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A systematic study on the reactivity of different grades of charged $Li[Ni_xMn_yCo_z]O_2$ with electrolyte at elevated temperatures using accelerating rate calorimetry

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HIGHLIGHTS

- $Li[Ni_{0.8}Mn_{0.1}Co_{0.1}]O_2$ shows serious reactivity with electrolyte above 110 °C.
- $Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]O_2$ shows the least reactivity with electrolyte at high temperature.
- $Li[Ni_{0.6}Mn_{0.2}Co_{0.2}]O_2$ and $Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O_2$ show intermediate reactivity.
- This work identifies important trade-offs between $Li[Ni_xMn_yCo_z]O_2$ grades.

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ABSTRACT

The reactivity between charged $Li[Ni_xMn_yCo_z]O_2$ (NMC, with $x + y + z = 1$, x:y:z = 1:1:1 (NMC111), 4:4:2 (NMC442), 5:3:2 (NMC532), 6:2:2 (NMC622) and 8:1:1 (NMC811)) and traditional carbonate-based electrolytes at elevated temperatures was systematically studied using accelerating rate calorimetry (ARC). The ARC results showed that the upper cut-off potential and NMC composition strongly affect the thermal stability of the various NMC grades when traditional carbonate-based electrolyte was used. Although higher cut-off potential and higher Ni content can help increase the energy density of lithium ion cells, these factors generally increase the reactivity between charged NMC and electrolyte at elevated temperatures. It is hoped that this report can be used to help guide the wise selection of NMC grade and upper cut-off potential to achieve high energy density Li-ion cells without seriously compromising cell safety.

1. Introduction

Li-ion batteries (LIB) are now widely used in numerous applications, from portable electronics to electrified vehicles. In order to meet the increasing demands of these applications, the development of advanced positive electrode is critical to help increase the energy density and safety of LIB [1].

The most common positive electrode material is layered structured lithium cobalt oxide, $LiCoO_2$ (LCO), which can be cycled with an average specific capacity of 140 mAh/g to 4.2 V [2], of 189 mAh/g to 4.5 V and of 225 mAh/g to 4.6 V [3]. However, its drawbacks (e.g. high cost, environmental contamination) limit its future development. Thus other alternative materials such as $LiFePO_4$ (LFP) [4,5], $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ (NCA) [6,7] and lithium-excess layered solid solution materials $xLi_2MnO_3 \cdot (1\text{-}x)LiMO_2$ [8,9] have been studied. Among all the alternative materials, the $Li[Ni_xMn_yCo_z]O_2$ (NMC) ($x + y + z = 1$) series of materials are outstanding because of their comparatively high specific capacity, low cost and thermal tolerance [10].

Lu et al. [11] showed that the electrochemical characteristics of the $Li[Ni_xMn_xCo_{1\text{-}2x}]O_2$ series, in particular, $Li[Ni_{0.375}Mn_{0.375}Co_{0.25}]O_2$ were basically equivalent to those of LCO. Ohzuku's group [12] showed that $Li[Ni_xMn_xCo_{1\text{-}2x}]O_2$ with $x = 1/3$ or $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ (NMC111) was also excellent. Between 2001 and the present day, various NMC grades have become widely used in LIBs and the properties of various compositions, including their reactivity with electrolyte, have been explored. For example, Wang et al. [13]

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showed that NMC111 had the best safety properties when compared to LCO and NCA. Since nickel-rich NMC can deliver high specific capacity, which contributes to high energy density, Li[$Ni_{0.5}Mn_{0.3}Co_{0.2}$]O_2 (NMC532) [14], Li[$Ni_{0.6}Mn_{0.2}Co_{0.2}$]O_2 (NMC622) [15] and Li[$Ni_{0.8}Mn_{0.1}Co_{0.1}$]O_2 (NMC811) [16,17] have drawn lots of attention as well. A recent excellent review by Kim et al. [10], compares the various tradeoffs between these common NMC grades and shows that the reactivity of these materials with electrolyte at elevated temperature increases with Ni content.

An alternative approach to high energy and lower cost NMC materials is to use materials from the Li[$Ni_xMn_xCo_{1-2x}$]O_2 series with high Mn content and charge cells to high potential. For example, Paulsen et al. [18] promoted Li[$Li_x(Ni_{0.42}Mn_{0.42}Co_{0.16})_{1-x}$]$O_2$ with x near 0.11 as an excellent positive electrode material with exceptional thermal stability compared to Ni-rich materials (See drawing 9 in the patent). Such materials have evolved to be called NMC442 and have been extensively studied by our group recently. Unlike NMC111, which appears to be structurally unstable during extended periods at high potential (>4.5 V) [19], NMC442 did not show any structural changes after sequential exposures to 4.7 and 4.9 V [20]. With appropriate electrolyte additives (NMC442)/graphite full cells have been shown to be able to be operated to 4.4 V for extended periods of time and for 500 cycles (>80% capacity retention) [21] and up to 4.5 V for 500 cycles (>80% capacity retention) [22].

Li-ion battery safety is a key factor and is influenced by the selection of the positive electrode material and the operating potential range. For example, how does the reactivity of NMC442 charged to 4.4 V compare to that of NMC811 charged to 4.1 V? There are no literature references that compare the reactivity between all NMC materials, charged to various potentials, and electrolyte at elevated temperatures using accelerating rate calorimetry. In this work, the reactivity of charged NMC111, NMC442, NMC532, NMC622 and NMC811 at different cut-off voltages with electrolyte was systematically investigated and compared using accelerating rate calorimetry (ARC). The data in this paper can be used to rank the thermal stabilities of charged NMC grades in traditional carbonate-based electrolytes. The advantage of some particular NMC materials at high voltage is revealed from a safety perspective.

2. Experimental

1.0 M $LiPF_6$ in ethylene carbonate (EC):ethyl methyl carbonate (EMC) (3:7 by weight, from BASF, water content was 12.1 ppm) was used as the control electrolyte.

2.1. Pouch cells

Dry (no electrolyte) NMC111/graphite, NMC442/graphite, NMC532/graphite NMC622/graphite and NMC811/graphite pouch cells balanced for 4.7 V operation were obtained from Li-Fun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000). The positive electrodes were made with a weight ratio of active material, carbon black and polyvinylidene fluoride (PVDF) binder of 96:2:2. Since the reaction rate at elevated temperatures during ARC testing depends on the surface area of electrode materials in contact with electrolyte [23], Table 1 shows a summary of the BET specific surface areas of all the NMC positive electrode materials. Fig. 1 shows the scanning electron microscope (SEM) images of the different NMC grades. The NMC422 used in these cells was supplied by Umicore (Chonan, Korea) while the other NMC grades were provided by Chinese suppliers.

All pouch cells were vacuum sealed without electrolyte in a dry room in China and then shipped to our laboratory in Canada. Before electrolyte filling, the cells were cut just below the heat seal and dried at 80 °C under vacuum for 12 h to remove any residual water. Then the cells were transferred immediately to an argon-filled glove box for filling and vacuum sealing. All the pouch cells were filled with 0.9 g of electrolyte. After filling, cells were vacuum-sealed with a compact vacuum sealer (MSK-115A, MTI Corp.). First, cells were placed in a temperature box at 40 ± 0.1 °C where they were held at 1.5 V for 24 h, to allow for the completion of wetting. Then, all the cells were charged at the current corresponding to C/20 to 3.5 V. After this step, all the cells were transferred and moved into the glove box, cut open to release any gas generated and then vacuum sealed. Then all the cells were charged at the current corresponding to C/20 to 4.5 V. After this step, all the cells were transferred and moved into the glove box, cut open to release any gas generated and then vacuum sealed again.

2.2. Accelerating rate calorimetry (ARC) experiments

After degassing, all the cells were discharged to 2.8 V. Then the cells were divided into four groups. Each group was charged to its selected upper cut-off potential (4.2 V, 4.4 V, 4.5 V or 4.7 V) at C/20. All the cells were then held at the set upper cut-off potential for around 3 h. After this step, the cells were transferred and moved into the glovebox and cut open to recover the jelly rolls. The jelly rolls were then unwound to get the positive electrode. All the charged NMC powder for the ARC tests was obtained by carefully scratching the electrodes. This was very time consuming because the electrodes were well-adhered to the Al foil current collectors.

In order to make the results comparable, the capacity that had been delithiated from each sample used in the ARC tests was kept the same (~15 mAh). This was done by adjusting the mass of charged positive electrode material added to each ARC sample tube. The following example shows how the mass of material to be added to each ARC tube was determined.

The mass of positive electrode material in an NMC111/graphite pouch cell was 1.14 g. When the cell was charged to 4.2 V, the capacity was ~175 mAh. So the specific capacity, $Q_{specific}$, of the NMC111 material charged to 4.2 V was:

$$Q_{specific} = 175\ mAh/(1.14\ g \times 0.96) = 160\ mAh/g$$

The number of moles, n, of delithiated lithium was:

$$n = 160\ mAh/g \cdot 3.6\ C/mAh \cdot M/F = 0.576$$

where M = 96.5 g/mole is the formula weight of NMC111 and F is Faraday's number in C/mole.

Thus the delithiated NMC111 at 4.2 V can be described as $Li_{(1-0.576)}[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$, or $Li_{0.424}[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$. The mass, m, of delithiated material required for the ARC test is therefore:

Table 1
Summary of the specific surface area for the positive electrode materials in the NMC111/graphite, NMC442/graphite, NMC532/graphite, NMC622/graphite and NMC811/graphite pouch cells. The instrumental error in each value is estimated to be ±0.03 m^2/g.

Material	NMC111	NMC442	NMC532	NMC622	NMC811
Specific surface area (m^2/g)	0.34	0.38	0.28	0.24	0.25