

Short communication

# Time-resolved XRD study on the thermal decomposition of nickel-based layered cathode materials for Li-ion batteries

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## Abstract

Structural changes for a series of nickel based layer structured cathode materials during heating from 25 to 450 °C in the presence of electrolyte were studied using time-resolved X-ray diffraction (XRD). These samples were electrochemically delithiated to  $\text{Li}_{0.33}\text{NiO}_2$ ,  $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , and  $\text{Li}_{0.2}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ . The structural changes of all these three samples follow a same trend, first convert from a layered structure to a disordered spinel structure, then the disordered spinel phase transforms to the NiO-like phase as the temperature increases. However, the onset temperature of the thermal decomposition reactions strongly depends on the nickel content of the material. The lower the nickel content, the higher the decomposition temperature. At the end of heating at 450 °C, the metallic nickel structure was observed only for  $\text{Li}_{0.33}\text{NiO}_2$  sample. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Time-resolved X-ray diffraction; Lithium rechargeable batteries;  $\text{LiNiO}_2$ ;  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ;  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$

## 1. Introduction

The emergence of portable telecommunication, computer equipment and ultimately hybrid electric vehicles has created a substantial interest in manufacturing lithium rechargeable batteries with lower cost, less toxicity, longer life, smaller size, and lighter weight. Problems of power-fade and safety in high power lithium-ion cells are the major technical barriers that have to be overcome for these more demanding applications. Safety is related to the occurrence of exothermic reactions in charged batteries at elevated temperatures that ultimately results in thermal runaway and catastrophic failure of the battery. The thermal runaway has been ascribed to reactions between the charged electrodes and the electrolyte. There is a lot of information we can learn from the reactions between the electrodes and electrolyte as the battery is heated. Calorimetric analysis (DSC, ARC and microcalorimetry) and the analysis of electrolyte and evolved gasses have been utilized to understand the cell and component

reactions, which contribute to the complex thermal behaviors of Li-ion cells [1–4]. However, there is very little information on reactions in the electrodes. Unfortunately, most temperature dependent diffraction studies on the charged electrodes have been performed in the absence of electrolyte/solvents [5–7]. Recently we used time-resolved XRD studies to monitor the thermal behavior of the charged electrode in the presence of electrolyte as a function of temperature [8]. In order to understand thermal degradation of the electrodes in Li-ion cells, we have monitored the structural changes of the charged cathode material in the presence of electrolyte using time-resolved X-ray diffraction (XRD). The results from a series of nickel based cathode materials are reported in this paper and the effects of nickel content on the thermal stability will be discussed.

## 2. Experimental

The cathodes were incorporated into cells with a Li foil (99.9% pure lithium ribbon from Aldrich Co.) anode, a Celgard separator, and a 1 M  $\text{LiPF}_6$  electrolyte in a 1:1 EC: DMC solvent (LP 30 from EM Industries, Inc.). The cells were assembled in an argon-filled glove box and were hermetically sealed

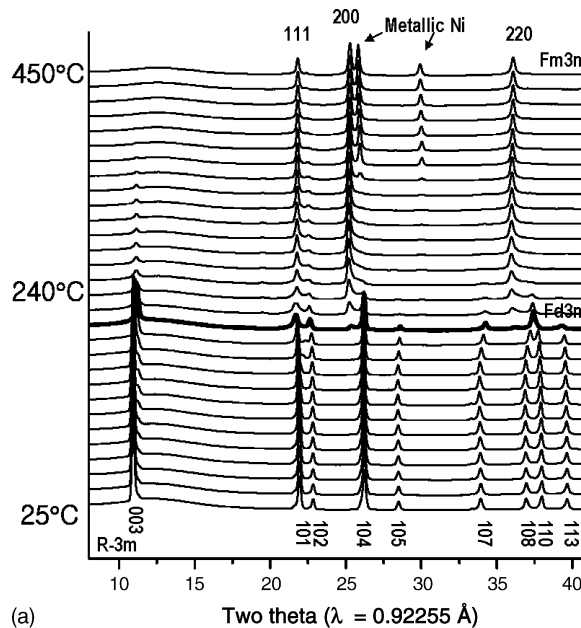
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in a housing that could be easily disassembled. The cells were charged to various stages of charge, outside the glove box. The cells were then transferred to the glove box for disassembly and transfer of charged cathode materials to quartz capillaries. Some of the charged cathode samples washed in THF in the glove box and were sealed in either 0.3 mm or 0.5 mm quartz capillaries. Other samples were not washed before loading the capillaries and wetted with a drop of excess electrolyte before sealing. These capillaries could withstand the pressure generated on heating. In order to simulate the real operating condition, excess electrolyte was added to the capillary to compensate the lost electrolyte during the disassembling of the cell. The capillaries were mounted in the thermal stage of diffractometers on beamline X7B, at National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), and XRD spectra were recorded as a set of circles on a Mar 345-image plate detector in the transmission mode. A complete XRD spectrum was taken on the image plate within  $\sim 1$  min exposure time and the image plate was scanned and the spectral information transferred to a computer in  $\sim 1.6$  min. Thus the total recording time for a spectrum is  $\sim 2.6$  min. Most of the capillaries were heated up to  $450^\circ\text{C}$  at a heating rate of  $2.4^\circ\text{C}/\text{min}$ .

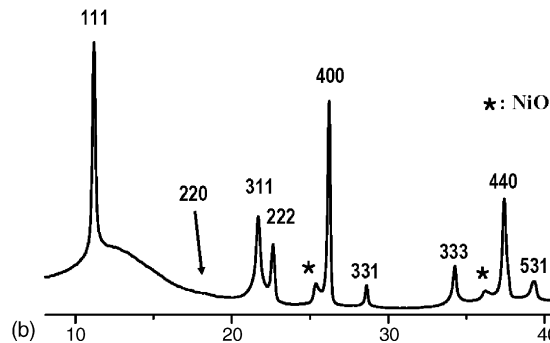
### 3. Results and discussion

In order to investigate structural changes in charged  $\text{Li}_{1-x}\text{NiO}_2$  cathodes during thermal decomposition, time-resolved XRD analysis was performed. Time-resolved XRD patterns for  $\text{Li}_{0.33}\text{NiO}_2$  in the presence of electrolyte in a temperature range from  $25$  to  $450^\circ\text{C}$  are shown in Fig. 1. The thermal decomposition reaction starts at about  $170^\circ\text{C}$ . In the interval between  $180$  and  $210^\circ\text{C}$  the coalescence of the  $(1\ 0\ 8)$  and  $(1\ 1\ 0)$  peaks in the layered structure is observed suggesting the formation of disordered spinel phase. The evolution of the  $(2\ 2\ 0)$  diffraction line also confirms the formation of the spinel phase (Fig. 1b), because the  $(2\ 2\ 0)$  reflection is prohibited under the hexagonal structure [7]. The broad shoulders at the lower angle side of the spinel  $(4\ 0\ 0)$  and  $(4\ 4\ 0)$  peaks observed in the spectrum at about  $210^\circ\text{C}$  grow into the sharp  $(2\ 0\ 0)$  and  $(2\ 2\ 0)$  peaks of the NiO-like structure when the sample was heated from  $210$  to  $250^\circ\text{C}$ . This NiO-like rock salt structure grows with temperature at the expense of the disordered spinel phase, and becomes the dominated structure at the end of heating at  $450^\circ\text{C}$ . At about  $370^\circ\text{C}$ , the formation of metallic Nickel is observed and the peaks representing this structure grow with the temperature up to  $450^\circ\text{C}$ .

It was reported that the poor thermal stability of  $\text{LiNiO}_2$  can be dramatically improved by doping it with Co, Al, and Mg [9]. Therefore, it is quite interesting to study the thermal decomposition of these doped materials in comparison with the undoped  $\text{LiNiO}_2$ . Fig. 2a shows time-resolved XRD patterns 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, in the temperature range from  $25$  to  $450^\circ\text{C}$ . Decomposition of the layered structure starts at about  $200^\circ\text{C}$ . In the interval between  $200$  and  $250^\circ\text{C}$  the coalescence of the  $(1\ 0\ 8)$  and  $(1\ 1\ 0)$  peaks in the layered structure is observed suggesting the formation of disordered spinel phase. Based on a  $2 \times 2 \times 2$  cubic rock salt lattice,



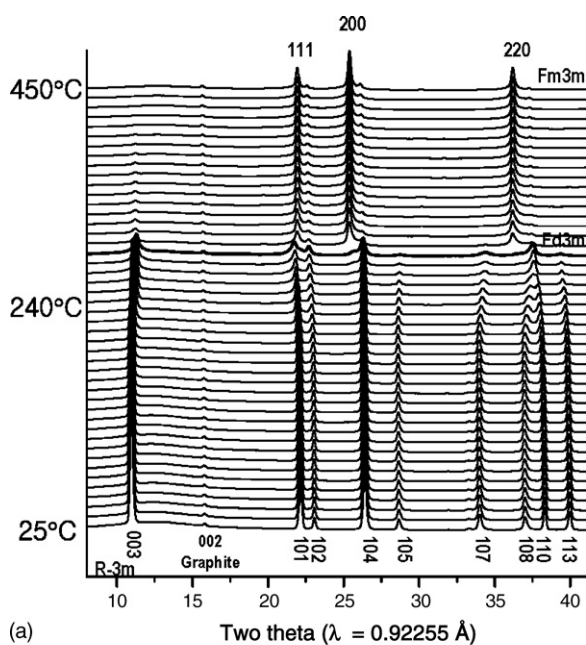
(a)



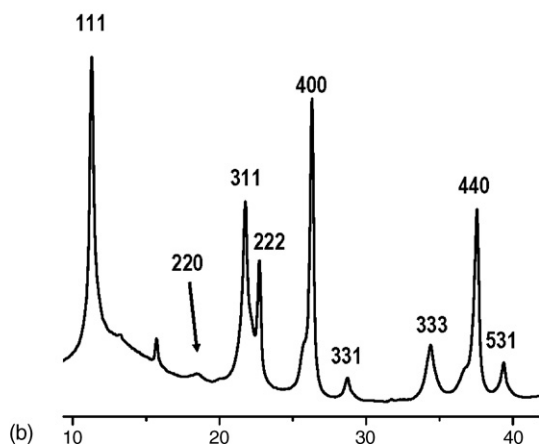
(b)

Fig. 1. (a) Time-resolved XRD patterns for  $\text{Li}_{0.33}\text{NiO}_2$  in the presence of electrolyte, heated in the temperature range from  $25$  to  $450^\circ\text{C}$ . (b) Time-resolved XRD patterns for  $\text{Li}_{0.33}\text{NiO}_2$  in the presence of electrolyte, heated to  $210^\circ\text{C}$ , this is an expanded view of the thick line in (a). The shoulders located at the lower angle sides of the spinel  $(4\ 0\ 0)$  and  $(4\ 4\ 0)$  peaks indicate the presence of a new phase.

this merged peak corresponds to the  $(4\ 4\ 0)$  peak in the cubic structure with space group  $Fd3m$  [10,11]. The evolution of the  $(2\ 2\ 0)$  diffraction line (marked in Fig. 2b) also confirms the formation of the spinel phase as described by Guilnard et al. [7]. As can be seen in Fig. 2b, in addition to the well-defined peaks of the spinel structure, broad shoulders located at the lower angle sides of the spinel  $(4\ 0\ 0)$  and  $(4\ 4\ 0)$  peaks are also seen. The appearance of these broad shoulders clearly indicates the formation of a new phase. When sample was heated to higher temperature, the new peaks become sharper and can be indexed to the NiO-like rock salt structure. The broad peaks at the lower angle sides of the spinel  $(4\ 0\ 0)$  and  $(4\ 4\ 0)$  peaks grow into sharp  $(2\ 0\ 0)$  and  $(2\ 2\ 0)$  peaks of the NiO-like structure at the expense of the disordered spinel phase. A clear rock salt structure is observed at  $290^\circ\text{C}$ , as marked by the thick line in Fig. 2a, indicating the formation of NiO-like phase. The disordered spinel phase transforms progressively to the NiO-like phase as the temperature increases. During the conversion from a spinel to a rock salt phase, lithium ions move to neighbor nickel layer and nickel



(a)

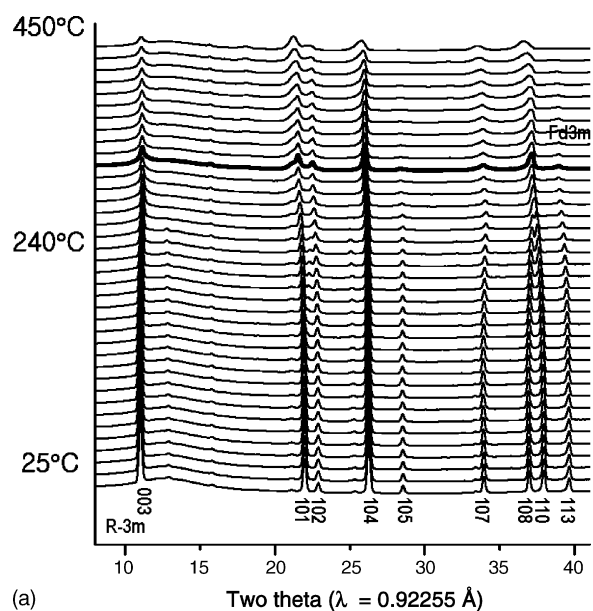


(b)

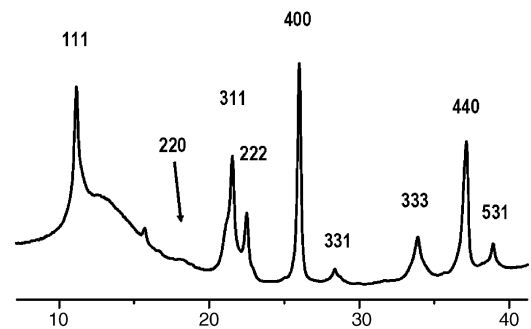
Fig. 2. (a) Time-resolved XRD patterns for  $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  in the presence of electrolyte, heated in the temperature range from 25 to 450 °C (thick line in (b)). (b) Time-resolved XRD pattern for  $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  at 280 °C. This is an expanded view of the thick line in (a). The shoulders located at the lower angel sides of the spinel (4 0 0) and (4 4 0) peaks indicate the presence of a new phase.

ions move to neighbor lithium layer, making these layers no longer distinguishable from each other. Therefore, the resulting rock salt phase has a unit cell with an axis of a half for the spinel phase. The transformation from the spinel phase to NiO-like rock salt phase is almost completed at the end of heating at 450 °C. The resulting peaks could be indexed assuming a cubic cell with a space group of  $Fm\bar{3}m$  [10]. Comparing with Fig. 1, the phase transitions from layered structure to disordered spinel and finally to a NiO-like rock salt structure in the temperature range of 25–450 °C are quite similar for  $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  and  $\text{LiNiO}_2$ . However, there are two interesting differences. One is the transition temperatures; another is the presence of the metallic nickel structure at the end of heating at 450 °C for  $\text{Li}_{0.33}\text{NiO}_2$ .

Recently, the layer structured  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  type materials have been widely studied due to their much better thermal stability over  $\text{LiNiO}_2$  material. Fig. 3a shows time-resolved XRD



(a)



(b)

Fig. 3. (a) Time-resolved XRD patterns for  $\text{Li}_{0.2}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  in the presence of electrolyte, heated in the temperature range from 25 to 450 °C. (thick line in (b)). (b) Time-resolved XRD pattern for  $\text{Li}_{0.2}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  at 335 °C. This is an expanded view of the thick line in (a).

patterns for  $\text{Li}_{0.2}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  in the presence of electrolyte in the temperature range from 25 to 450 °C. Compared to the other two nickel-based layered compounds ( $\text{Li}_{0.33}\text{NiO}_2$  and  $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ), decomposition reaction starts at much higher temperature (245 °C versus 170 °C for  $\text{Li}_{0.33}\text{NiO}_2$  and 200 °C for  $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ). In the interval between 265 and 335 °C the coalescence of the (1 0 8) and (1 1 0) peaks in the layered structure is observed suggesting the formation of disordered spinel phase. The evolution of the (2 2 0) diffraction line also confirms the formation of the spinel phase (Fig. 3b). If we use the lowest temperature at which the NiO-like rock salt structure is observed to measure the thermal decomposition, it is 210 °C for  $\text{Li}_{0.33}\text{NiO}_2$ , 290 °C for  $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , and 340 °C for  $\text{Li}_{0.2}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ . Another indicator is the absence of metallic structure at the end of heating at 450 °C for both  $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  and  $\text{Li}_{0.2}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ . Therefore, the overall thermal decomposition of  $\text{Li}_{0.2}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  takes place at much higher temperature than those of  $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  and  $\text{Li}_{0.33}\text{NiO}_2$ . From the structural point of view,  $\text{Li}_{0.2}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  shows much better thermal stability than the other two materials. This is in good agreement

with the previous DSC results [12,13]. It is also interesting to note, with decreasing content of Ni, the thermal decomposition of  $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  and  $\text{Li}_{0.2}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  takes place at higher and higher temperatures, showing the clear negative effects of nickel content in thermal stability.

#### 4. Conclusion

Time-resolved XRD analysis has been carried out to investigate thermal behavior of electrochemically delithiated  $\text{Li}_{0.33}\text{NiO}_2$ ,  $\text{Li}_{0.27}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , and  $\text{Li}_{0.2}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  in the presence of electrolyte, in a heating temperature from 25 to 450 °C. For all of these three high degree charged cathode materials, the structural changes followed a same trend, first convert from a layered structure to a disordered spinel structure, then the disordered spinel phase transforms to the NiO-like phase as the temperature increases. The difference is the transition temperature: the onset temperature of thermal decomposition reactions strongly depends on the nickel content in the structure. The lower the nickel content, the higher the decomposition temperature. At the end of heating at 450 °C, the metallic nickel structure was observed for  $\text{Li}_{0.33}\text{NiO}_2$  sample.

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