Structural changes and thermal stability of Ni based cathode material for Li-ion batteries studied by *in-situ* XRD

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Abstract

The three-component system $Li[Ni_xCo_yMn_z]O_2$ has outstanding electrochemical properties by taking advantage of the high capacity of $LiNiO_2$, thermal stability and low cost of manganese in $LiMnO_2$ and layered characteristics of $LiCoO_2$.[1] While capacity of $Li[Ni_xCo_yMn_z]O_2$ is similar to capacity of $LiCoO_2$, it is a promising alternative in terms of performance, safety and cost. Various material combinations are being developed to achieve the higher capacity by increasing Ni content while retaining its advantages. Although higher Ni content contributes to better capacity in $Li[Ni_xCo_yMn_z]O_2$, but on the other hand, it tends to decrease the thermal stability of electrode material.

The purpose of this study is to understand the thermal behavior of high-Ni $Li[Ni_xCo_yMn_z]O_2$ cathode material through structural analysis. Structural changes and thermal stability of charged $Li_{1-x}Ni_{0.6}Co_{0.2}Mn_{0.2}O_2$ and $Li_{1-x}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2$ have been studied using *in-situ* X-ray diffraction (XRD) in a wide temperature range from 25 to 600 ºC. In addition, *in-situ* thermal XRD experiments have been carried out in the presence and absence of electrolyte and 2-states of charge, 33% and 66% of Li extraction from $Li[Ni_xCo_yMn_z]O_2$.

Interesting phase transition behavior during heating is observed in $Li_{0.66}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode samples. $Li_{0.66}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2$ without electrolyte converts from a layered (R-3m) structure to disordered LiM_2O_4-type spinel (Fd3m) around 337 ºC. Upon further heating, M_3O_4-type spinel (Fd3m) appears and co-exists with LiM_2O_4-type spinel (Fd3m) from 454 ºC and remains in this structure up to 600 ºC. In the absence of electrolyte, small peaks of MO-type rock salt phase (Fm3m) start to appear around 572 ºC whereas in the presence of electrolyte, further phase transition from M_3O_4-type spinel (Fd3m) to MO-type rock salt phase (Fm3m) takes place above 362 ºC.

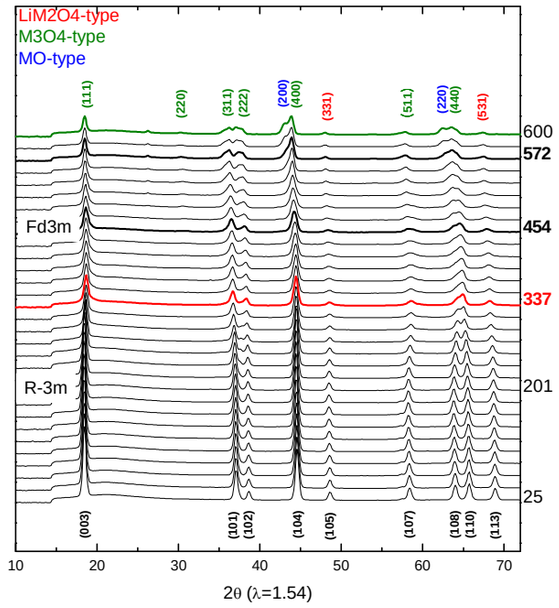
The electrolyte accelerates the thermal decomposition of charged cathode materials. The presence of electrolyte alters the paths of structural changes and lowers the onset temperatures of thermal decomposition reactions.[2] In case of $Li_{0.66}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2$ with electrolyte, more dramatic structural changes are observed in comparison with the one in the absence of electrolyte. The sample with electrolyte shows the structural decomposition to MO-type rock salt phase at 362 ºC, in the early stage of heating.

Thermal behavior of $Li_{0.33}Ni_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode material is similar to the $Li_{0.66}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2$. $Li_{0.33}Ni_{0.6}Co_{0.2}Mn_{0.2}O_2$ without electrolyte converts from a layered (R-3m) structure to disordered LiM_2O_4-type spinel (Fd3m) around 328 ºC. Upon further heating, M_3O_4-type spinel (Fd3m) co-exists with LiM_2O_4-type spinel (Fd3m) from 540 ºC and maintains this structure up to 600 ºC. Presence of electrolyte initiates additional phase transitions in this cathode material. M_3O_4-type spinel (Fd3m) starts to convert into MO-type rock salt phase (Fm3m) at 436 ºC. Above 560 ºC, pure MO-type rock salt phase (Fm3m) is observed.

This result of thermal behavior of $Li_{1-x}Ni_{0.6}Co_{0.2}Mn_{0.2}O_2$ and $Li_{1-x}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2$ is contributed to better understanding for thermal stability of Ni-based cathode materials.

Working on other samples and more detailed discussion will be presented at the time of meeting.

(a)



(b)

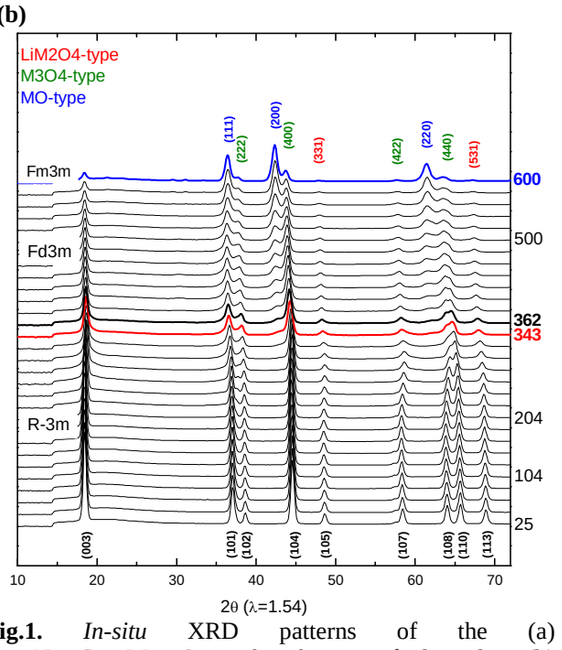


Fig.1. *In-situ* XRD patterns of the (a) $Li_{0.66}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2$ in the absence of electrolyte (b) $Li_{0.66}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2$ in the presence of electrolyte heated from 25 to 600 ºC.

Reference

[1]K.-W. Nam et al. Journal of Power Sources 189 (2009) 515–518

[2] Y.-H. Cho et al. Journal of Alloys and Compounds 562 (2013) 219–223