**Using Real-time Electron Microscopy to Explore the Effects of Transition Metal
Composition on the Local Thermal Stability in Charged $\text{Li}_x\text{Ni}_y\text{Mn}_z\text{Co}_{1-y-z}\text{O}_2$
Cathode Materials**

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1   **Abstract**

2   In this work, we use in-situ transmission electron microscopy (TEM) to
3   investigate the thermal decomposition that occurs at the surface of charged
4    $\text{Li}_x\text{Ni}_y\text{Mn}_z\text{Co}_{1-y-z}\text{O}_2$ (NMC) cathode materials of different composition (with y, z=0.8,
5   0.1 and 0.6, 0.2 and 0.4, 0.3), after they have been charged to their practical upper
6   limit voltage (4.3V). By heating these materials inside the TEM, we are able to
7   directly characterize near surface changes in both their electronic structure (using
8   electron energy loss spectroscopy) and crystal structure and morphology (using
9   electron diffraction and bright-field imaging). The most Ni-rich material (y, z = 0.8,
10   0.1) is found to be thermally unstable at significantly lower temperatures than the
11   other compositions – this is manifested by changes in both the electronic structure and
12   the onset of phase transitions at temperatures as low as 100°C. Electron energy loss
13   spectroscopy indicates that the thermally induced reduction of Ni ions drives these
14   changes, and that this is exacerbated by the presence of an additional redox reaction
15   that occurs at 4.2V in the y, z = 0.8, 0.1 material. Exploration of individual particles
16   shows that there are substantial variations in the onset temperatures and overall extent
17   of these changes. Of the compositions studied, the composition of y, z = 0.6, 0.2 has
18   the optimal combination of high energy density and reasonable thermal stability. The
19   observations herein demonstrate that real time electron microscopy provide direct
20   insight into the changes that occur in cathode materials with temperature, allowing
21   optimization of different alloy concentrations to maximize overall performance.

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1   **Introduction**

2   Increasing the energy density of cathode and anode materials has been a
3   primary goal of research in lithium ion batteries (LIB) since their commercialization.
4   This is because increased energy density translates directly to an increase in the
5   operation time of portable devices following a single charge. However, with increasing
6   emphasis on the potential incorporation of LIBs in large-scale applications such as
7   electric vehicles (EVs), they must meet substantially more stringent requirements.
8   These include high energy and power density, longer lifetime, lower cost, and
9   improved safety.¹

10   Since the successful commercialization of LiCoO_2 as a cathode material, there
11   have been extensive investigations of the effects of incorporating other transition
12   metals into lithium metal oxides (e.g. LiMO_2 , where $\text{M}=\text{Co}, \text{Ni}, \text{Mn}$, etc.). Transition
13   metals act to relieve the charge imbalance that occurs during either the insertion or
14   removal of lithium from the structure during the reduction or oxidation process, and
15   thus their incorporation strongly affects the overall electrochemical performance. In
16   general, the incorporation of Ni increases the overall capacity of the cathode; however,
17   Ni-rich cathodes have also been associated with significant safety issues. Mn offers
18   improved structural stability, but this comes at the expense of overall capacity. Co
19   improves the rate performance of the cathode, but it is both expensive and toxic.² As a
20   result of the different advantages and disadvantages that these elements impart, there
21   is strong interest in determining the composition that obtains the optimal cathode
22   performance. The alloy lithium nickel manganese cobalt oxide ($\text{Li}_x\text{Ni}_y\text{Mn}_z\text{Co}_{1-y-z}\text{O}_2$,
23   NMC) attempts to balance these competing effects: in particular, NMC materials with
24   compositions of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ have been widely
25   investigated.²⁻⁴ However, demands for higher energy density have led to the

1 exploration of new compositions with even higher capacity, but which still guarantee
2 the safe usage.

3 Ni-rich cathode materials generally have higher energy density. However,
4 when in a charged state, the Ni^{4+} ions are easily reduced when exposed to elevated
5 temperatures. Consequently, because of this thermodynamic instability, a series of
6 phase transitions occurs with increasing temperature: the layered $\text{R}\bar{3}\text{m}$ structure first
7 transitions to the disordered spinel structure ($\text{Fd}\bar{3}\text{m}$), and then finally to the rock-salt
8 ($\text{Fm}\bar{3}\text{m}$) structure.⁵ These phase transitions are accompanied by the evolution of
9 oxygen from the structure:⁶ this becomes a serious safety threat, as this oxygen can
10 react with the flammable electrolytes inside of the battery system, potentially
11 resulting in a catastrophic explosion. EVs that are intended to be powered by LIBs
12 will necessarily require substantially larger batteries than small appliances, and as a
13 result, the possibility of invoking unwanted hazardous reactions by accidental heat
14 exposure becomes higher and the effects of explosion become more substantial. These
15 facts motivate this study: it is critical to understanding how these cathode materials
16 respond to temperature increases.

17 There have been many attempts to optimize the composition of Ni-rich NMC
18 material such that they maintain both maximum energy density and thermal stability.
19 As a result, there have been many investigations of the structure of NMC materials as
20 a function of composition, primarily using x-ray based techniques such as x-ray
21 diffraction,⁶ and x-ray absorption spectroscopy.⁷ Bak *et al.*⁸ recently studied the
22 thermal stability of NMC materials using combined in-situ XRD and mass
23 spectroscopy, and demonstrated that specific phase transitions in Ni-rich NMC
24 materials lead to considerable release of oxygen from the structure.

1   These x-ray based techniques provide valuable information regarding the
2 overall thermal stability of NMC cathode materials: however, few studies have
3 investigated the changes that occur at the near-surface region of these materials, how
4 the reaction fronts proceed during charging or discharging, or how particle to particle
5 variations occur as a function of increasing temperature. Here, we take advantage of
6 real time transmission electron microscopy methods to investigate these issues during
7 thermal degradation of NMC materials with several different compositions. Bright
8 field (BF) images, selected area electron diffraction (SAED) patterns, and electron
9 energy loss (EEL) spectra from the oxygen K-edge and transition metal (TM: nickel,
10 manganese, cobalt) L-edges of charged NMC cathode materials are recorded from
11 individual particles as a function of increasing temperature. As the transition metal
12 content varies within the structure, the initial charge capacity and thermal stability are
13 highly affected: high Ni content provides a high initial charge capacity but has a
14 strong negative effect on the stability of the cathode, leading to abrupt structural
15 transitions at low temperatures. Statistical analysis for several particles is also
16 performed in order to examine particle-to-particle variation, which becomes
17 significant in NMC having a high Ni content. This study demonstrates that the
18 transition metal content has a strong impact on both the electrochemical properties
19 and the thermal stability of charged NMC materials.

21   **Experimental Details**

22   Commercially available lithium nickel manganese cobalt oxide –
23 $\text{Li}_x\text{Ni}_y\text{Mn}_z\text{Co}_{1-y-z}\text{O}_2$ with y and z of 0.8 and 0.1, 0.6 and 0.2, 0.4 and 0.3 (referred to as
24 NMC811, NMC622, NMC433, respectively) – were electrochemically delithiated at a
25 rate of C/10 using a galvanostatic condition with a cutoff voltage of 4.3 V. The

1 cathode part was prepared from a mixed slurry of 80 wt.% of active material (NMC),
2 10 wt.% of conducting agent (Denka Black) and 10 wt.% of polyvinylidene fluoride
3 (PVDF) binder in a n-methyl pyrrolidone (NMP) solvent. This slurry was then coated
4 onto an Al foil, which acted as a current collector. The cathode was incorporated with
5 Li metal as an anode, a Celgard separator, and an electrolyte of 1 M LiPF₆ dissolved
6 in ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate
7 (DMC) solvent (1:1:1 by volume) to assemble a 2032 type coin cell.

8 After reaching a potential of 4.3 V, the coin cells were disassembled, and the
9 cathode part was soaked in a pure DMC solution to remove the residual salts. Charged
10 NMC particles were obtained by abrading the Al foil for subsequent analysis.
11 Supersonic vibration was applied to ensure adequate dispersion of powder samples in
12 the pure DMC solution before dropping onto lacey carbon TEM grids. Sample
13 preparation and loading into a TEM sample holder were done in either an argon-filled
14 glove box or in a dry room to minimize the exposure of the samples to air and
15 moisture.

16 The thermal decomposition process was investigated in real time using a
17 Tecnai G² F20 (FEI) TEM at an accelerating voltage of 120 kV, with a 652 double-tilt
18 heating holder (Gatan), and temperatures ranging from room temperature (25 °C) to
19 400 °C. Electron energy loss (EEL) spectra were acquired using a Quantum 963 GIF
20 system (Gatan). EEL spectra were obtained in image-coupled TEM mode. A selected
21 area aperture was utilized to confine the signal from the areas of interest. The energy
22 resolution of the EEL spectrum – determined by measuring the full-width at half
23 maximum of the zero loss peak (ZLP) – was around 1 eV. The backgrounds of all
24 spectra were subtracted using the power law method embedded in Digital Micrograph
25 software (Gatan).

Results and Discussion

The average crystallographic structure of NMC as a function of composition was determined by x-ray diffraction before electrochemical charging. The result is shown in Figure S1(a). All NMC particles have α -NaFeO₂ layered structure with a Space Group of $R\bar{3}m$. The relative atomic ratio of nickel, manganese, and cobalt was investigated through the use of atomic absorption spectroscopy (AAS). As shown in Figure S1(b), the compositions of the transition metals broadly corresponded to the expected compositions.

Figure 1(a-c) BF images and (d-f) SAED patterns from pristine NMC811 at room temperature, 200 °C, and 400 °C, respectively. (g-j) EEL spectra of the oxygen K-edge, and Mn, Co, Ni L_{2,3} edges, respectively as a function of temperature. SAED patterns and EEL spectra were acquired from the areas indicated in the BF images.

The thermal stability of pristine (before charging) NMC samples is investigated as a reference. Figure 1 presents real-time bright field (BF) images, selected area electron diffraction patterns (SAED), the oxygen K-edge, and the TM (Mn, Co, Ni) L_{2,3} edges electron energy loss (EEL) edges acquired from NMC811 as a function of temperature. We chose to investigate NMC811 as the reference, as this

1 is suspected to be the most thermally unstable composition because of its high nickel
2 content. EEL spectra (which reflect the energy density of states above the Fermi
3 level)⁹ are used to examine the changes in the electronic structure of NMC samples
4 during heating. The oxygen K-edge EEL spectrum of lithium metal oxides (LiMO₂)
5 with the R $\bar{3}$ m layered structure is composed of two main peaks, including a pre-edge
6 peak at around 527~530 eV and a main peak at around 538.5~540 eV. The pre-edge
7 peak is attributed to the transition of electrons from the 1s core state to unoccupied 2p
8 states hybridized with 3d states in TMs.¹⁰ The main peak originates from a transition
9 of electrons from the 1s state to hybridized states of O 2p and metal 4sp states.¹¹ The
10 L_{2,3} edge of TMs is attributed to transitions from 2p states into the highly localized 3d
11 states near the Fermi level. The splitting of the L edge stems from the degeneracy of
12 the 2p states into 2p_{1/2} and 2p_{3/2} levels due to spin-orbit coupling.¹² We found that
13 uncharged NMC811 (no lithium extraction) maintained broadly constant
14 crystallographic and electronic structure, as well as general morphology upon heating
15 from room temperature to 400 °C. Additionally, the surface structure of pristine
16 NMC622 and 433 are also stable against additional heat, as presented in Figures S2
17 and S3, respectively.

Figure 2(a) Initial charge curve of NMC433, 622, 811 at a rate of C/10 with a cutoff voltage of 4.3 V (b) corresponding differential capacity vs. voltage curve.

Figure 2(a) shows the charge profiles of NMC433, 622, and 811 half-cells at a rate of C/10. 4.3 V is set as a cutoff voltage, as this voltage corresponds to the highest energy state of LIBs for normal operation in most applications. After the initial charge, the capacity of NMC433, 622, and 811 is 169.78, 205.72, and 213.26 mAh/g, respectively, confirming that the NMC with a higher Ni content can deliver a higher capacity when subjected to the same electrochemical testing conditions. At around 4.2 V, an additional plateau is observed for NMC811 and differential capacity vs. voltage curves [Fig. 2(b)] clearly show an additional peak near 4.2 V. This extra redox peak is known to be caused by a hexagonal two-phase reaction.^{13,14}

Figure 3 Modification in (a) the oxygen K-edge, (b) Mn (c) Co and (d) Ni $L_{2,3}$ edges EEL spectra of charged NMC811 with increasing temperature. (e), (f) BF image and SAED pattern of the area where the EEL spectra were obtained at room temperature and (g), (f) at 200 °C. (i) summary of changes in the EEL spectra with ΔE from the oxygen K-edge and the L_3/L_2 ratios of the three transition metals. SAED patterns and EEL spectra were acquired from the areas indicated in the BF images.

Figure 3 presents the thermal behavior of charged NMC811. Modifications in the electronic structure of the cathode material are apparent from the EEL spectra [oxygen K-edge, the Mn $L_{2,3}$, the Co $L_{2,3}$, and the Ni $L_{2,3}$ edges, shown in Fig. 3(a), (b), (c), (d), respectively]. As the temperature increases, a noticeable shift of the oxygen K-edge pre-edge peak to a higher energy loss is observed. In the case of the transition metal edges, an obvious change takes place in the intensity ratio of L_3 to L_2 during heating. Figure 3(i) summarizes the changes in the EEL spectra by describing a ΔE (the difference of the energy loss values at the highest point of pre-edge peak and main peak) for the oxygen K-edge and the L_3/L_2 intensity ratios for the transition

metals. Previous x-ray absorption near edge structure measurements (which can provide superior energy resolution than EELS) have demonstrated that the pre-edge of oxygen K-edge consists of three distinct peaks: a peak at 528.5 eV attributed to a transition of electrons from the $1s$ state to the hybridized O $2p$ -TM^{3+/4+} $3d$ orbitals, a peak at 531.8 eV originating from a transition of electrons from the $1s$ state to the hybridized state of O $2p$ -TM²⁺ $3d$ orbitals.¹¹ In the case of EELS, each peak in the pre-edge peak is difficult to resolve, but changes in the pre-edge can be expressed as a peak shift. Thus, a pre-edge peak shift to higher energy loss indicates a reduction of the TMs around the oxygen sites upon heating. This leads to a decrease of the ΔE values and thus, ΔE can be considered as a measure of the reduction of the transition metals around the oxygen sites.^{15,16} The white line intensity ratio (L_3/L_2) also reflects the valence of the transition metals:¹⁷ this ratio becomes higher during reduction for Mn,¹⁷ Co,¹⁸ and Ni ions.¹⁹ While the pristine NMC811 is thermally stable up to 400 °C (Figure 1), a major change in the electronic structure occurs at temperatures as low as 100 °C for the charged NMC811. A broad oxygen K-edge pre-edge peak at 100 °C indicates that a number of oxidation states of Ni, Mn, and Co coexist. Meanwhile, the higher values of the L_3/L_2 intensity ratio for both Ni and Co at 100 °C demonstrates that reduction of Ni and Co ions has already initiated. As a consequence, the partial reduction of Ni and Co contributes to form a number of O $2p$ -TM²⁺ $3d$ hybridized states, leading to O $1s \rightarrow 2p$ transitions with a broad energy loss range rather than a sharp peak. During further heating over 100 °C, the oxygen K-edge of charged NMC811 barely changes, while L_3/L_2 intensity ratios of Mn, Co, and Ni L edges continue to increase: this means that the TMs are continuously reduced with increasing temperature.

In addition to the observed modification of the electronic structure in charged

1 NMC811, both the morphology and the crystallographic structure also undergo
2 significant changes. An SAED pattern from the charged NMC811 at room
3 temperature [Fig. 3(f)] is indexed as the 0001 zone-axis of the layered structure with
4 faint spots from the 111 zone-axis of the disordered spinel structure. $\{10\bar{1}0\}$
5 reflections also appear in the SAED because of the presence of Li/TM substitutional
6 disorder within the $R\bar{3}m$ layered structure.²⁰ Strong reflections from the layered
7 structure along with faint spots from the spinel structure in the SAED indicate that the
8 original layered structure is mostly retained, even though there is an incipient phase
9 transition to the spinel at room temperature. A maximum temperature of 200 °C is
10 selected to compare the degree of evolution in the crystallographic structure among
11 the NMC cathode materials with different TM composition. At 200 °C – where
12 significant changes of electronic structures have already been found for charged
13 NMC811 based on the EEL spectra – the SAED pattern in Fig. 3(h) indicates a phase
14 transition to the rock-salt structure has already occurred, based on the fact that the
15 SAED pattern is consistent with the 111 zone-axis of rock-salt structure. Along with
16 the observed changes in the crystal structure, porosity arises at the surface of charged
17 NMC811 [Fig. 3(g)] as a result of the oxygen release that accompanies the phase
18 transitions.²¹ As the phase transformations occur concomitant with a release of
19 oxygen gas from the structure, these structural transitions are irreversible.²² Therefore,
20 substantial changes in both the electronic and crystallographic structure, as well as
21 morphology have already occurred below 200 °C at the surface of NMC811.
22 Morphological changes and SAED patterns taken as the sample temperature increases
23 to 400 °C are shown in Figures S4, S5.

Figure 4 Modification in the EEL spectra of the (a) oxygen K-edge, (b) Mn (c) Co and (d) Ni L_{2,3} edges of charged NMC622 with increasing temperature. (e), (f) BF image and SAED pattern from the area where the EEL spectra were obtained at room temperature and (g), (f) at 200 °C. (i) summary of changes in EEL spectra expressed as ΔE of oxygen K-edge and L₃/L₂ ratios of transition metals. SAED patterns and EEL spectra were acquired indicated areas in BF images.

The changes that occur in charged NMC622 upon heating are presented in Figure 4. Although changes in the structure of NMC811 are found to initiate at temperatures as low as 100 °C, the onset of changes in NMC622 – as evidenced by changes in the EEL spectra – occurs at significantly higher temperatures. This is shown by the changes that occur in the L₃/L₂ ratios [Fig. 4(i)]: the spectra indicate that the Ni ions in charged NMC622 are the first TM component to reduce (near 200 °C), followed by reduction of both Mn and Co ions at higher temperatures. In addition to the L₃/L₂ ratios, the oxidation state of the transition metals can be

1 determined by the shape of $L_{2,3}$ edge.²³ This shape change is very distinct in the Mn
2 L_3 edge in Fig 4(b). The L_3 edge of Mn has a small shoulder at the lower energy loss
3 side of the peak at room temperature. However, as the temperature increases, there is
4 a significant change in this lower energy loss feature: it becomes larger, leading to a
5 increasing shift of the main peak toward the shoulder until the main peak shifts all the
6 way to the original position of the shoulder at 350 °C. This indicates that most of Mn
7 ions have become reduced.²⁴ This trend is most obvious in the Mn L_3 edge, however
8 the shapes of Co and Ni L_3 edges change in the same way. Along with the reduction
9 of the TM, the pre-edge of the oxygen K-edge is also modified, showing an abrupt
10 decrease in ΔE value from 250 °C to 300 °C.

11 SAEDs of charged NMC622 show similar trends as the EELS spectra, with
12 delayed thermal degradation in NMC622 compared to NMC811. After the initial
13 charge, the crystallographic structure remains the layered structure at room
14 temperature [Fig. 4(f)]; however, upon heating to 200 °C a phase transition to spinel
15 initiates, resulting in an SAED showing mixed phases of layered and spinel [Fig. 4(g)].
16 The presences of strong and distinct diffraction spots which originate from the spinel
17 structure indicate that a considerable amount of spinel structure has already appeared.
18 Additionally, based on the EELS results in Figure 4(i), we can conclude that very
19 little of the material has undergone a phase transition to the rock-salt structure in the
20 charged NMC622, because the valence of transition metals is relatively unaltered up
21 to 200 °C. It should be noted that in the case of charged NMC811 the phase transition
22 to rock-salt has already occurred and is accompanied by significant reduction of the
23 TMs at temperatures as low as 200 °C.

Figure 5 Modification in (a) oxygen K-edge, (b) Mn (c) Co (d) Ni $L_{2,3}$ edges EEL spectra of charged NMC433 with increasing temperature. (e), (f) BF image and SAED of the area where EEL spectra obtained at room temperature and (g), (f) at 200 °C. (i) summary of changes in EEL spectra with ΔE of oxygen K-edge and L_3/L_2 ratios of transition metals. SAED patterns and EEL spectra were acquired indicated areas in BF images.

Figure 5 shows EEL spectra, BF images and SAEDs from charged NMC433 during heating. We can discern noticeable electronic structure changes from 250 °C to 300 °C with a drop in ΔE of the oxygen K-edge and an increase in the L_3/L_2 ratio of the Ni L edge. Further decrease in ΔE is observed concomitant with an increase in the L_3/L_2 ratio of Co upon heating to higher temperatures. The SAED pattern from NMC433 at 200 °C in Figure 5(h) consists of distinct spots from the 0001 zone-axis of the layered structure and additional weak reflections from the 111 zone-axis of the spinel structure, indicating that NMC433 is the most robust composition against phase

1 transitions during heating. Based on these results, it is clear that there is a direct
2 correlation between thermal stability and TM valence in NMC cathode materials.

3 Our previous work regarding the thermal stability of one promising cathode
4 materials ($\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ - NCA) demonstrates that there is a huge particle-to-
5 particle variation in the onset temperature of thermal decomposition even at the same
6 state of charge.¹⁶ That work indicated that the investigation of particle-to-particle
7 variations may be of significant importance to ensuring the safety of lithium ion
8 batteries. Thus, five particles of each NMC composition were selected to further
9 examine the thermal stability of NMC cathode materials. Particle-to-particle
10 variations in the EEL spectra of pristine NMC materials (before charge) of each
11 composition during heating are shown as a reference in Figure S6, and almost no
12 changes are observed among particles. Figure 6 presents changes in the ΔE of the
13 oxygen K-edges measured from 5 different particles of each composition as a
14 function of increasing temperature. For NMC433 and 622, all charged particles
15 present a similar tendency to show a gradual decrease in ΔE over 200 °C, indicating
16 that particle-to-particle variations are not significant. On the contrary, we find
17 significant particle-to-particle variation in the ΔE of charged NMC 811: one particle
18 [the bottom of Fig. 6(c)] shows a comparable ΔE transition to NMC 433 or 622, but
19 most particles have an abrupt drop of ΔE around 100 °C, indicating that significant
20 structural evolution has occurred even at 100 °C. Notably, this is a low enough
21 temperature to be reached in normal operation.

Figure 6 Particle-to-particle variations in oxygen K-edge of charged NMC cathode materials expressed by ΔE with increasing temperature. In some cases, an additional pre-edge peak was observed with increasing temperature; the figure indicates this by showing those instances with hollow symbols of the same shape.

Figure 7 Particle-to-particle variations in transition metal L edges of charged NMC cathode materials expressed by L_3/L_2 intensity ratios with increasing temperature.

Changes in the L_3/L_2 intensity ratios of the TM upon heating are also monitored, from the same 5 particles that were used to investigate the changes in ΔE in Fig. 6. Figure 7 summarizes the results by presenting an average and standard deviation of the L_3/L_2 ratios of Mn, Co, Ni L edges acquired from individual particles. The reduction of the TM starts with nickel upon heating, showing a sharp increase in L_3/L_2 at 250, 200, and 100°C for the charged NMC433, 622, and 811, respectively. Co and then Mn ions undergo the reduction process at higher temperatures. Overall the changes in the TM L edges are well matched with those seen in the oxygen K-edge.

From our results, it is clear that the different thermal behavior of NMC materials is directly related to the relative TM composition ratios between Ni, Mn,

1 and Co. For the case of pristine $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathode materials, the valence of
 2 each TM is known to be Ni^{2+} , Mn^{4+} , Co^{+3} .³ By controlling the relative composition of
 3 the TMs, the overall oxidation states of TMs can be adjusted to maintain a total
 4 oxidation state of the TM contribution as +3. Figure S7 presents the L_3/L_2 intensity
 5 ratio of each TM of pristine NMC materials at room temperature. As Ni contents
 6 become larger, the L_3/L_2 intensity ratios of Ni and Co become lower, indicating that
 7 both ions are oxidized, but the L_3/L_2 intensity ratio of Mn becomes larger (in the case
 8 of NMC811), suggesting that a reduction of Mn ions occurs in NMC811 to maintain
 9 overall charge neutrality. First principle calculations have demonstrated that $\text{Ni}^{2+}/\text{Ni}^{3+}$
 10 and $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox couples occur in the range of $1/3 \leq x \leq 1$, and thus a $\text{Co}^{3+}/\text{Co}^{4+}$
 11 redox couple occurs in the range of $0 \leq x \leq 1/3$ in $\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathode
 12 materials.²⁵ Ni-rich NMC materials have oxidized Ni ions even before they are
 13 charged; thus, the probability of having Ni^{4+} becomes higher as a result of Ni redox
 14 during lithium removal. This means that the Ni^{4+} ions are thermodynamically unstable
 15 and are readily reduced to more stable forms during heating. The net result is that Ni-
 16 rich NMC cathode materials are significantly more thermally unstable.

17 It is intriguing that NMC811 exhibits significantly worse thermal stability than
 18 NMC622, especially when considering the smaller difference that is seen when
 19 comparing NMC433 and 622. Even though the L_3/L_2 intensity ratio of Ni (i.e. the
 20 valence of the Ni ions) in the pristine NMC622 and 811 are comparable, the 811
 21 composition is much more susceptible to phase transitions upon heating, showing
 22 instantaneous changes in electronic structures at 100 °C. We suspect that this
 23 particular thermal instability is attributed to the observation of the additional redox
 24 signature that is seen at around 4.2 V in the differential capacity vs. voltage curve for
 25 NMC811 in Figure 2(b). This redox peak correlates with a multi-phase transition

1 wherein the hexagonal structure exhibits a sharp drop in the c lattice parameter,^{13,26}
 2 leading to a noticeable volume contraction. This volume contraction during the initial
 3 charge has been considered as the prime factor that leads to structural instability.¹⁴
 4 Our results here suggest a direct correlation between this phase change and the
 5 considerable modifications we see in the crystallographic and electronic structure as
 6 well as the morphology of charged NMC811 at such low temperatures (100 °C).

7
 8 **Figure 8 Scheme that summarizes this work.**

9 Figure 8 summarizes our findings. We exploited electron microscope to
 10 investigate thermal degradation occurring near surface of NMC cathode materials.
 11 The properties of cathode materials can be directly controlled by the choice of
 12 transition metal ratio in the layered structure: high Mn content (representatively,
 13 NMC433) offers improved thermal stability in the charged state but at the expense of
 14 overall capacity. High Ni content (NMC811) provides high capacity but leads to poor
 15 thermal stability. Thus, optimizing the composition of transition metal ions is an
 16 effective way to achieve both high capacity and enhanced stability; from our results
 17 NMC622 represents a good compromise with its fairly high capacity, and relative
 18 thermal stability.

Conclusion

Analytical characterization with real time transmission electron microscopy has been exploited to investigate the thermal degradation of $\text{Li}_x\text{Ni}_y\text{Mn}_z\text{Co}_{1-y-z}\text{O}_2$ materials with compositions of NMC433, 622, 811. Changes in the transition metal content strongly affect both the initial charge capacity and the thermal stability: high Ni content leads to high capacity but at the expense of thermal stability. Investigation of particle-to-particle variation in structure and morphology indicate that these are significant in the high Ni content alloy (NMC811). We find that the poor thermal stability of NMC811 is caused by the relatively large percentage of Ni^{4+} ions present in the charged state as well as the additional redox reaction that occurs at around 4.2 V. Among the compositions we studied in this work, NMC622 has well balanced properties, having both high storage capacity and good thermal stability. It may be possible that the addition of another element in the alloy could provide an additional degree of freedom to optimize the electrochemical properties of cathode materials. This work provides a systematic approach to investigate the effects of each element on the overall electrochemical properties of electrode materials.

“Supporting Information Available: XRD pattern and AAS analysis of pristine NMC materials, BF/ SAED/ EEL spectra of pristine NMC622, 433 materials, BF/ SAED of charged NMC particles up to 400 °C, particle-to-particle variation in ΔE of oxygen K-edge and L_3/L_2 ratios of TM of pristine NMC materials during heating, L_3/L_2 ratio of pristine NMC materials at room temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.”

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1 **Figure captions**

2 **Figure 1.** (a~c) BF images and (d~f) SAED patterns from pristine NMC811 at room
3 temperature, 200 °C, and 400 °C, respectively. (g~j) EEL spectra of the oxygen K-
4 edge, and Mn, Co, Ni L_{2,3} edges, respectively as a function of temperature. SAED
5 patterns and EEL spectra were acquired from the areas indicated in the BF
6 images.

7 **Figure 2.** (a) Initial charge curve of NMC433, 622, 811 at a rate of C/10 with a cutoff
8 voltage of 4.3 V (b) corresponding differential capacity vs. voltage curve.

9 **Figure 3.** Modification in (a) the oxygen K-edge, (b) Mn (c) Co and (d) Ni L_{2,3} edges
10 EEL spectra of charged NMC811 with increasing temperature. (e), (f) BF image and
11 SAED pattern of the area where the EEL spectra were obtained at room temperature
12 and (g), (f) at 200 °C. (i) summary of changes in the EEL spectra with ΔE from the
13 oxygen K-edge and the L₃/L₂ ratios of the three transition metals. SAED patterns and
14 EEL spectra were acquired from the areas indicated in the BF images.

15 **Figure 4.** Modification in the EEL spectra of the (a) oxygen K-edge, (b) Mn (c) Co
16 and (d) Ni L_{2,3} edges of charged NMC622 with increasing temperature. (e), (f) BF
17 image and SAED pattern from the area where the EEL spectra were obtained at room
18 temperature and (g), (f) at 200 °C. (i) summary of changes in EEL spectra expressed
19 as ΔE of oxygen K-edge and L₃/L₂ ratios of transition metals. SAED patterns and
20 EEL spectra were acquired indicated areas in BF images.

21 **Figure 5.** Modification in (a) oxygen K-edge, (b) Mn (c) Co (d) Ni L_{2,3} edges EEL
22 spectra of charged NMC433 with increasing temperature. (e), (f) BF image and
23 SAED of the area where EEL spectra obtained at room temperature and (g), (f) at
24 200 °C. (i) summary of changes in EEL spectra with ΔE of oxygen K-edge and L₃/L₂
25 ratios of transition metals. SAED patterns and EEL spectra were acquired indicated

1 areas in BF images.

2 **Figure 6.** Particle-to-particle variations in oxygen K-edge of charged NMC cathode
3 materials expressed by ΔE with increasing temperature. In some cases, an additional
4 pre-edge peak was observed with increasing temperature; the figure indicates this by
5 showing those instances with hollow symbols of the same shape.

6 **Figure 7.** Particle-to-particle variations in transition metal L edges of charged NMC
7 cathode materials expressed by L_3/L_2 intensity ratios with increasing temperature.

8 **Figure 8.** Scheme that summarizes this work.

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