



Role of transition metal ratio on electrochemical and thermal properties of $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ layered materials for lithium-ion batteries

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Abstract: To reveal how the performance of $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM) changes as a function of transition metal (TM) composition, the effect of TM ratio on the structure, morphology, electrochemical performance and thermal behavior of different NCMs was systematically investigated. Increasing Ni content leads to higher reversible capacity but worse rate capability and cycling stability. Inhibited kinetics of Li^+ and poor electronic conductivity cause major capacity loss in Ni-rich NCMs. Comparison of thermal behaviors was carried out via in-situ and ex-situ micro-calorimetry. With the decrease of Ni content, the thermal stability is significantly improved. The oxygen release related to phase transitions was evaluated based on Li residuals in delithiated NCMs, which verifies that Ni-rich materials exhibit severer structural deterioration, lower onset temperature and more heat release. Comprehensive characterization identifies that $\text{LiNi}_{0.5}\text{Co}_{0.3}\text{Mn}_{0.2}\text{O}_2$ strikes a well-balanced combination of electrochemical performance and safety features.

Key words: lithium–nickel–cobalt manganese oxide; thermal stability; structural evolution; ternary material; lithium ion battery safety

1 Introduction

To address global carbon emissions, lithium-ion batteries (LIBs) have been introduced as an ideal carrier of green energy for hybrid electric vehicles (HEVs) and electric vehicles (EVs) due to their high reversible capacity, good rate capability and low cost [1–3]. Among the promising cathode materials, $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM) layered material makes full use of the virtues of three metals and is touted for greater capacity at lower cost [4,5]. Each transition metal (TM) in NCM has a distinct impact on its overall performance. Thus, ternary materials behave

differently as the proportion of TMs varies [6–8]. For instance, an increased Ni ratio ensures high energy density due to the great $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple, but severe structural deterioration and limited stability. High delithiation or heating further exacerbates the thermal instability due to the oxygen release, which is significantly depended on Ni content. Indeed, the lack of safety remains the primary obstacle to widespread implementation of Ni-rich NCMs [9,10]. Therefore, an in-depth investigation of the effect of TM proportion on the electrochemical performance and thermal behaviors of NCMs is critical to improving the battery performance while maintaining the thermal safety.

Considerable efforts have been put forth to

investigate the structural changes and decay mechanisms of different nickel–cobalt manganese (NCM) materials, utilizing a range of techniques including X-ray diffraction (XRD) [11,12], scanning electron microscopy (SEM) [13], transmission electron microscopy (TEM) [5,14], nuclear magnetic resonance (NMR) [11,15] measurement and X-ray absorption spectroscopy (XAS) [7,16]. KO et al [5] investigated the TM content of degraded NCM materials and determined the microstructural origin of the dissolution of TMs through TEM coupled with X-ray energy dispersive spectroscopy. ZHENG et al [17] used XRD to discuss the relation between structural change and capacity degradation. Meanwhile, NMR tests were carried out to detect the Li chemical environment. However, the majority of research has been focused on individual NCM material and its electrochemical evolution without exploring the impact of varying TM ratios on both battery performance and thermal characteristics. Moreover, there are few reports that systematically elucidate the relationship among Ni ratios, battery performance and thermal characteristics.

In this study, NCM ternary materials including $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM111), $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523), $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622) and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811) are systematically investigated from the standpoint of structure, morphology, electrochemical performance and thermal behavior. The thermal safety consisting of dynamic heat generation of NCM half-cells and thermal stability of fully-charged NCM materials are quantitatively determined via in-situ and ex-situ micro-calorimetry. The oxygen release of delithiated NCMs are also evaluated by combining experimental and theoretical analysis.

2 Experimental

2.1 Sample preparation

Coin cells of CR2032 type were utilized to regulate the lithium content in the NCM materials. The cathode electrodes were fabricated from NCMs supplied by Cyber Electrochemical Materials Co., polyvinylidene fluoride (PVDF), and acetylene black, all in a mass ratio of 8:1:1. The cathode electrodes had an average mass loading of $(4.28 \pm 0.03) \text{ mg/cm}^2$ and a thickness of 400 μm . A sheet of porous polypropylene membrane was

utilized as a separator. Lithium plates were used as the negative electrode. All materials were soaked in the electrolyte solution of 1.0 mol/L LiPF_6 /ethylene carbonate (EC) and diethyl carbonate (DEC) in a mass ratio of 1:1.

2.2 Characterization

The surface morphology of NCM materials was observed using SEM (FEI Sirion200). After charging to a specific voltage limit, the cells were disassembled in an argon-filled glovebox (Vigor SG2400/750TS). The charged cathodes were thoroughly washed with dimethyl carbonate (DMC, Aladdin, 99.9%) to remove residual lithium salt. Then, the crystal structure of cathode particles scraped from current collector was investigated by the XRD (Cu K_{α} , MXPAAHF) instrument in the 2θ range of 10° – 110° with a step of 0.02° . And the Rietveld Refinement was carried out using GSAS software [18]. The accurate content of TM elements in cathode was evaluated by inductively coupled plasma source mass spectrometer (ICP-MS, PlasmaQuad 3, USA). The Li-containing residuals (mainly Li_2CO_3 and LiOH) on the particle surface were quantitatively measured through titration with dual indicator method (bromocresol green-methyl red indicator and phenolphthalein indicator).

2.3 Electrochemical test

A Neware battery cycler was initially employed for pre-cycling at a current rate of $0.2C$ prior to other tests. Electrochemical measurements were then conducted in constant current modes based on a charge and discharge voltage range of 2.8–4.2 V. The experimental protocol employed current rates of $0.5C$, $0.75C$ and $1.0C$ for the dynamic heat flow test. The rate capability of NCM materials was evaluated at room temperature (RT). Electrochemical impedance spectroscopy (EIS) was conducted by using a CHI 604A electrochemical workstation with an amplitude of 5 mV over a frequency range from 10^5 to 10^{-2} Hz.

Powder electrical resistivity measurements were conducted by using an in-house-built pellet press. 100 mg of powder was placed between two stainless steel pressing rods that were designed to fit into a Teflon-lined cylindrical sleeve. The rods have a diameter of 1 cm and a manual hydraulic press was utilized to apply pressure. The bulk electrical resistance of the pressed powder was

recorded based on true pressure using a 4-wire measurement and a Keithley–2700 multimeter. Each measurement was performed three times, and the average resistance was calculated.

2.4 In-situ heat generation measurement

The dynamic heat generation data were collected using a multiple mode calorimetry (Netzsch, MMC 274 Nexus, German) equipped with a high-temperature coin cell module (HTCC). By coupling this device with a battery cycler, real-time cycling and corresponding heat generation data were monitored with high accuracy and precision. Differential signals from the sensor were obtained by comparing the measurement with a sample and RMS noise of $10\text{ }\mu\text{W}$. To simulate normal working conditions, an isothermal mode of $35\text{ }^{\circ}\text{C}$ was selected.

2.5 Thermal stability at high temperature

The selection of cathode materials significantly impacts battery safety performance, emphasizing the importance of investigating thermal stability. To examine this, differential scanning calorimetry-thermal gravimetric analysis (Netzsch, DSC-TGA, German) is one of the most popular methods. To prepare for the thermal testing, cells with different NCM materials were charged to 4.2 V with a constant current–constant voltage charging protocol and a $0.02C$ cut-off current. The

electrode powder was separated from the aluminum current collector and rinsed with DMC solvent in a glove box. Then, the thermal stability tests were conducted in a nitrogen atmosphere from RT to $600\text{ }^{\circ}\text{C}$ at a rate of $5\text{ }^{\circ}\text{C}/\text{min}$. Each NCM sample in the test had the mass of $3\text{--}5\text{ mg}$. The entire test process is summarized in Fig. S1 of Supplementary materials (SM).

3 Results and discussion

3.1 Morphology, structure and composition of NCM materials

The surface morphology analysis was first conducted to determine the particle distribution of original powders. Figure 1 illustrates the SEM images of commercial NCM materials. The particle sizes were characterized using Image J software, as displayed in the inserts. High magnification SEM images for the surface morphology are shown in Fig. S2 of SM. In general, smaller particles provide a larger surface area for the electrode–electrolyte interaction, resulting in shorter Li^+ diffusion path and higher current rates during Li insertion/extraction. It can be seen that materials with different element proportions display similar mean particle diameters, ranging from 4 to $10\text{ }\mu\text{m}$. Previous research [19] indicated that the current density within the $0.2C\text{--}2C$ range has little impact on the energy density when the secondary particle

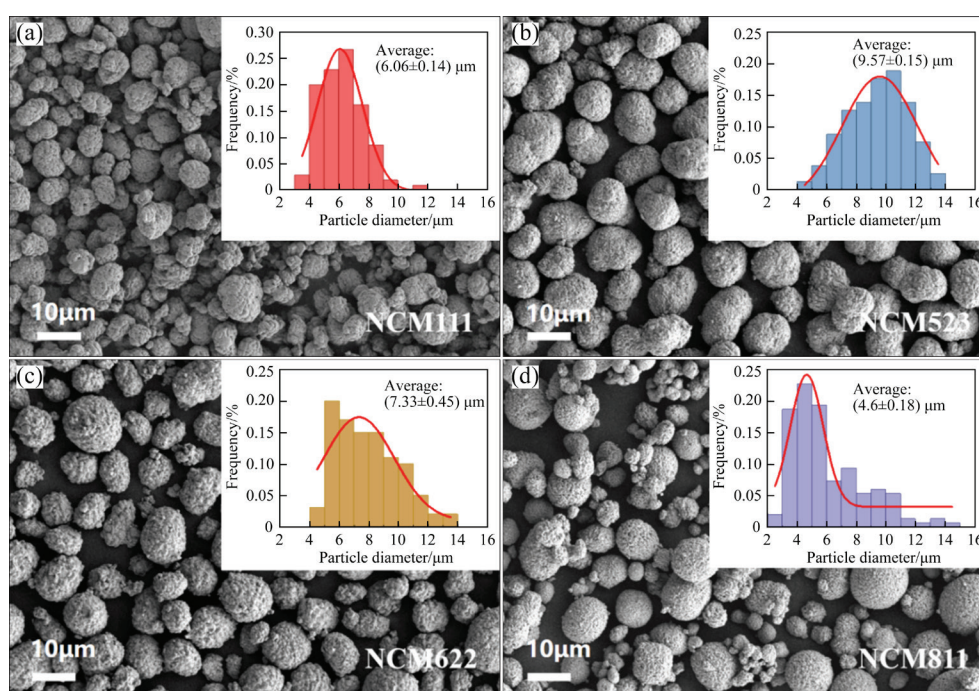


Fig. 1 SEM images and particle size distribution of NCM111 (a), NCM523 (b), NCM622 (c), and NCM811 (d)

size is in the range of several micrometers. Regarding primary particles, NCM111 displays the largest particle size, followed by NCM523 and NCM622, and NCM811 shows the smallest particle size (see Fig. S2 in SM). When the secondary particle sizes are similar, smaller primary particles cause more grain boundaries and greater reaction with the electrolyte.

Figure 2 displays the XRD patterns of the four materials, all of which reveal a hexagonal-type structure group ($R\bar{3}m$). A comparison of the crystal structures is made by obtaining the a - and c -axis lattice parameters with standard errors of different NCMs from Rietveld refinement (Table 1). In Table 1, R_{wp} represents the quality of refinement. All R_{wp} values are less than 5%, indicating the high reliability of fit results. The low radius of Co and Mn ions results in the contraction of the a -axis, while the c -axis slightly expands as the Ni content decreases. From a valence state perspective in NCM, an increase in the tetravalent Mn content enlarges the ratio of $Ni^{2+}/(Ni^{2+}+Ni^{3+})$ to maintain charge conservation, causing c parameter to increase accordingly due to the large radius of Ni^{2+} . Additionally, the weakening of the Ni—O bond (spontaneous conversion of Ni^{3+} to Ni^{2+}) leads to the formation of active O^{2-} [20] and consumption of the surface Li^+ . As a result, the internal Li^+ migrates to the surface, inducing cation mixing and inert Ni^{2+} (NiO). Due to their similar radii, the mixing of cations is primarily manifested in the confusion of Li^+ and Ni^{2+} . Therefore, atomic occupancy is refined based on the XRD patterns (Table 1). The results indicate that the Ni present in Li sites increases rapidly with increasing Ni content in NCMs. This could be due to the fact that most Ni existed as Ni^{2+} , which is similar to Li^+ in terms of ion radius. Moreover, more Li is present on the surface, leading to significant phase transformation.

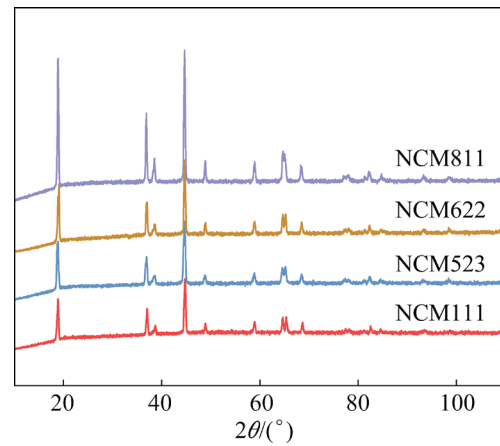


Fig. 2 XRD patterns of NCM materials with different TM proportions

This result is consistent with a previous opinion that the Ni/Li exchange is most likely to occur in NMC materials with a higher Ni content [21].

To further support this hypothesis, we discussed the relationship between Li residuals on the surface and the Ni content. Mass fractions of Li_2CO_3 and $LiOH$ ($w(Li_2CO_3)$ and $w(LiOH)$) in Table S1 of SM show that free Li on the surface increases significantly in Ni-rich NCM, resulting in more pronounced surface reconstruction or side reactions with the electrolyte, which is considered responsible for the capacity loss in the first cycle. Furthermore, the specific composition of TM elements is measured by ICP-MS, and the results shown in Table S2 of SM are found to be close to the expected values.

3.2 Electrochemical performance

As one of the main materials of power batteries, NCMs have an essential function in influencing the electrochemical performance of the battery. In this study, the electrochemical properties of various NCM materials were evaluated through

Table 1 Rietveld Refinement results of different NCMs

Material	Occupancy/%				$a/\text{\AA}$	$c/\text{\AA}$	$R_{wp}/\%$
	Li_{3b}	Ni_{3b}	Ni_{3a}	Li_{3a}			
NCM111	0.9511	0.0489	0.2845	0.0489	2.8726(1)	14.2907(8)	4.6
NCM523	0.9435	0.0565	0.4435	0.0565	2.8759(1)	14.2694(9)	4.5
NCM622	0.9412	0.0588	0.5412	0.0588	2.8797(1)	14.2661(6)	4.87
NCM811	0.9245	0.0755	0.7245	0.0755	2.8835(1)	14.2608(6)	3.83

$$n(Li_{3b})+n(Ni_{3b})=1; n(Ni_{3a})+n(Li_{3a})=1-n(Co_{3a})-n(Mn_{3a}); n(Ni_{3b})=n(Li_{3a})$$

the assembly of CR2032-type coin cells. The curves of the first and second cycles between 2.8 and 4.2 V are presented in Figs. 3(a) and (b), respectively. Typically, the Ni content in NCMs has a dominant role in boosting the capacity density because almost all the reversible capacities are associated with the $\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$ redox reaction within this voltage range [22]. Consequently, Ni-rich NCM materials demonstrate a higher discharge capacity, fluctuating

from 146 to 172 $\text{mA}\cdot\text{h}/\text{g}$ with an increase in Ni ratio from 1/3 to 0.8. Table 2 reveals the coulombic efficiency (CE) for the initial and second cycle of NCM materials. The values in the first cycle gradually decline as Ni content increases, manifesting severer capacity loss in the first charging process, whereas the subsequent cycles achieve a CE close to 100% (Figs. 3(c–f)). The capacity loss may occur due to multiple factors,

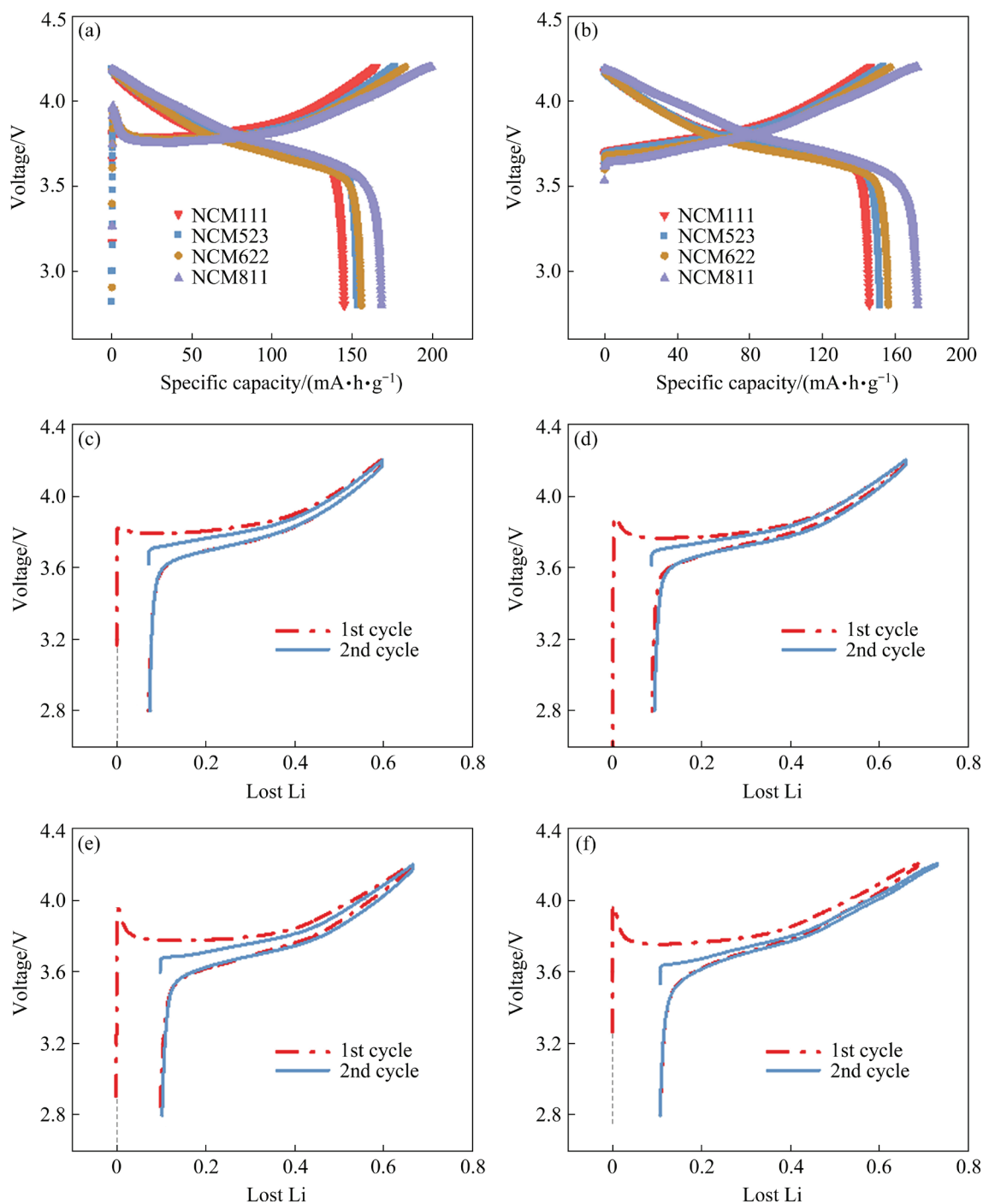


Fig. 3 Charge/discharge profiles of NCMs in the first cycle (a) and the second cycle (b), and comparison of two cycles in NCM111 (c), NCM523 (d), NCM622 (e) and NCM811 (f) (Lost Li is $1-n$ in $\text{Li}_n\text{Ni}_x\text{Co}_y\text{Mn}_z\text{O}_2$)

Table 2 Coulombic efficiency (CE) of the first and second cycle of NCMs

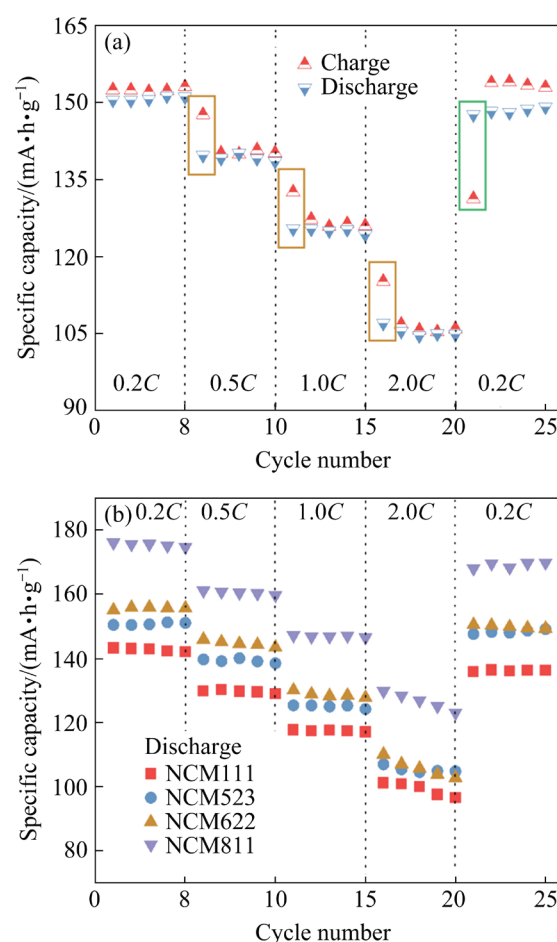
Material	CE/%	
	1st cycle	2nd cycle
NCM111	87.9	99.7
NCM523	86.4	99.5
NCM622	86.3	99.4
NCM811	85.7	99.5

including the parasitic reaction at the electrode–electrolyte interface, irreversible phase change on the particle surface, and the inhibited kinetic process of Li^+ [23,24]. Although the first two factors are irreversible, the loss caused by the alteration of dynamic characteristics is discovered to be recoverable, accounting for more than 60% of capacity loss. Adjusting the charge/discharge rate or implementing a constant-voltage mode is expected to recover this portion of the loss.

Rate performance of NCM materials shown in Figs. 4(a) and (b) conclusively demonstrates that the discharge capacity always decreases as the current rate increases. Taking NCM523 for example, a larger current rate leads to a higher over-potential in the beginning, causing an earlier reach for cut-off voltage and a decline in capacity. Furthermore, polarization in lithiation process contributes to a more distinct drop in discharge capacity. However, decreasing the current rate from 2.0C to 0.2C results in a higher discharge capacity than the charge capacity (CE>100% inside the green boxes), indicating that the lithium lost in previous cycles is recovered with the decrease in current rate (CE<100% inside the yellow boxes). Additionally, Fig. 4(b) shows that the rate capabilities of different NCMs are progressively deteriorated with increasing current rate, but gradually recover when the current decreases.

Electronic conductivity is considered to be related to the element ratio and size of particles in NCM materials. In the three metallic elements, Co as a crucial element in NCM chemistry, has an average intermediate oxidation state that fosters an itinerant electron system, leading to strong electronic correlation and polaronic effects. As Co content increases, contact impedance reduces, improving electronic conductivity. Furthermore, smaller secondary particle sizes enhance the rate performance by bringing active material and

conductive agent into closer contact. Based on SEM results, the particle diameters of NCMs are comparable. Therefore, NCM111 is likely to exhibit the best rate performance due to the higher cobalt content, whereas that of the NCM811 is the worst. However, NCM622 performs worse than NCM811, which has the highest Ni content. Figures 1(c) and (d) show that most particles of NCM622 are larger than those of NCM811. For NCMs with low Co content, particle size may have a great influence on electronic conductivity. Powder resistivity tests with an in-house-built pellet press (Fig. S3 in SM) show that NCM622 presents the highest resistance, aligning with its inferior electronic conductivity and rate performance well.

**Fig. 4** Rate capability of NCM523 (a) and all NCM materials (b)

To better illustrate the redox behavior of NCM materials during charge and discharge, the corresponding differential capacity vs voltage profiles (dQ/dV) are obtained in Fig. 5. It is observed that NCM111 exhibits two prominent redox peaks, occurring at 3.78 V during charge and

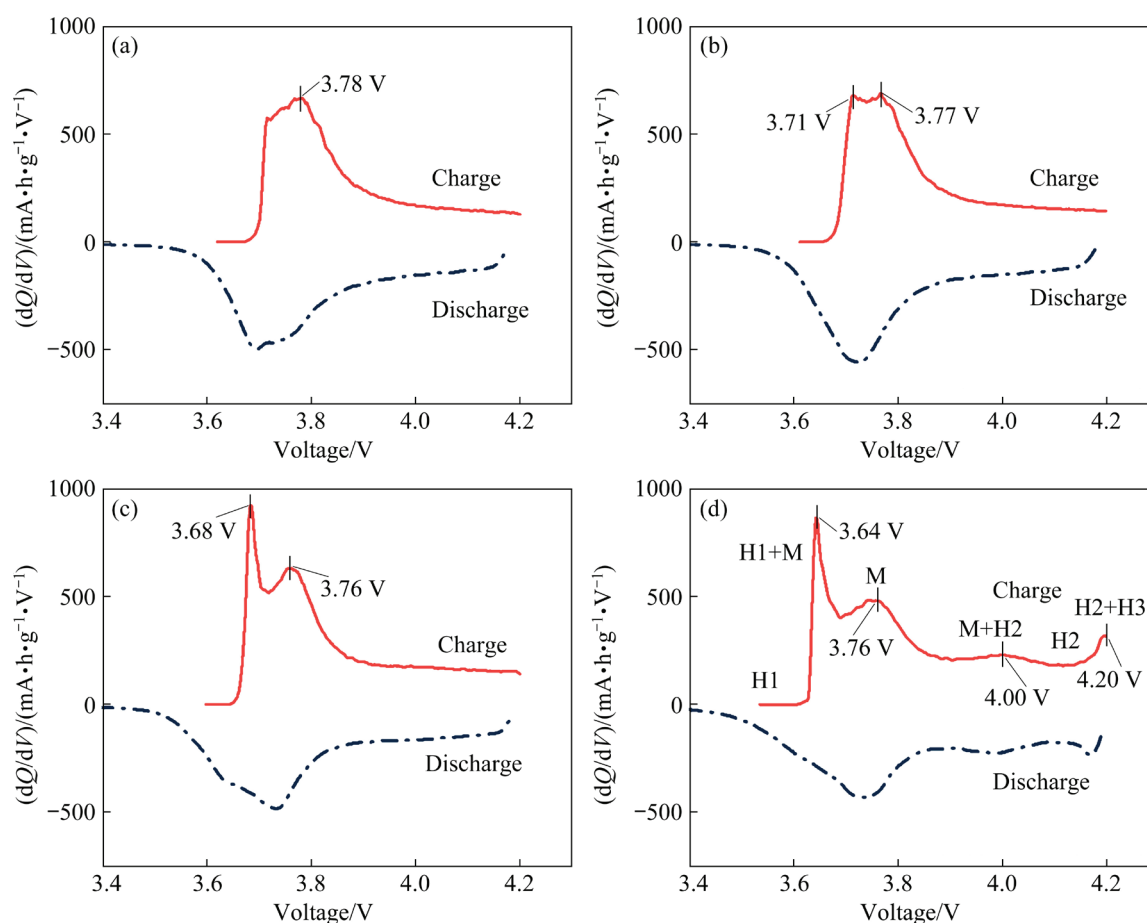


Fig. 5 Differential capacity versus voltage curves of NCM111 (a), NCM523 (b), NCM622 (c), and NCM811 (d) (H and M represent hexagonal and monoclinic, respectively)

3.70 V during discharge, respectively. These peaks indicate the main plateaus in the cycling process of NCM111. However, as the Ni content increases from one-third to half, a new oxidation plateau arises around 3.71 V, which moves to lower potentials with further increment in Ni content. This transition can be attributed to the shift from hexagonal to monoclinic, encouraged by the high content of Ni. The NCM811 displays more complex redox behaviors, as shown in Fig. 5(d), and these alterations are highly depended on the subsequent phase transitions. In addition, the structural conversion from H2 to H3 causes swift volume contraction, leading to accelerated capacity fading, whereas NCMs with lower Ni content do not undergo this adverse process, hence exhibiting greater stability and reversibility.

3.3 Dynamic heat generation

NCMs are commonly used in power batteries for transportation due to their superior electrochemical performance. However, besides electro-

chemical performance, thermal safety is also a crucial aspect that requires further development and attention. Heat generation is a significant safety concern that can be controlled with the help of thermal management system (TMS). In order to effectively build up TMS, it is essential to apply accurate experimental data to validate the model. Therefore, we monitored the dynamic heat flow of half-cells to evaluate the impact of Ni content on in-situ thermal behaviors. Figure 6 illustrates the results of NCMs in charge and discharge at current rates of 0.5C, 0.75C and 1.0C. The dynamic heat flow shows that higher currents result in an expanded heat flux [25]. Regardless of the proportion of TM elements, when using different currents, the results exhibit similar line shapes but differ in magnitude. The major contribution to the accumulation of internal heat stems from Joule heat and reversible heat, as both of them are proportional to current changes. Joule heat polarization is considered as the dominant factor here. As the current increases, the charge transfer resistance on the surface

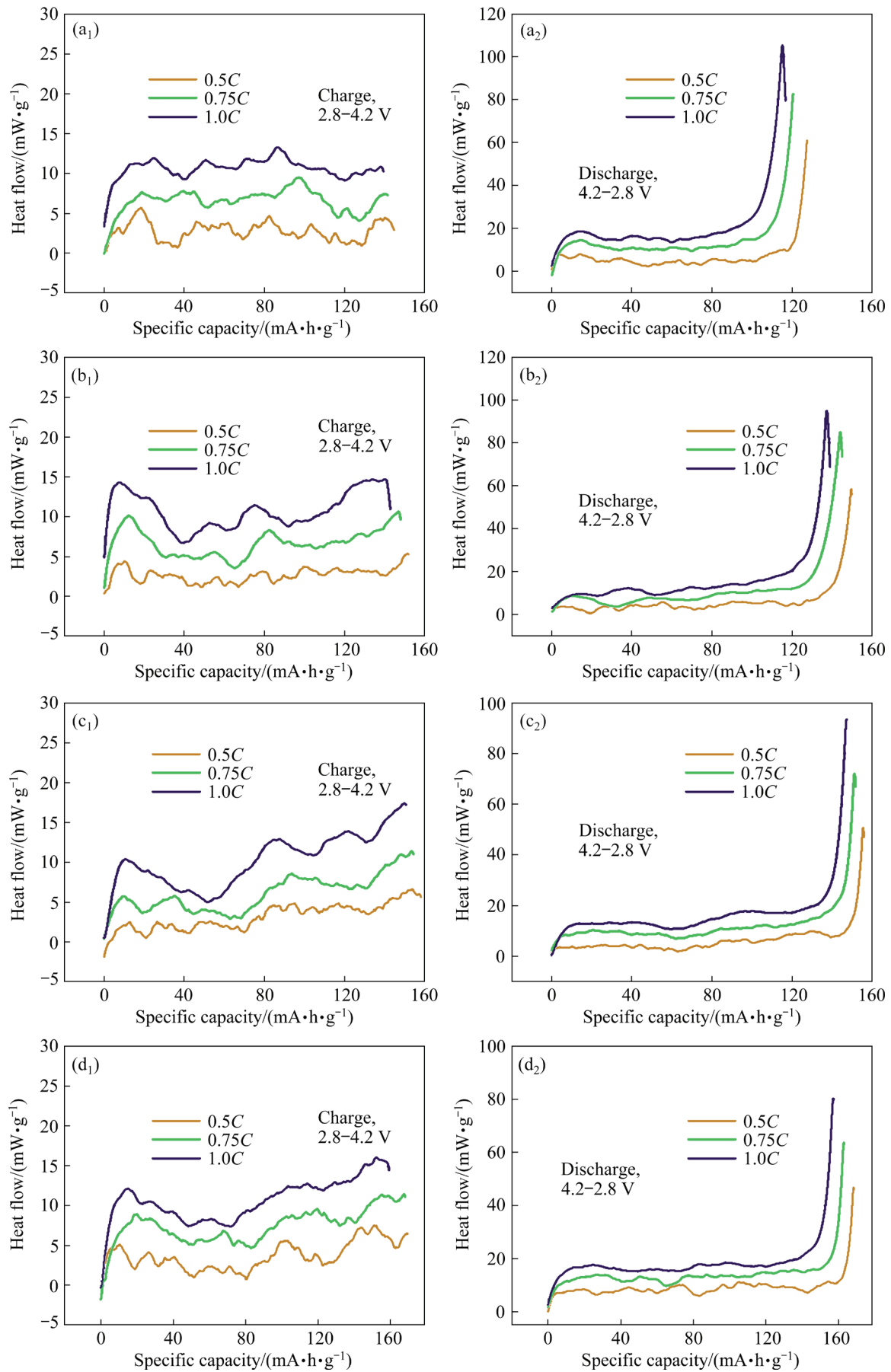


Fig. 6 Dynamic heat flow of NCM111 (a), NCM523 (b), NCM622 (c), and NCM811 (d) during charge and discharge

and mass transfer limitations become apparent. This extends polarization resistance and accelerates heat generation, leading to the sharp exothermic peak observed at the end of discharge. Additionally, Li insertion generates much more heat compared to Li extraction, which can be explained by the barrier of Li diffusion dynamics due to the first-level transition [26,27].

Regarding NCMs with different Ni contents, there is no significant change in heat flow during discharging, while the presented feature during charge varies widely. NCM111 (Fig. 6(a₁)) shows a mild trend and barely changes with state of charge (SOC), whereas the heat generation rate at the end of charge increases dramatically with elevated Ni content. Two reasons can interpret this contrast. First, due to the lower Ni migration barrier, Ni-rich materials exhibit strong surface segregation of antisite defects (mainly Li/Ni mixing) [28], which results in a surface rock-salt NiO phase that may impede charge transfer and Li⁺ transport at the electrode–electrolyte interface. Additionally, this may lead to further structural deterioration arising from the chaotic arrangement of Ni in the Li plane. Rietveld refinements were carried out as listed in Table 1 to understand the extent of surface segregation of Ni/Li mixing.

The AC impedance was used to depict the resistance in Fig. S4 of SM. The corresponding charge transfer impedance (R_{ct}), resistance of Li⁺ through material surface (R_f), and the ohmic resistance (R_s) are listed in Table 3. The values for R_s and R_f are relatively insignificant, while R_{ct} progressively increases with rising Ni content. This observation is in harmony with the enhanced Li/Ni disordering detected via the Rietveld refinement highlighted in Table 1. It is suggested that Li/Ni disordering exhibits inverse trends relative to the proportion of Ni²⁺. As a result, ion transportation in Ni-rich materials is hindered, contributing significantly to the intense heat discharge encountered during the charging termination. Furthermore, the

researchers developed a technique for quantifying ion transport kinetics by calculating the Li⁺ diffusion coefficient using EIS and galvanostatic intermittent titration technique [29–31].

The impact of high Ni⁴⁺ content on the Ni-rich NCM electrode resulting from a significant quantity of Li extraction represents the second contributing factor. This phenomenon accelerates surface chemical evolution by promoting reactions between the charged electrode and electrolyte, which leads to an increase in resistance and additional heat release. Furthermore, oxidation of Ni²⁺ to Ni³⁺ and Ni⁴⁺ lowers the oxygen stability. With more than half of the Li ions removed, the layered structure tends to convert into a spinel structure, releasing oxygen and promoting the reaction between O₂ and the electrolyte that eventually triggers the heat accumulation.

Figure 7 demonstrates that the heat generation associated with discharge (delithiation) is significantly greater than that associated with charge (lithiation), indicating the safety hazards during Li extraction. In addition, higher current rates and NCMs with greater Ni content correspond to more unstable states.

To further quantify the influence of Ni content, heat generation values of NCMs at 1.0C are shown in Fig. 8. As mentioned above, NCM111 and NCM523 exhibit lower heat generation per unit mass at the expense of lower capacity, while NCM811 displays the most significant heat release during discharge (Fig. 8(a)). However, increasing Ni content can not only result in higher energy density, which is beneficial to the practical applications, but also bring thermal hazards. Therefore, to comprehensively assess the safety property and electrochemical performance, the heat generation per unit capacity is evaluated with respect to Ni content, as presented in Fig. 8(b). The results indicate that NCM111 and NCM622 experience higher thermal instability during Li extraction and insertion, respectively, compared to other NCMs. In addition, the energetic efficiency (η) is determined by comparing heat values (Q) and electrical power (W) during charge and discharge using the following equations:

$$\eta_c = \frac{Q_c}{W_c + Q_c} \quad (1)$$

$$\eta_d = \frac{Q_d}{W_d + Q_d} \quad (2)$$

Table 3 EIS fitting results of different NCM materials

Material	R_s/Ω	R_f/Ω	R_{ct}/Ω
NCM111	2.21	39.20	20.22
NCM523	3.61	11.63	71.53
NCM622	2.55	29.37	157.4
NCM811	2.63	38.33	197.5

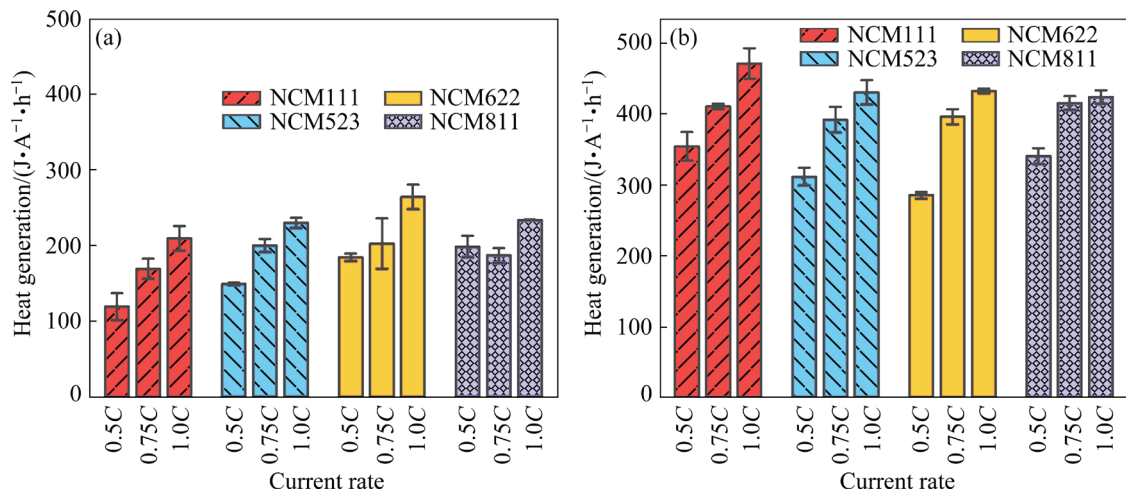


Fig. 7 Heat generation of NCMs versus current rate during charge (a) and discharge (b)

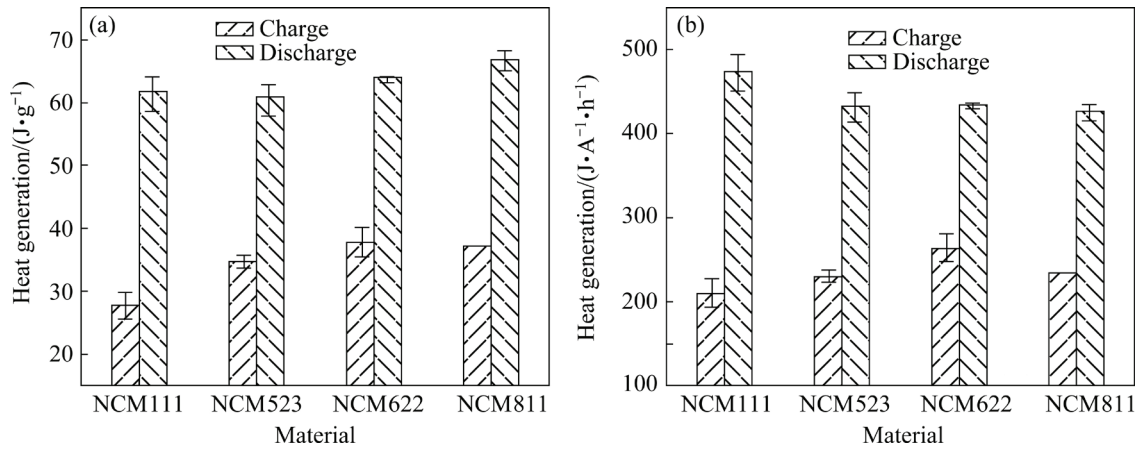


Fig. 8 Comparison of heat generation per unit mass (a) and heat generation per unit capacity (b) in different NCMs at 1.0C

where the terms “c” and “d” are used to represent the processes of charge and discharge, respectively. A summary of these processes is given in Table 4, which illustrates that the efficiency values for heat generation are similar for the materials. However, there is a notable disparity in the overall efficiencies during charge and discharge. Specifically, the largest efficiency values during charging and discharging are 0.0176 for NCM622 and 0.0336 for NCM111.

Table 4 Calculated energetic efficiencies of NCMs

Material	η_c	η_d
NCM111	0.0148	0.0336
NCM523	0.0171	0.0311
NCM622	0.0176	0.0314
NCM811	0.0165	0.0305

3.4 Thermal stability

The cathode materials in a fully charged battery have the potential to produce an excessive amount of heat, thereby increasing the overall thermal hazards. In order to assess the role of NCM cathode materials in this regard, Fig. 9 displays the thermal behaviors and mass losses of delithiated NCM111, NCM523, NCM622 and NCM811, identified by a DSC–TGA. As highlighted in our previous study [32], during high delithiation or heating of NCMs, the oxygen release significantly affects safety characteristics. Oxygen can react with the organic electrolyte and reduce the thermal stability of system, increasing the probability of thermal runaway. Consequently, it is essential to conduct a comprehensive analysis of mass loss, which indicates O_2 release. The TGA curves depicted in Fig. 9(a) exhibit a significant variation

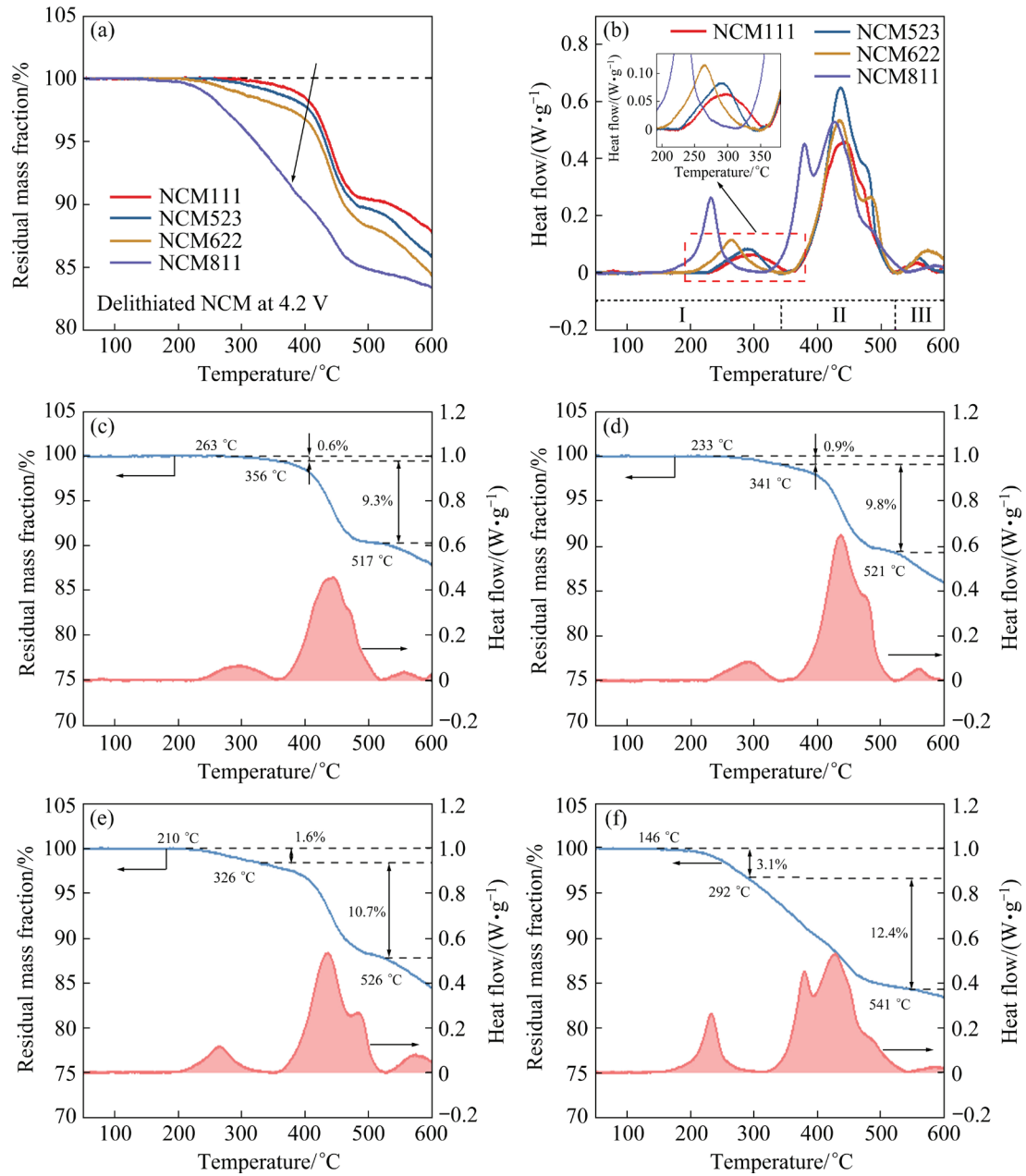
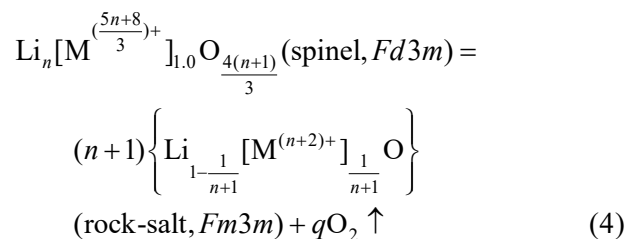
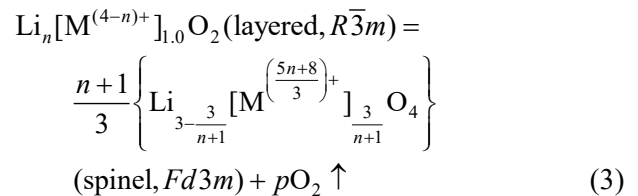


Fig. 9 TGA (a) and DSC (b) curves of all NCMs and integrated analysis of NCM111 (c), NCM523 (d), NCM622 (e) and NCM811 (f)

depending on the Ni content, and the onset temperatures of the three different stages are demonstrated in Table S3 of SM, much like the previous results [33]. According to Refs. [7,34], these mass losses are mainly attributed to O_2 release due to two main phase transitions: layered ($R\bar{3}m$) $\rightarrow$ spinel ($Fd\bar{3}m$) and spinel ($Fd\bar{3}m$) $\rightarrow$ rock-salt ($Fm\bar{3}m$). In addition, the transition process is mainly determined by the amount of residual lithium and the mixed oxidation states of TMs, as shown in Eqs. (3) and (4) [35]:



where M represents $\text{Ni}_x\text{Co}_y\text{Mn}_z$; n represents the remaining Li in Li_nMO_2 ; p and q represent the released O_2 from phase transitions. The theoretical values of O_2 release are displayed in Table 5. It is important to note that the total O_2 production ($p+q$) increases with Ni content. This increase is ascribed to the ability of Ni-rich NCMs to possess a higher average valence of TMs after Li removal. The resulting increase in Ni^{4+} contributes to the production of stable Ni^{2+} , facilitating electron extraction in the hybrid orbitals between O 2p and TM 3d. This further promotes the release of O_2 . The values of the residual Li are dependent on different ratios of practical capacities of NCMs to their theoretical counterparts. For instance, the NCM811 exemplifies 38% Li remaining after Li delithiation, with the following phase transition equations:

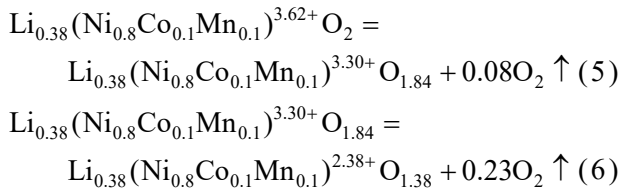


Table 5 Residual Li and theoretical values of O_2 release in delithiated NCMs during phase transition

Material	n	p	q	$p+q$
NCM111	0.476	0.016	0.246	0.262
NCM523	0.454	0.031	0.242	0.273
NCM622	0.437	0.042	0.240	0.282
NCM811	0.380	0.080	0.230	0.310

Severe delithiation and oxygen evolution can render electrode materials in thermodynamically unstable states leading to surface decomposition, thereby reducing thermal stability. Our analysis on the thermal behavior of delithiated NCM formulations indicates a similar trend in thermal behavior from RT to 600 °C, with a close correlation to phase transition, as depicted in Fig. 9(b). This correlation is further supported by our theoretical model, which satisfactorily agrees with experimental mass loss ratio presented in Table S3 of SM. Overall, our results suggest that the initial temperature of mass loss decreases with elevated Ni content and the mass loss ratio increases at each stage. Of the samples, NCM811 stands out with a comparatively higher mass loss ratio (15.5%) compared to NCM111 (9.9%). This

difference is mirrored in three exothermal processes in heat flow profile, with the major heat release identified between 350 and 520 °C. Along with the increased structural instability, NCM811 undergoes more rapid decomposition, exhibiting poor thermal stability at low temperatures. It is found that heat release time is also longer as Ni content increases, leading to larger heat accumulation. Thereby the initial reaction temperature is lower, accompanied by amplified total heat generation (147 °C and 734.09 J/g for delithiated NCM811). Conversely, the reduction in Ni content leads to an alleviation in the thermal stability (202 °C and 572.46 J/g for NCM622, 227 °C and 599.89 J/g for NCM523, and 238 °C and 484.02 J/g for NCM111). Thus, the thermal stability of the delithiated NCMs ranging from RT to 600 °C follows the order of NCM811 < NCM622 < NCM523 < NCM111. We attribute the enhanced stability of NCMs with lower Ni content to increased Co and Mn contents, as evidenced by the decrease in the occupancy of Ni ions in the Li layer, which relieves cation ordering and stabilizes the layered structure. Mn content, on the other hand, stabilizes the structure and prevents structural collapse [34,36].

Figure 10 summarizes the key properties of NCM materials. NCMs with higher Ni content exhibit a high capacity, although they are prone to harmful phase-transition and have higher heat generation while cycling. As a result, this can lead to severe structural deterioration when exposed to heat. Conversely, NCM111 contains a Ni ratio of 1/3, which provides better safety characteristics,

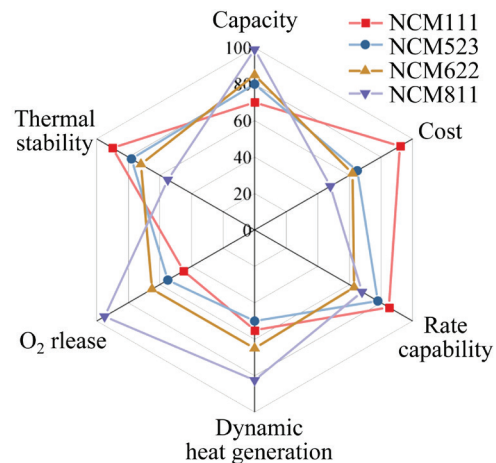


Fig. 10 Radar chart showing performance comparison of NCMs with different Ni contents

including thermal stability and rate capability. However, NCM111 has limited energy density and higher material costs due to the increased content of Co and Mn. Therefore, Ni plays a specific role in determining the appropriate balance between safety risks and higher capacity contributions. As a result, the challenge is to limit the former while enhancing the latter.

4 Conclusions

(1) The increase in Ni content causes high cation mixing and poor electronic conductivity, leading to a considerable reduction in capacity and rate capability.

(2) Ni-rich NCM exhibits increased total heat generation, particularly during the charging process, while NCM111 with a lower Ni ratio delivers higher heat per unit capacity due to the limited energy density.

(3) The TM ratio plays a significant role in enhancing the thermal safety of NCMs. The increase in Ni ratio induces severer structural deterioration, promoting phase transition at lower temperature and expanding associated oxygen release.

(4) Based on comprehensive analysis, NCM523 is identified as a superior material in NCMs.

(5) The results provide comprehensive assessment of electrochemical and thermal properties of NCMs with different TM compositions, which serves as a foundation for developing effective methodologies to enhance capacity and thermal stability.

CRedit authorship contribution statement

Chen LIANG: Conceptualization, Writing – Original draft; **Bang TONG:** Methodology, Data curation; **Shi LI:** Investigation, Validation; **Ze-sen WEI:** Validation, Visualization; **Jin-hua SUN:** Resource, Supervision; **Qing-song WANG:** Data curation; Writing – Review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary materials in this paper can be found at: http://tnmsc.csu.edu.cn/download/16-p1936-2022-1381-Supplemental_materials.pdf.

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过渡金属比例对锂离子电池 $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ 层状材料 电化学性能及热特性的影响

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摘要: 为了揭示 $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM)的性能随过渡金属(TM)成分的变化规律, 系统研究 TM 比例对不同 NCM 材料的结构、形貌、电化学性能和热行为的影响。镍含量的增加能够提高可逆容量, 但速率性能和循环稳定性变差。在富镍 NCM 中, Li^+ 的动力学抑制和电子导电性差是容量损失的主要原因。通过原位和非原位微量热法对不同 NCM 的热行为进行对比。结果表明, 随着 Ni 含量的降低, 材料的热稳定性显著提高。通过对 NCM 中 Li 剩余量的分析, 对相变相关的氧释放量进行评估。结果表明, 富镍材料在脱锂后出现更严重的结构恶化, 起始温度更低, 热释放量更多。综合表征表明, $\text{LiNi}_{0.5}\text{Co}_{0.3}\text{Mn}_{0.2}\text{O}_2$ 在电化学性能和安全性能间实现良好的平衡。

关键词: 镍钴锰酸锂; 热稳定性; 结构演变; 三元材料; 锂离子电池安全

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