



Short communication

Structural changes and thermal stability of charged $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material for Li-ion batteries studied by time-resolved XRDKyung-Wan Nam^a, Won-Sub Yoon^{a,b,*}, Xiao-Qing Yang^a^a Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA^b School of Advanced Materials Eng., Kookmin University, Seoul 136-702, South Korea

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ABSTRACT

Structural changes and their relationship with thermal stability of charged $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode samples have been studied using time-resolved X-ray diffraction (TR-XRD) in a wide temperature from 25 to 600 °C with and without the presence of electrolyte in comparison with $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes. Unique phase transition behavior during heating is found for the $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode samples: when no electrolyte is present, the initial layered structure changes first to a LiM_2O_4 -type spinel, and then to a M_3O_4 -type spinel and remains in this structure up to 600 °C. For the $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode sample with electrolyte, additional phase transition from the M_3O_4 -type spinel to the MO-type rock salt phase takes place from about 400 to 441 °C together with the formation of metallic phase at about 460 °C. The major difference between this type of phase transitions and that for $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ in the presence of electrolyte is the delayed phase transition from the spinel-type to the rock salt-type phase by stretching the temperature range of spinel phases from about 20 to 140 °C. This unique behavior is considered as the key factor of the better thermal stability of the $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials.

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1. Introduction

The research and development of hybrid electric vehicle (HEV), plug-in hybrid electric vehicle (PHEV) and electric vehicle (EV) are intensified due to the energy crisis and environmental concerns. Having the highest energy density among all rechargeable batteries, lithium-ion battery is considered as the best candidate of rechargeable batteries for transportation applications. In order to meet the challenging requirements of powering HEV and PHEV, the safety characteristics of lithium battery need to be thoroughly studied and significantly improved. The thermal stability of the cathode materials is one of the key issues of the safety characteristics, which is related to the occurrence of exothermic reactions in charged batteries at elevated temperatures that ultimately result in thermal runaway and catastrophic failure of the battery. The thermal runaway has been attributed to the reactions between the charged electrodes and the electrolyte. Therefore, in-depth understanding of the structural changes of the charged cathode material during thermal decomposition, with or without the presence of electrolytes and

their relationship to the thermal stability of the cathode material is very important. We have reported our studies on the structural changes of the charged nickel based cathode materials such as $\text{Li}_{1-x}\text{NiO}_2$, $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, and $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ with and without the presence of electrolyte during heating, using synchrotron based time-resolved X-ray diffraction (TR-XRD) [1–3].

Recently, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material has attracted a lot of interest due to its advantages such as low cost, high specific capacity, and good thermal stability [4–7]. The thermal properties of this material have been characterized by various techniques such as differential scanning calorimetry (DSC), thermogravimetry/differential thermal analysis (TG/DTA), accelerated rate calorimetry (ARC), and micro-calorimetry [8–11]. However, not much information on the structural changes of charged $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode during heating has been reported. In this paper, the results of our studies using TR-XRD technique on the structural changes of the charged $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode with and without the presence of electrolyte during heating up to 600 °C are reported. New findings of the unique phase transition behaviors of the charged $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode during thermal decomposition will be discussed in comparison with other nickel-based cathode materials such as $\text{Li}_{0.33}\text{NiO}_2$ and $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$.

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2. Experimental

The cathode consists of 84% $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (Seimi, Japan), 8% carbon black (Chevron), and 8% PVdF (Kureha). The cathodes, coated on Al foil current collector, were incorporated into 2-electrode test cells. Each of these cells was made of a Li foil anode, a Celgard separator, and a 1.2 M LiPF_6 electrolyte in a 3:7 EC:EMC solvent. The cell was charged at a C/18 rate to a level corresponding to a cathode composition of $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and then transferred to the glove box for disassembly. Charged cathode materials were scratched from the current collector and loaded into quartz capillaries in glove box. For the electrolyte-free samples, the charged cathodes were washed in DMC in the glove box. For the electrolyte containing samples, a drop of excess electrolyte was added in the capillaries after the unwashed samples were loaded. The capillaries were sealed in a glove box before being mounted on the thermal stage of the diffract-photometer of beamline X7B, at National Synchrotron Light Source at Brookhaven National Lab. The wavelength used at X7B was $\sim 0.9212 \text{ \AA}$. XRD spectra were recorded as a set of circles on a Mar 345-image plate detector in the transmission mode for $\sim 1 \text{ min}$ of exposure time. The total recording time for a spectrum is $\sim 2.6 \text{ min}$ because of the scanning time of the image plate and transferring time of the spectral information. In order to make an easy comparison with the results in the literature, all the 2θ angles in this paper have been converted to the values corresponding to the Cu $K\alpha 1$ radiation ($\lambda = 1.54 \text{ \AA}$).

3. Results and discussion

For comparison purpose, we reprocessed our previously published time-resolved XRD (TR-XRD) spectra for charged $\text{Li}_{0.33}\text{NiO}_2$ sample [3] with electrolyte during heating by converting all 2θ angles into the values corresponding to the Cu $K\alpha 1$ radiation ($\lambda = 1.54 \text{ \AA}$) and plotted them in Fig. 1. The spectra in Fig. 1 provide a good road map for the structural changes of nickel-based cathode materials during heating. As shown in Fig. 1, when heated from 25 to 450°C , the sample went through a whole series of phase transitions. The structural change starts at about 170°C . In the temperature range between 180 and 210°C , the (1 0 8) and (1 1 0) peaks for the original layered structure gradually coalesce into a new peak, indicating the formation of a new structure, the disordered spinel phase. In the temperature range from 220 to 280°C , two new peaks (assigned as (2 0 0) and (2 2 0) for the rock salt structure of NiO)

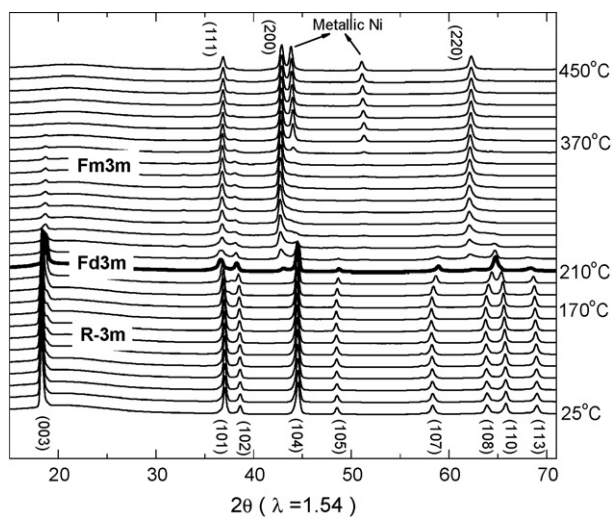


Fig. 1. TR-XRD patterns of the charged $\text{Li}_{0.33}\text{NiO}_2$ in the presence of electrolyte heated from 25 to 450°C .

appear at lower angle sides of the (4 0 0) and (4 4 0) peaks for the disordered spinel. These two new peaks increase their intensity with increasing temperature, indicating the growing amount of the NiO-like structure at the expense of the disordered spinel phase. A new intermediate structure, Ni_2O_3 phase was also reported in the XRD patterns for $\text{Li}_{0.33}\text{NiO}_2$ in the temperature range between 220 and 370°C [2]. From 370 to 450°C , another new phase, the metallic nickel phase forms, grows, and co-exists with the rock salt NiO phase up to 450°C . These phase transitions show clearly that the crystal structure of the sample changes from the layered hexagonal to the disordered spinel cubic and then to the rock-salt cubic by increasing the levels of cation mixing (migration of Li and Ni cations) with increased temperature.

The different phase transition behavior of charged $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material during heating with or without the presence of electrolyte can be seen in Figs. 2 and 3. Fig. 2 (a) shows the time-resolved XRD (TR-XRD) patterns of $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in the absence of electrolyte as a function of temperature. The $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ sample at room temperature shows a hexagonal layered structure with a $R\text{-}3m$ space group, just like in the $\text{Li}_{0.33}\text{NiO}_2$ sample. The structural change starts at about 236°C , which is much higher than the 170°C starting temperature for $\text{Li}_{0.33}\text{NiO}_2$ shown in Fig. 1. In the

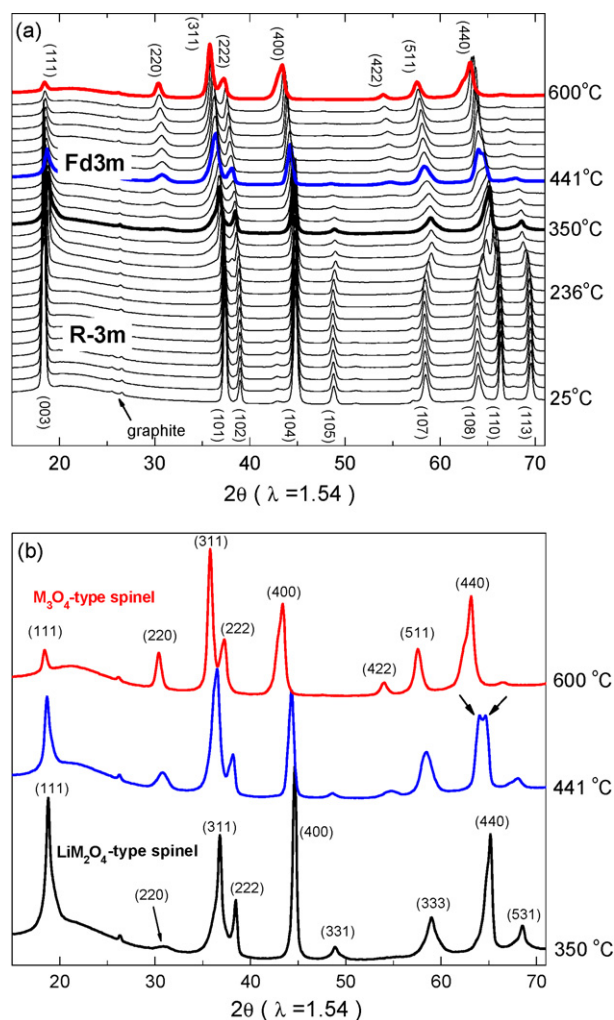


Fig. 2. (a) TR-XRD patterns of the charged $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in the absence of electrolyte heated from 25 to 600°C . (b) Three selected XRD patterns from Fig. 1 (a) for the sample heated to 350, 441 and 600°C .

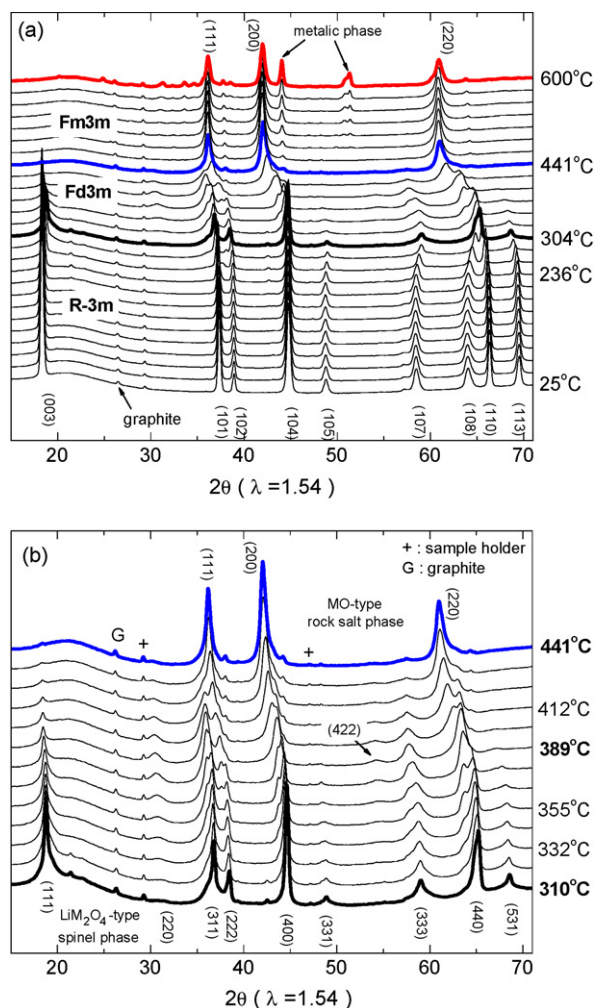


Fig. 3. (a) TR-XRD patterns of the charged $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in the presence of electrolyte heated from 25 to 600 °C. (b) Same TR-XRD patterns as in Fig. 3(b) in temperatures between 310 and 441 °C with smaller temperature step.

temperature range from 236 to 350 °C, the coalescence of the original (108) and (110) forms a new peak (marked as (440)), giving clear indication for the formation of a disordered LiM_2O_4 -type spinel phase with a unit cell containing $2 \times 2 \times 2$ cubic rock salt unit cells. This new peak is indexed as (440) reflection for the cubic structure with a space group of $Fd3m$ [12]. The spinel-type cubic symmetry is preserved up to the temperature as high as 600 °C, the terminating temperature of the experiment. No further decomposition to MO-type rock salt phase is present at all. However, there are noticeable changes in the diffraction lines in the temperature range from 350 to 600 °C. The evolution of the (220) diffraction line at $\sim 31^\circ$ in the XRD pattern after 350 °C shown in Fig. 2 (a) was used as confirmation of the formation of disordered LiM_2O_4 -type spinel phase in the literature [13]. However, in the spectra for $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode in Fig. 2(a), the appearance and growing of the new (220) peak are concurrent with the appearance and growing of another new peak (422), as well as the disappearance of the old peaks of (331) and (531). This tells us that the spinel structure at the end of heating at 600 °C is not the same LiM_2O_4 -type spinel, but a complete new phase. Three selected TR-XRD patterns for the sample heated to 350, 441, and 600 °C in Fig. 2 (a) are plotted in Fig. 2 (b). While the intensity of (220) line gets stronger together with the new (422) diffraction line at $\sim 54^\circ$, the intensity of (331) and (531)

peaks gets weaker with increasing temperature towards 600 °C. The TR-XRD pattern at 600 °C can be indexed to the M_3O_4 -type spinel structure (e.g., Co_3O_4 , JCPDS No. 43-1003) with the same $Fd3m$ space group as for the disordered LiM_2O_4 -type spinel phase. The major differences of these two types of spinel are the different lattice parameters and different cation distribution. The two-phase co-existence region can be seen clearly in the XRD pattern at 441 °C in Fig. 2 (b): the old (331) and (531) peaks of LiM_2O_4 -type spinel phase co-exist with the new (220) and (422) peaks for M_3O_4 -type spinel phase, in concurrence with the peak splitting of (440) line (marked by two arrows in Fig. 2 (b)). It should be noted that the coexistence of two different types of spinel phase during thermal decomposition has not been observed in the nickel based cathodes such as $\text{Li}_{1-x}\text{NiO}_2$ [3], $\text{Li}_{1-x}\text{Ni}_{0.89}\text{Al}_{0.16}\text{O}_2$ [13], and $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. [1]. This might be a unique phase transition behavior of Mn containing layered materials only. More detailed studies are planned to confirm this.

Fig. 3(a) shows the TR-XRD patterns for $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in the presence of electrolyte as a function of temperature. Compared to the sample without electrolyte, dramatic electrolyte induced structural changes are observed. Although not so much difference of starting temperature for structural change is observed, the completion of phase transition from the layered structure to the disordered LiM_2O_4 -type spinel phase is lowered from 340 to 304 °C. In addition, further thermal decomposition from the M_3O_4 -type spinel phase to a MO-type rock salt phase (space group: $Fm3m$) is observed from ~ 400 to 441 °C. From ~ 460 to 600 °C, new metallic phases (most likely Ni) are formed. These results show that electrolyte accelerates the thermal decomposition of the charged cathode materials. The presence of electrolyte changes the paths of the phase transitions and lowers the temperatures of the reactions. According to Wang et al., the electrolyte can modify the stability of pure cathode by catalyzing electrode decomposition reaction at the electrode surface and adding exothermic heat to the overall reaction due to its combustion with liberated oxygen from the cathode decomposition [14]. In addition, the electrolyte combustion equilibrium can create a low oxygen chemical potential in the system, which will reduce the cathode at lower temperature than for a pure cathode [14].

The TR-XRD patterns with smaller temperature steps from 310 to 441 °C are plotted in Fig. 3 (b). From 310 to 389 °C, the structure transforms from the LiM_2O_4 -type spinel phase to the M_3O_4 -type spinel phase as evidenced by the growing intensity of (220) and (422) peaks. From 389 to 441 °C, new diffraction peaks appear in the left side of the M_3O_4 -type spinel (400) and (440) peaks. These new peaks grow in intensity and get sharper with increased temperature. These two peaks are indexed as (200) and (220) peaks for the MO-type phase with rock salt structure. The phase transition from the M_3O_4 -type spinel structure to the MO-type rock salt structure is completed at 441 °C.

In order to compare the thermal decomposition behavior of the $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and the $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes in the presence of electrolyte in more detail, our previously published TR-XRD patterns for the $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode (Fig. 4(a) of reference [1]) were re-processed using the same 2θ angles as in this paper. The re-processed patterns are plotted in Fig. 4. Please note that this sample was heated up to 450 °C, not 600 °C as in this work. Decomposition of the layered structure starts at about 200 °C. Upon heating, phase transitions from the layered to the spinel-type phase and then to the NiO-type rock salt phase are clearly seen. However, there are several noticeable differences between the thermal decomposition behaviors of the $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and the $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes in the presence of electrolyte. Firstly, the $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ shows higher beginning and ending temperatures of the phase

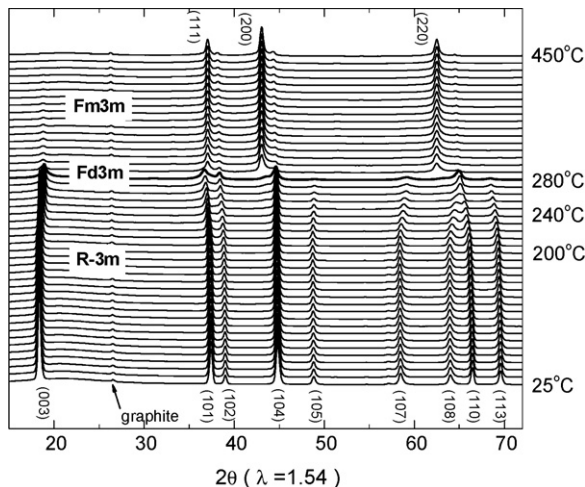


Fig. 4. TR-XRD patterns of the charged $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ in the presence of electrolyte, heated from 25 to 450 °C.

transitions from layered to the spinel-type, and from spinel-type to the rock salt-type phases than those of the $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, indicating better thermal stability. For $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, the ending temperatures for the transition from layered to spinel-type phase and from spinel-type to rock salt-type phase in the presence of electrolyte are 304 and 441 °C, while for $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, they are 280 and ~300 °C respectively. These results are consistent with our previously published conclusion about the negative effects of nickel content on the thermal stability of layered cathode materials. [3] Secondly, the $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ sample remains in the spinel structures (LiM_2O_4 and M_3O_4 -types) in a quite wider temperature range of about 140 °C from 304 to 441 °C. In contrast, for $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, the spinel structure lasts only in a very narrow temperature range of about 20 °C before totally converted into the MO-type rock salt structure. Since the phase transitions from the spinel-type phase to the rock salt-type phase are accompanied by oxygen loss, better thermal stability of the $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ than that of the $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ in the presence of electrolyte can be attributed to the higher phase transition temperature from spinel-type phase to the rock salt-type phase during heating. This unique thermal decomposition characteristic of the $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathodes is believed to be originated from the existence of Mn^{4+} ions in the $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material.

4. Conclusions

Unique phase transition behavior during heating is found for the $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode samples: when no electrolyte

is present, the initial layered structure changes first to a LiM_2O_4 -type spinel in a temperature range from 236 to 350 °C, and then to a M_3O_4 -type spinel from 350 to 441 °C, and remains in this structure up to 600 °C. For the $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode sample with electrolyte, additional phase transition from the M_3O_4 -type spinel to the MO-type rock salt phase takes place from ~400 to 441 °C together with the formation of metallic phase at about 460 °C. The major difference between this type of phase transitions for the $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode sample and that for $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ in the presence of electrolyte is the delayed phase transition from the spine-type to the rock salt-type phase by stretching the temperature range of spinel phases from about 20 to 140 °C. In this 140 °C range, the phase transition from the LiM_2O_4 -type spinel to the M_3O_4 -type phase takes place in the $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode sample. This unique behavior is considered as the key factor of the better thermal stability of the $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials than that of the other nickel based materials such as $\text{Li}_{1-x}\text{NiO}_2$ and $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. This behavior is very likely originated from the existence of Mn^{4+} in $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials.

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