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Deciphering the thermal behavior of lithium rich cathode material by *in situ* X-ray diffraction technique

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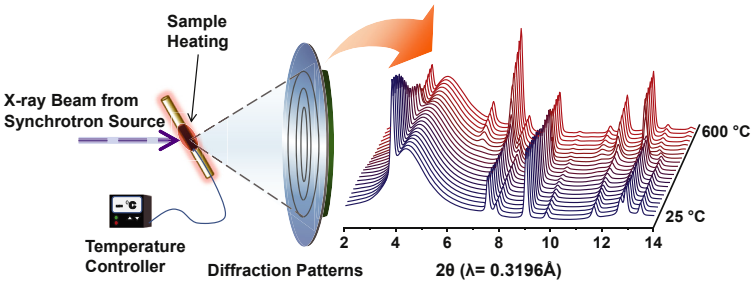
HIGHLIGHTS

- Thermal degradation mechanism of lithium rich electrode material is investigated.
- In the absence of electrolyte, LMC shows better thermal stability compared to NMC.
- In the presence of electrolyte, thermal decomposition of LMC is accelerated.
- Catalytic activity of electrolyte in thermal decomposition is electrode dependent.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermal stability is one of the critical requirements for commercial operation of high energy lithium-ion batteries. In this study, we use *in situ* X-ray diffraction technique to elucidate the thermal degradation mechanism of $0.5Li_2MnO_3$-$0.5LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ lithium rich cathode material in the absence and presence of electrolyte to simulate the real life battery conditions and compare its thermal behavior with the commercial $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ cathode material. We show that the thermal induced phase transformations in delithiated lithium rich cathode material are much more intense compared to similar single phase layered cathode material in the presence of electrolyte. The structural changes in both cathode materials with the temperature rise follow different trends in the absence and presence of electrolyte between 25 and 600 °C. Phase transitions are comparatively simple in the absence of electrolyte, the fully charged lithium rich cathode material demonstrates better thermal stability by maintaining its phase till 379 °C, and afterwards spinel structure is formed. In the presence of electrolyte, however, the spinel structure appears at 207 °C, subsequently it transforms to rock salt type cubic phase at 425 °C with additional metallic, metal fluoride, and metal carbonate phases.

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1. Introduction

Lithium-ion batteries were introduced in 1990 by Sony Corporation. Since its successful debut, various transition metal oxides have been synthesized and investigated as new lithium ion battery electrode materials to fulfill the ever demanding high capacity requirements. Recently composite layered material between Li_2MnO_3

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and $LiMO_2$ (where M = Mn, Co, Ni), also known as the lithium rich cathode material, has received pronounced attention and has been considered as promising cathode material due to its high discharge capacity of ~250 mAh g^{-1} [1]. However, there are several intrinsic problems associated with this material family that need to be solved; e.g., the voltage as well as the capacity decay during cycling, the high irreversible capacity loss in the first cycle, poor rate capability, and oxygen release during cycling, in order to adopt these materials in practical cells [2–4]. Thermal stability is another challenge which could greatly impact the safety of lithium-ion batteries, however it has received little attention unlike the widely studied electrochemical performance and reaction mechanism of this material.

In this study, we synthesized $0.5Li_2MnO_3$-$0.5LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (LMC) and applied the *in situ* XRD to monitor the in depth thermal behavior of this cathode material in the presence and absence of electrolyte as a function of temperature. XRD is a powerful technique to study the crystal structure and can provide the roadmap on average bulk structural changes during thermal decomposition, which is crucial to understand the thermal behavior of electrode materials [5–7]. Utilization of this technique during heating the electrode materials in the presence of electrolyte can simulate the real life battery conditions and provides meaningful information about the thermal decomposition of the electrode materials. In our previous studies, we have successfully employed this technique to study the thermal degradation mechanism of nickel-based cathode materials [8–12]. Monoclinic Li_2MnO_3 phase in a lithium rich cathode material acts as additional lithium sources and provides the anomalous high capacity when lithium rich cathode material is cycled above 4.4 V. In order to evaluate the impact of Li_2MnO_3 on the thermal stability of this cathode material, thermal induced phase transitions of this selected lithium rich cathode material were comparatively studied with the commercial $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ cathode material, also known as NCM. Outcomes of this study furnish the fundamental understanding of phase transitions in lithium rich cathode material under the thermal abuse and provide guidelines for further research and development in this material for commercial applications.

2. Experimental

$0.5Li_2MnO_3$-$0.5LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ powder was synthesized by a sol–gel method [13]. 0.05 mol of lithium acetate $Li(CH_3COO).2H_2O$ and stoichiometric amounts of nickel acetate $Ni(CH_3COO)_2.4H_2O$, cobalt nitrate $Co(NO_3)_2.6H_2O$, and manganese acetate $Mn(CH_3COO)_2.4H_2O$ were dissolved in 190 ml distilled water. The mixed metal solution was added drop-wise to aqueous solution of 10 ml (60%) nitric acid HNO_3, 15 ml of citric acid $C_6H_8O_7$, and 15 ml of ethylene glycol $C_2H_6O_2$ with constant stirring. The pH of the resulting solution was adjusted to 7.5 using ammonium hydroxide before solvent evaporation to get a transparent viscous gel. This gel was calcined at 950 °C for 5 h in air to obtain the desired cathode material.

High resolution synchrotron X-ray powder diffraction (HRPD) measurements of the synthesized $0.5Li_2MnO_3$-$0.5LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ powder were carried out at 9B HRPD beam line at Pohang Light Source-II in South Korea. The pristine powder sample was scanned from 10 to 130.5° with step size of 0.01°. The incident X-rays were vertically collimated using a mirror and monochromatized to wavelength of 1.5475 Å using a double-crystal Si (111) monochromator. The detector arm of diffractometer consisted of soller slits with an angular resolution of 2°, a flat Ge (111) crystal analyzer, an antiscatter baffle, and a scintillation detector.

The electrodes were prepared by mixing 8 wt% PVDF (Kureha) and 8 wt% carbon black (Chevron) in synthesized cathode material to prepare the slurry. The electrode films were formed on Al foil current collector by slurry coating technique. 2032-type coin cells were assembled in the dry room by using Celgard separator, lithium foil as counter electrode, and 1.3 M $LiPF_6$ electrolyte dissolved in ethylene carbonate/dimethyl carbonate (3:7 by volume) solvent. The cells were fully charged at low current rate of 0.05C to cut-off voltage of 4.7 V using constant current and constant voltage mode, and the net charge capacity of 311 mAh g^{-1} was achieved. The electrode material was scratched from the current collector and loaded into quartz capillaries whereas for the electrolyte-free samples, charged electrodes were washed with excess dimethyl carbonate in the glove box. For the electrolyte containing, a drop excess electrolyte was added in the capillaries after the samples were washed and loaded. The capillaries were sealed in glove box before mounting on the thermal stage of the diffract-photometer of beamline X7B at National Synchrotron Light Source, Brookhaven National Laboratory. The wavelength used at X7B was 0.3196 Å. The spectra were recorded as a set of circles on Mar 345-image plate detector in transmission mode for ~1 min of exposure time while temperature was raised at the rate of 2.5 °C min^{-1}. 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 CuKα radiation (λ = 1.54056 Å). Rietveld refinement of recorded HRPD pattern and Pawley fitting of *in situ* XRD patterns were performed by using GSAS-II package [14].

3. Results and discussion

High resolution powder diffraction pattern and Rietveld refined fit of the synthesized $0.5Li_2MnO_3$-$0.5LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ powder are shown in Fig. 1, and detailed structural parameters are tabulated in Table 1. Most of the peaks in the pattern were indexed based on a hexagonal α-$NaFeO_2$ type structure with *R-3m* space group. The weak peaks between 20 and 30° are originated from monoclinic Li_2MnO_3-like *C2/m* super lattice, caused by local ordering of Li and Mn in the transition metal layers [15]. Clear splitting of the (006)/(102) and (108)/(110) reflection pairs indicates a well-defined hexagonal structure [16]. Excellent agreement between observed and calculated pattern in Rietveld fit shows that the desired lithium rich composition was successfully synthesized. *In situ* XRD patterns of the fully charged $0.5Li_2MnO_3$-0.5 $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ and $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ cathode materials during heating from 25 to 600 °C in the absence of electrolyte are shown in Fig. 2. XRD patterns for charged $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ were obtained by

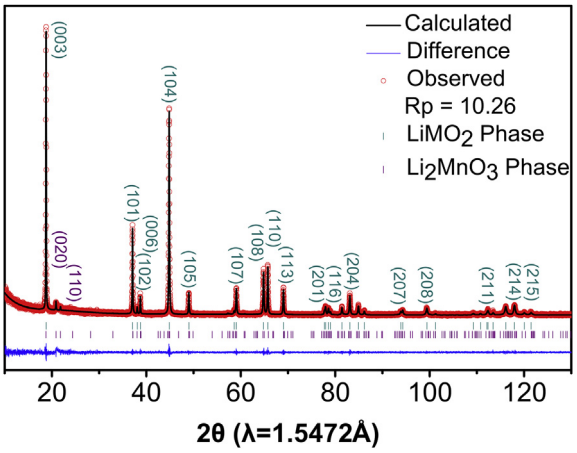

Fig. 1. The Rietveld refined fit of $0.5Li_2MnO_3$-$0.5LiMn_{0.33}Co_{0.33}Ni_{0.33}O_2$ pristine powder HRPD spectrum.

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