Thermal Behavior of Charged Cathode Materials Studied by Synchrotron-Based X-ray Techniques

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Comparison of the gravimetric and volumetric energy densities of rechargeable lithium batteries with those of other systems.
A laptop explodes at a conference in Japan
Introduction

- **Safety of Li rechargeable batteries**
  - a major technical barrier for more demanding applications such as EV and HEV
  - related to the exothermic reactions in charged batteries at elevated temperatures that results in thermal runaway and catastrophic failure of the battery
  - thermal runaway: reactions between the charged electrodes and the electrolyte

- **Improving the thermal stability of the electrode materials**
  - many approaches: doping, surface coating, particle size, and so on
  - better understanding of thermal behavior of the charged electrode
Highly deintercalated Li$_{x}$CoO$_2$ is decomposed to layered LiCoO$_2$ and electrochemically inactive Co$_3$O$_4$ at about 250 °C. The reaction process is shown below as

$$\text{Li}_{x<0.4}\text{CoO}_2 \rightarrow [(1-x)/3]\text{Co}_3\text{O}_4 + x\text{LiCoO}_2 + [(1-x)/3]\text{O}_2$$

LiMn$_2$O$_4$ is generally considered a safer compound than either LiCoO$_2$ and LiNiO$_2$. It is reported that the oxygen release from $\lambda$-MnO$_2$ starts at about 400 °C. The reaction process is shown below as

$$\lambda\text{-MnO}_2 \rightarrow (1/2)\text{Mn}_2\text{O}_3 + (1/4)\text{O}_2$$

The layered Li$_{0.5}$NiO$_2$ converts to the spinel LiNi$_2$O$_4$ when heated near 200 °C. The transformation is accompanied by no weight loss or heat generation. In contrast at higher degrees of deintercalation than $x = 0.5$, the conversion to spinel is apparently accompanied by significant oxygen evolution and heat generation. Above 400 °C, all of Li$_{x-y}$Ni$_{2-x}$O$_2$ undergo the following reaction:

$$\text{Li}_{x-y}\text{Ni}_{2-x}\text{O}_2 \rightarrow \text{Li}_{x-y}\text{Ni}_{2-x}\text{O}_{2-y} + (y/2)\text{O}_2$$

**Literature review**

**Temperature-induced structural changes in nickel-based cathodes**

\[
\text{Li}_{1-x}\text{NiO}_2 \rightarrow (2-x)\text{Li}_{(1-x)/(2-x)}\text{Ni}_{1/(2-x)}\text{O} \text{ (Fm3m)} + x/2 \text{O}_2 \text{ at } \sim 200^\circ\text{C}
\]


\[
\text{Li}_{1-x}\text{NiO}_2 \rightarrow (1-2x)\text{LiNiO}_2 \text{ (R-3m)} + x\text{LiNi}_2\text{O}_4 \text{ (Fd3m)} \text{ (x<0.5)}
\]
\[
\rightarrow \text{[Li}_{1-x}\text{Ni}_{(2x-1)/3}\text{][Ni}_{(4-2x)/3}\text{O}_{(8-4x)/3} \text{ (Fd3m)} + (2x-1)/3 \text{O}_2 \text{ (x>0.5)}
\]


\[
\text{LiNi}_{1-x}\text{M}_x\text{O}_2 (M = \text{Mn, Co, and Al})
\]

The decomposition occurs in two steps:

1st transition – layered to spinel-type phase

2nd transition – pseudo-spinel phase to NiO-type phase through a highly disordered R-3m phase


Most temperature dependent diffraction studies of the structure of the charged electrodes have been performed in the absence of electrolyte/solvents.

Need to investigate the structural changes of the charged cathode materials in the presence of electrolyte using in situ x-ray diffraction
In-situ XRD data: Electrolyte effect

$\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ with/without electrolyte (50\%SOC)

Yoon et al., ESSL, 2005

Electrolytes accelerate the thermal decomposition and change the decomposition path !!
TR-XRD study on thermal stability of \( Li_{0.33}NiO_2 \) with electrolyte (as a reference)

**In situ time-resolved (TR) XRD of charged cathode materials during heating**

- \( Li_{0.33}NiO_2 \)
  - A good road map for the structural changes of nickel-based cathode materials during heating.

\( \Rightarrow \) \( Li_{0.33}NiO_2 \) goes through a whole series of phase transitions (i.e., thermal decomposition) when heated up to 450 °C.
Thermal stability of charged $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) with electrolyte

At $\sim 265^\circ C$, the (220) spinel layer and (440) peaks are observed. This indicates the formation of a disordered spinel layer.

Heating up to $450^\circ C$ results in changes in the crystal structure, as shown in the X-ray diffraction patterns. The peaks at 25$^\circ C$ and 260$^\circ C$ are associated with the graphite phase.

Much better thermal stability than $Li_{0.33}NiO_2$.

Narrow temperature range ($\sim 20^\circ C$) for the disordered spinel region. (boxed region)
Thermal stability of charged $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) with electrolyte

Heating up to $600 \, ^\circ\text{C}$

Much wider temperature range (~140 $^\circ\text{C}$) for the disordered spinel region (boxed region) due to the stabilization of two different spinel-type structures.

⇒ much better thermal stability!!

Comparison of thermal stability of charged layered cathodes *with* electrolyte

**NCM cathode shows the best thermal stability** due to the large spinel stabilized temperature region. **why?** ⇒ Need better understanding of role of each elements during thermal decomposition.
**Mn** K-edge XANES and EXAFS of charged \(Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2\) (NCM) during heating

In depth analysis of better thermal stability of NCM cathode using XAS

**EXAFS : local atomic structure**

\(\Rightarrow\) Preserving local structure around Mn during heating.

**XANES : Oxidation state**

\(\Rightarrow\) No reduction of Mn ions during heating.

**⇒ Excellent thermal stability of Mn\(^{4+}\) ions in the charged \(Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2\) cathode.**

\(\Rightarrow\) likely due to the high preference of octahedral coordination of Mn\(^{4+}\) ions.
In-situ XRD data
Comparison of Li_{0.33}Ni_{1-x}Co_xO_2 with MgO-coated Li_{0.33}Ni_{1-x}Co_xO_2

Uncoated Li_{0.33}Ni_{1-x}Co_xO_2

MgO-coated Li_{0.33}Ni_{1-x}Co_xO_2

Much slower decomposition!!
In-situ XRD data: first charging curve

**Li$_{1.2}$Ni$_{0.133}$Co$_{0.133}$Mn$_{0.533}$O$_2$** after first charge activation

- C-rate
  
  C/C = C/16
  C/V = C/80
- Cut off: 4.7V
- A.M / Current
  
  Activation: 3.7014 mg
  C/C = 0.0854 mA
  C/V = 0.0168 mA

**Li$_{1.2}$Ni$_{0.133}$Co$_{0.133}$Mn$_{0.533}$O$_2$ = 0.5Li$_2$MnO$_3$-0.5LiNi$_{0.333}$Co$_{0.333}$Mn$_{0.333}$O$_2$**
In-situ XRD data

\[ \text{Li}_{1.2}\text{Ni}_{0.133}\text{Co}_{0.133}\text{Mn}_{0.533}\text{O}_2 \] after first charge activation

Li-rich layered cathode shows more complicating decomposition reaction with electrolyte.
Thermal Abuse: In situ XRD
Olivine cathode (LiMnPO₄) : electrolyte effect

LMP pure (100% charge:with electrolyte)

LMP pure (100% charge:without electrolyte)

$2\text{MnPO}_4 \rightarrow \text{Mn}_2\text{P}_2\text{O}_7 + 0.5\text{O}_2$

Olivine cathode shows less sensitivity with electrolyte.

ICSD # :047137 : $\text{Mn}_2\text{P}_2\text{O}_7$
Thermal Abuse: In situ XRD
Olivine cathode (LiMn$_{0.88}$Mg$_{0.1}$Zr$_{0.02}$PO$_4$) : doping effect

2MnPO$_4$ → Mn$_2$P$_2$O$_7$ + 0.5O$_2$

Doped olivine cathode shows better thermal stability with electrolyte.

ICSD #: 047137 : Mn$_2$P$_2$O$_7$
- Synchrotron based X-ray results clearly elucidate the thermal decomposition mechanism of charged cathode materials in the presence of electrolyte.

- The electrolyte accelerates the thermal decomposition of the charged cathode materials.

- The presence of electrolyte alters the paths of the structural changes and lowers the onset temperatures of the reactions.

- The electrolyte induced thermal decomposition of nickel containing layered cathode can be successfully suppressed by MgO surface coating.

- Li-rich layered compounds show more complicating decomposition reaction compared to other nickel containing layered compounds.

- Olivine cathode materials show less sensitivity in the presence of electrolyte.

- The thermal XRD study helps design thermally stable and safer cathode materials.
In honor of the wonderful scientist, Dr. James McBreen...
Thank you !!!