in a Li-ion cell

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Abstract

The 12 V overcharge instability of the LiCoO₂ cathode material was improved by the physical blending it with LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂. Even though a Li-ion cell containing a LiCoO₂ cathode did not exhibit thermal runaway at 12 V at the 1 C overcharging rate, it showed thermal runaway at the 2 C overcharging rate, and the cell surface temperature reached more than 400 °C. However, the LiCoO₂ cell containing 40, 50, and 60 wt.% LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ did not exhibit thermal runaway at the 2 C overcharging rate. In conclusion, 60 wt.% LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ in the LiCoO₂ cathode showed the lowest cell surface temperature of <90 °C even at a 3 C overcharging rate.

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1. Introduction

Li-ion cell safety is one of the most important issues among the various cell performance test items, and a cell that does not meet the safety guidelines cannot be used in mobile applications [1]. However, only protective devices tend to secure the cell's safety. In this regard, all Li-ion cell producers have installed protective devices either in the battery pack itself or they produce batteries that block the high temperature, high current, overcharging and have safety pressure-release rupture vent. On the other hand, many accidents involving smoke, fire or explosions due to defects or malfunction of the devices have been reported [2]. Among the safety tests for Li-ion cells, an overcharge test to 12 V is the most important one according to the guidelines [1]. In this test, a cell is forced to charge to the limit of the power supply, 12 V, and for example, LiCoO₂ using an electrolyte without any additives that can retard the flammable nature of the electrolyte that undergoes an incendiary explosion at 12 V [2,3]. Among the cell components, the violent exothermic reactivity of a delithiated cathode with the flammable electrolytes leads to substantial heat

generation, which has been reported to be a trigger point for thermal runaway [4–8]. This is accompanied by a build-up of pressure, leading to the cell rupturing, or catching fire as a result of an internal short circuit. Therefore, the guidelines recommend that a cell that emits smoke, catches fire or explodes during the abuse tests are unacceptable for practical applications.

Several studies have reported that additives in the electrolytes can prevent thermal runaway [9–12]. For instance, additives, such as phosphorus compounds or aromatic compounds with two methyl groups, can reduce the flammable nature of the electrolytes. However, these additives damaged the electrochemical properties of the cathode and anode materials. Recently, Cho et al. reported that LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode materials exhibited enhanced thermal stability above 4.5 V, compared to LiCoO₂, and decreased heat generation from the reaction between electrolyte and the delithiated cathode [13,14].

Therefore, this study investigated the dependence of the overcharge behavior in a LiCoO₂ cathode material as a function of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ addition on overcharge behavior at 2 and 3 C rates. The cell surface temperature was monitored using a type K thermocouple attached to the center of the largest face of the prismatic cell and was measured as a function of time.

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2. Experimental

The standard capacity of the Li-ion cell was set to 900 mAh (cell size: $3.4 \times 65 \times 50 \text{ mm}^3$ (thickness \times length \times width)). LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, and physical mixture of these materials were used as the cathode, and the anode material was synthetic graphite. BET surface areas of the LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ were 0.5 and 1 g m^{-2} , respectively. A mixture of LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ was prepared by the physical blending of these materials with of 40:50, 50:50, and 40:60 wt.% ratios (LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$). $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ starting powders consisting of spherical particles ($\sim 13 \mu\text{m}$ in diameter) were prepared by co-precipitation from a solution containing stoichiometric amounts of nickel/cobalt/manganese nitrates and adding a NaOH and NH_4OH solution in a specially designed reactor to produce spherical particles [14]. LiCoO_2 was directly prepared from Co_3O_4 and Li_2CO_3 with a mole ratio of 1 and 1.01 at 900°C for 20 h.

The discharge capacities of the cathodes were 155 and 185 mA h g^{-1} at a 4.3 V charge cut-off in a coin-type half-cell at a 0.1 C rate (for C rates of LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ was 14 and 18 mA g^{-1} , respectively). The anode to cathode capacity ratio was set at 1.2:1. The electrolyte used was 1.03 M LiPF_6 with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (EC/DEC/EMC) (3/3/4 vol.%). The cathodes for the battery test cells were made from the cathode material, Super P carbon black, and polyvinylidene fluoride (PVdF) binder (Kureha Company) in a weight ratio of 96:2:2. On the other hand, the anodes for the battery test cells were made from PHS synthetic graphite and (PVdF) binder (Kureha Company) in a weight ratio of 94:6. All the fresh cells were cycled at the rate of 0.2 C (a charge limit was 4.2 V) for two cycles before further tests. The rate-capability tests of the Li-ion cells were carried with a discharge rate of 0.2, 0.5, 1, and 2 C (while the charge rate was fixed at 0.5 C).

For the 2 and 3 C overcharge experiments to 12 V, fresh cells were initially cycled at a 0.2 C rate for 1 cycle, and charged to 4.2 V with a constant current corresponding to 1 C (=900 mA). The end charge capacities for the cells just prior to the overcharge abuse test was 900 mAh ($\pm 5 \text{ mA h}$), and each five cells were used for 2 and 3 C overcharge tests. This was followed by holding the cell at 4.2 V until the current decreased to 30 mA. The cells were subsequently charged to 12 V at a rate of 1 C (equivalent to $140 \text{ mA g}^{-1} = 0.9 \text{ A}$) using an identical charging method to that at 4.2 V.

3. Results and discussion

Fig. 1 shows a comparison of the rate capabilities of the Li-ion cells containing pure LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, and the composites ($\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$: LiCoO_2 = 40:50, 50:50, and 60:40 wt.%) at discharge rates of 0.2, 0.5, 1, and 2 C (the charge rate was set at 0.5 C). In contrast to

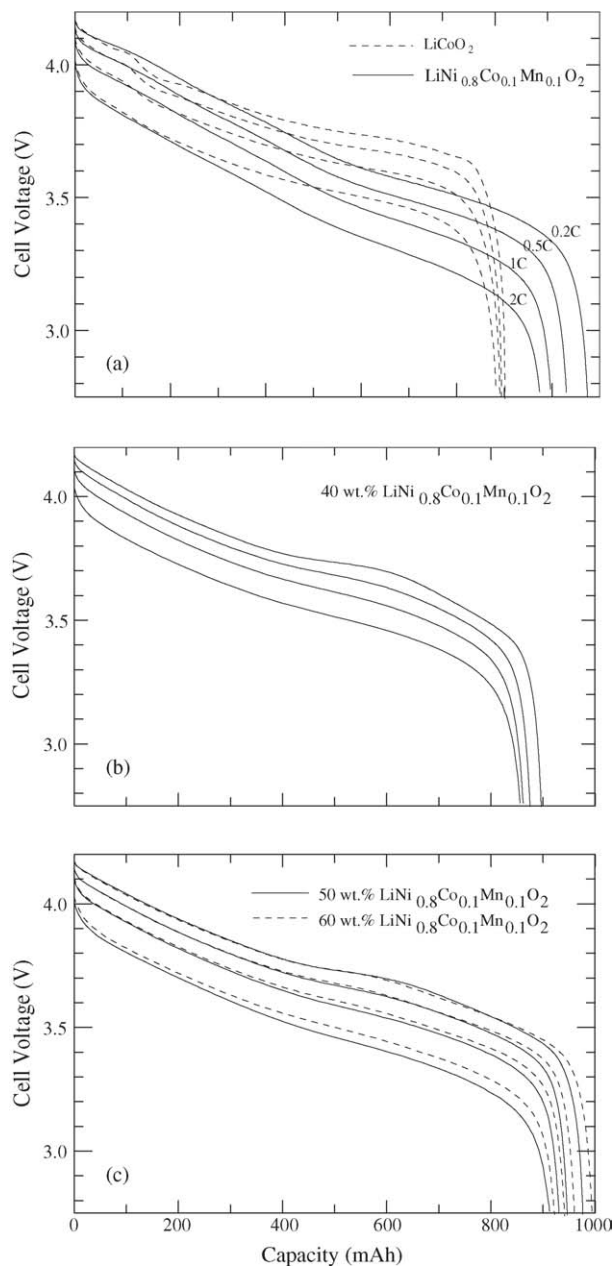


Fig. 1. Plot of the rate capabilities of Li-ion cells containing: (a) pure LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$; (b) 40 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$; and (c) 50 and 60 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$. The cell was charged at the rate of 0.5 C to 4.2 V (1 C = 900 mA).

pure LiCoO_2 , which showed excellent capacity retention with 98% retention even at the 2 C rate, compared with the capacity at the 0.2 C rate, pure $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ showed only 91% capacity retention when the C rate was increased from 0.2 to 2 C. This indicates that the electronic conductivity of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ is inferior to LiCoO_2 . In the case of LiCoO_2 with 40 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, the rate capabilities appeared similar to those of pure LiCoO_2 . However, the capacity retention of the cell containing 50 and 60 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ was approximately 2% lower than to the cathode with 40 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$.

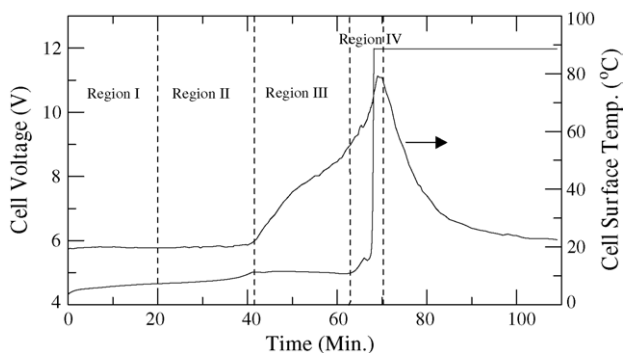


Fig. 2. Plot of the cell voltage and cell surface temperature as a function of time in the course of overcharging to 12 V.

Although the capacity at the 0.2 C rate was about 900 mA h for both pure LiCoO_2 and 40 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, it increased to ~ 1000 mA h in the case of both 50 and 60 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, indicating that the capacity contribution from the $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ began to dominate over LiCoO_2 .

Cells of the above materials with the same discharge capacities were performed at 12 V overcharge tests at 2 and 3 C rates. Figs. 2 and 3 compares the 12 V overcharge reaction divided into four regions, and a diagram of the factors affecting the increase in the cell temperature during a portion of the overcharge tests. Regions III and IV should be particularly noted, where the cell surface temperatures increased faster than in the other regions. The cell surface temperature in region III rather slowly increases mainly due to the decomposition of the electrolyte, anode and its SEI layer decompositions. However, the cell surface temperature rises faster in region IV as a result of the exothermic decomposition of the cathode within a short time, producing oxygen. This reaction plays a dominant role in determining the cell safety, and no explosion of the cell would be expected despite the short-circuiting as long as the delithiated cathode remains stable. In terms of the cell

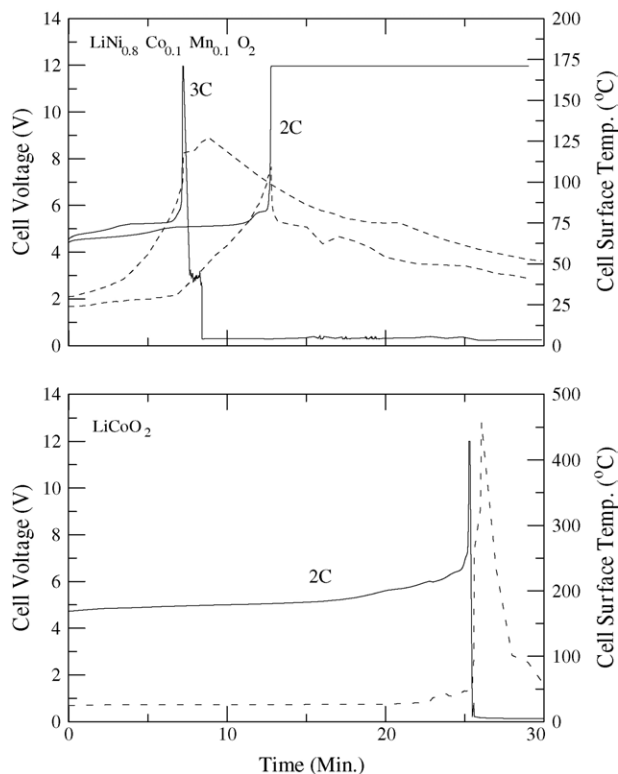


Fig. 4. Plot of the cell voltage and cell surface temperature as a function of time during overcharging. The cells were charged to 12 V at a 1 C rate, and held at that voltage until the applied current decreased to 30 mA.

geometry, when the heat dissipation rate is higher than the rate of heat accumulation, the cell will not explode [15].

Fig. 4 compares the 12 V overcharge behavior of pure LiCoO_2 with that of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$. A Li-ion cell containing pure LiCoO_2 exhibited thermal runaway with fire and explosion at the 2 C rate overcharge. That is, upon shooting to 12 V, the cell was short-circuited, which was followed by a sudden drop in the cell voltage to almost 0 V. This is a typical result when the cell shows thermal runaway

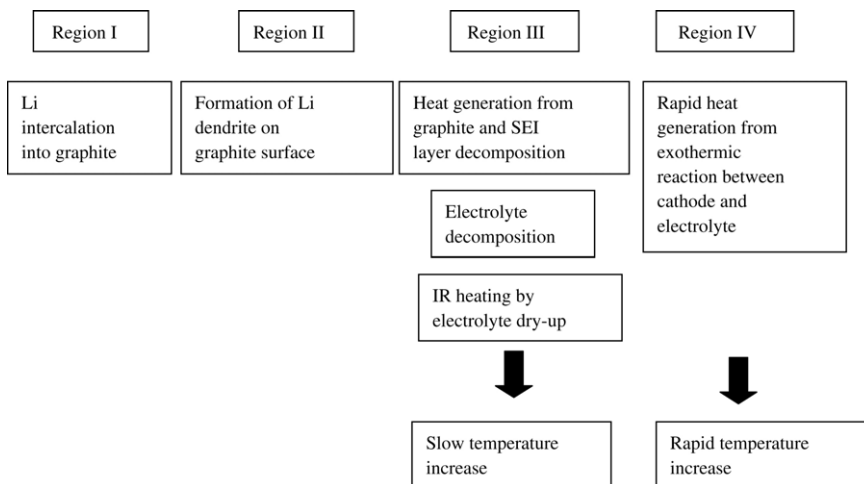


Fig. 3. Diagram of the reactions governing the cell temperature increase in the four regions shown in Fig. 2.

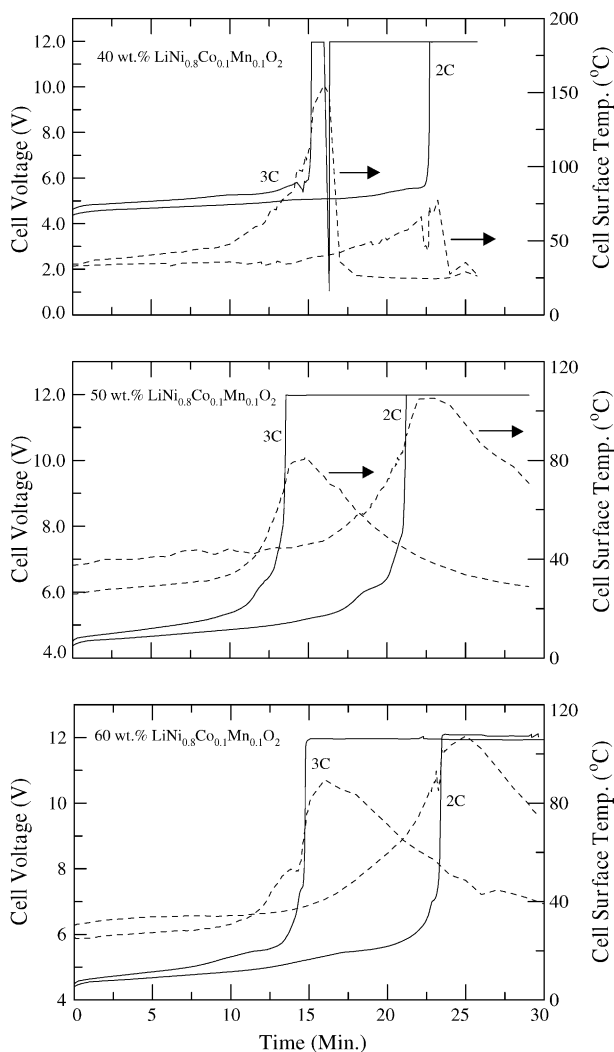


Fig. 5. Plots of the cell voltage curves and the cell surface temperature vs. time in the cells with 40, 50, and 60 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$. The cells were charged 12 V at a 2 and 3 C rates, and held at that voltage until the applied current decreased to 30 mA.

and exhibits cell a surface temperature $>450^\circ\text{C}$. At this temperature, the internal cell temperature was over 550°C , and all the electrodes were totally burnt. In contrast, the cells containing $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ did not exhibit the thermal runaway at 12 V with no short-circuit, and the maximum cell surface was maintained at below 100°C during a 2 C rate overcharging. A further increase to 3 C led to a short-circuit of the cell at 12 V, but the cell did not exhibit thermal runaway, as evidenced by the cell surface temperature ($\sim 125^\circ\text{C}$). This behavior is closely related to the decomposition characteristics of the cathode, which exhibited spiking to 12 V approximately 10 min earlier than Li_xCoO_2 . This phenomenon is due to the fact that $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ accelerates its exothermic decomposition reaction with the electrolyte below 4.5 V, resulting in an earlier separator shut-down. However, above 4.5 V, its reaction is drastically reduced, as evidenced by the DSC results [13]. On the other

hand, Li_xCoO_2 shows a continuously increasing exothermic peak height up to 4.9 V [14]. This does not lead to thermal runaway, securing the overcharge safety.

Fig. 5 shows the voltage profiles and cell temperature changes as a function of time at the 2 and 3 C overcharging rate to 12 V in Li-ion cells containing different weight fraction of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ and LiCoO_2 . Note that the LiCoO_2 with 40 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ can block the thermal runaway, and the cell surface temperature can be maintained to below 150°C even at a 3 C overcharging rate. A more interesting phenomenon is that both LiCoO_2 with 50 and 60 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ shows that the maximum cell temperature at the 3 C overcharging rate is smaller than that at the 2 C overcharging rate. The cause of this is currently under investigation.

On the contrary to 12 V overcharge test, the nail-penetration test result of Li-ion cells at 4.35 V charge (corresponding to 4.5 V versus Li metal), which is considered to stimulate an internal short in a Li-ion cell. This test directly showed the thermal stability of the cathodes because a sudden internal short accompanying an abrupt increase joule heat is induced in the cathode [14]. Hence, maximum surface temperature of 400°C was observed in the cell with bare $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ with spark and fire [14]. However, 12 V overcharge test is sensitive to the cumulative heat generation of the cathode during a longer time because continuous current is applied even after all the lithium ions were removed from the cathode. In this regard, $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ did not show the thermal runaway as explained above.

4. Conclusions

A physical blend of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ with LiCoO_2 noticeably improved the 12 V overcharge stability. Thermal runaway, which occurred in pure LiCoO_2 at a 2 C rate charging, was completely removed by 40 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ without sacrificing the cell capacity. The addition of 50 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ in LiCoO_2 gave rise to a capacity increase by approximately 100 mA h.

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