nature portfolio

Peer Review File

Thermal processing to modulate surface chemistry and bulk charge distribution in nickel-rich layered lithium positive electrodes

Corresponding Author: Professor Feng Lin

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The article entitled “Thermal processing to modulate surface chemistry and bulk charge distribution in layered cathodes” introduces a simple thermal processing method which can regulate the valence state of nickel and the distribution of lithium on the surface of high-nickel NCM material, enhance the stability of particle surface, and improve the uniformity of charge distribution in secondary particles, so that the prepared NCM material exhibited favourable cycling performance under high voltage. Besides, this simple modification method can help to reduce the cost in the manufacturing process of NCM cathode. This manuscript has some similarities with Advanced Energy Materials 9, 1901915 (2019), therefore, I hope the authors can further highlight their innovative points. The following concerns need to be addressed before the manuscript can be accepted.
1. What is the accurate/approximate cooling rate of the NMC-S in oxygen flow and NMC-Q quenched in the air? What are some other environmental conditions (such as the humidity of the air)? Since the thermal processing parameters and environmental conditions have a significant impact on the properties of the prepared materials, it is recommended to enrich the relevant details of the experiment.
2. Fig. 1c describes that NMC-Q has a lower Ni oxidation state than NMC-S at 10~nm depth in TEY mode, while the Ni oxidation state remains virtually the same for NMC-S and NMC-Q at the ~50 nm probing depth based on the FY mode. If the author discusses the conclusion, it may be nice.
3. Please explain the decrease in first turn capacity after heat treatment.
4. It is recommended to add TEM characterization to further investigate the recrystallization process of the particles during quenching.
5. The rise in capacity during cycling in Fig. 3c,d. Why? Please explain.
6. The inconsistency between the initial segment capacity rise in Fig. 3a, b and Fig. 3c.t. Why?
7. The experimental results showed that the distribution of Li in NCM-S and NCM-Q prepared in two ways is different. According to Figure 2e, quenching could enrich lithium on the surface of the NCM particles, while slower cooling appeared to reduce the lithium content of the surface with an increase in the valence state of nickel. Figure S5c supports the above result, and the Li-deficient layer (ca. 20~400 nm) can also be observed in Figure S5c. What is the mechanism of regulating Li distribution by quenching?
8. It is proposed to add the cross-sectional primary particle morphology (Fig. 2e) and elemental distributions to verify the effect of air quenching on the internal structure of particles as well as the migration trend of Li to the outer surface of particles.
9. For NCM811 high nickel positive electrode air quenching, quenching at different humidity may affect the surface Li2CO3 content, please give a description about the quenching environmental condition control.
10. The quenching of NCM-Q is carried out in air. According to the XPS result, there is more Li2CO3 on the surface of NCM-Q. Does this mean that besides high cooling-rate, the air (especially CO2 and H2O in the air) also plays a nonnegligible role in promoting the enrichment of lithium on the surface and enhancing the surface stability?
11. Li2CO3 is often regarded as a surface residue which is unfavorable to the performance due to its low conductivity. Ref 24 (Advanced Energy Materials 9, 1901915 (2019)) compared samples cooled at different rates in the air and it was found that there was less Li2CO3 on the surface of the quenched sample, so the quenched NCM had a lower impedance. In this manuscript, the NCM-S was cooled in oxygen airflow, and the content of Li2CO3 on its surface is less than that of the quenched NCM-Q, but the impedance of NCM-S is higher. It seems to be contrary to the conclusion of Ref 24. How to understand this phenomenon?

12. The increased content of Li_2CO_3 on the surface does not affect the cycling performance of the material, but rather enhances the cycling performance. Why? Please elucidate the mechanism.
13. It seems that poly(vinylidene difluoride) is abbreviated to PVDF in most literature. It is suggested to amend "poly(vinylidene difluoride, as the binder) (PVdF)" to "poly(vinylidene difluoride) (PVDF, the binder)" in the section "Electrochemical measurements.
14. It is recommended that the full name of all abbreviations should be given when they first appear, such as TXM.
15. If the author adds dQ/dV, CV, rate, Gitt, lithium ion diffusion coefficient, etc., it will be better for supporting the electrochemical performance.
16. Please elucidate the mechanism of uniform distribution of charge in secondary particles for enhancing material properties.

Reviewer #2

(Remarks to the Author)
This work reported the use of a thermal processing technique to improve the quality of layered cathode materials. NMC811 is used as a platform to validate the process. The study is also supported by several synchrotron techniques, including transmission x-ray microscopy. The work also shows elemental distribution in NMC polycrystalline particles can be manipulated by regulating the cooling rate. The process creates a surface Ni reduction layer to decrease the surface reactivity. It is also demonstrated that the process allows the redox reactions to proceed more homogeneously throughout polycrystalline particles, leading to more favorable capacity retention cycled to high voltages. The reported technique is innovative and the underlying mechanism has been fully revealed in the work. The study has a great combination of phenomenon-mechanism demonstrations. It can be accepted in publication in NC after addressing the following aspects:

1. The complete parameters of the Rietveld refinement should be included as a table in SI.
2. More discussion on how the surface residue Li carbonate may impact full cell performance would be great.
3. Since surface reduction can also happen during electroltye soaking of Ni-rich materials, will it have similar impacts on the charge distribution and performance discussed in this work?
4. Adding more discussion on how the processing technique may impact the manufacturing facility would be good. Will the proposed technique save energy?

Reviewer #3

(Remarks to the Author)
This manuscript reports on a quenching treatment for NCM811 cathodes during calcination to generate Li_2CO_3 and reduce Ni oxidation states near the particle surface. The cathodes exhibit few side reactions and charge distribution homogeneity, and show a more stable cycling retention at 4.5 V. However, there have been many reports on the fast-cooling treatment for Ni-rich cathode (Electrochimica Acta 2017, 227, 225; Advanced Energy Materials 2019, 9, 1901915), and the author does not clearly illustrate the surface-bulk interactions. This work is not recommended for publication in Nature Communications, and several questions are desirable to be addressed as follows:
1. Please provide more experimental details about the quenching method. Was it in ambient environment or dry air? Were the treatments and the results controllable?
2. It is unreasonable to compare the Ni-rich cathodes that slowly cooled in O_2 and that quenched in the air. It is known that Ni-rich cathodes are vulnerable in the ambient environment with residual lithium species generated on the surface, leading to inferior performance.
3. Does the surface lithium species here contain only Li_2CO_3? Why would it benefit to the performance? The author claims that the Li ions diffuse out of the lattice, then would the lack of Li ions in the bulk influence the electrochemical performance?
4. The surface difference between the two cathodes needs more characterization. Do the Li-containing species cover the particle surface evenly? Why the surface Ni ions are reduced after quenching. The surface of Ni-rich cathodes tends to be reduced with oxygen loss and form an inactive rock-salt phase. What about the surface situation here? Finally, how do the above two features induce charge homogeneity?
5. On Page 17, Line 340, the author states that the charge homogeneity may promote higher chemo-mechanical stability, which is indeed a critical factor influencing the cathode performance. What about the chemo-mechanical performance of the two cathodes in this work? Please provide related evidence.
6. Why does the capacity of NMC-Q increase in the first few cycles?
7. The author states that this thermal processing is a simple and scalable step and could be a promising CAM manufacturing path forward. Did the author attempt to perform a scalable application and validation in pouch cells?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have well addressed all the concerns raised by the reviewers. The manuscript will be ready for publication after

revising the following question:
1. In Figure 4c, there is a problem with the format of “Ni L3high/L3low”. Please modify it.

Reviewer #2

(Remarks to the Author)
The author has revised the manuscript point-to-point.The innovation and quality of the manuscript have met the requirements of Nat.Commun. journal, and we recommend it for publication.

Reviewer #3

(Remarks to the Author)
The authors have extended their manuscript and improved the quality to a certain extent. The reviewer has also carefully read through the comments from other reviewers and the responses from the authors. However, the major concern of the reviewers remains unsolved. In particular, the mechanism how the surface properties can impact the bulk reactions is not clarified, which is one of the core concepts of this work. It is unreasonable to directly build an interaction relationship between the surface and the bulk simply via the individual experimental consequences. Does the NMC-S and NMC-Q only have the difference in surface? For example, it is likely that the quenching induces the change of strain or defects distribution in the crystal bulk, which can cause the more homogenous charge distribution. Besides, there are still several issues listed below. Therefore, this work cannot be accepted at the current state.
1. From the Li 1s XPS spectra, compared with the 81.0% proportion of NMC-Q, there is 68.0% Li2CO3 of NMC-S, which should be derived from residual lithium. Does the left 13.0% Li2CO3 come from the Li diffusion in the lattice and induce the improved performance of NMC-Q?
2. The composition of the surface Li layer remains elusive. Chemical titration can be useful technique to distinguish the Li2CO3 and LiOH.
3. The author states that Li and O loss and the subsequent Li2O formation contribute to the surface Li2CO3 layer. However, it is known that Li/O loss is accompanies with the formation of inert rock-salt NiO-like phase, which deteriorates the cathode performance. What about the NMC-Q here?
4. To clearly clarify the difference of the two cathodes, STEM images showing surface crystal structures should be provided.
5. Typically, the Ni reduction corresponds to the Ni L edge EELS peak shifting to low energy loss. However, there is no peak shift in the supplemented Figure S1.
6. Please explain the mechanism of the reduced valence of surface Ni in the quenching process.
7. To elucidate the chemo-mechanical stability, cross-section SEM images of the cycled cathode particles should be provided to observe the evolution of cracks.

Version 2:

Reviewer comments:

Reviewer #3

(Remarks to the Author)
The author has addressed the reviewer's concerns and this work can be accepted.

Response letter

Dear Reviewers,

Thank you for reviewing our manuscript (***NCOMMS-23-48088***) entitled "***Thermal processing to modulate surface chemistry and bulk charge distribution in layered cathodes for lithium batteries***". We sincerely appreciate all the insightful comments and valuable suggestions, which we believe have helped us greatly improve the manuscript. We have carefully considered these comments and thoroughly revised our manuscript.

In this revised manuscript, we addressed review comments point by point and annotated the changes in the revised manuscript. For ease of reference, our response is in blue, and all changes in the revised manuscript are highlighted in yellow.

We appreciate your attentiveness and earnestness and thank you once again for your consideration and support.

With our best regards,

Feng Lin
On behalf of all coauthors

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The article entitled "Thermal processing to modulate surface chemistry and bulk charge distribution in layered cathodes" introduces a simple thermal processing method which can regulate the valence state of nickel and the distribution of lithium on the surface of high-nickel NCM material, enhance the stability of particle surface, and improve the uniformity of charge distribution in secondary particles, so that the prepared NCM material exhibited favorable cycling performance under high voltage. Besides, this simple modification method can help to reduce the cost in the manufacturing process of NCM cathode. This manuscript has some similarities with Advanced Energy Materials 9, 1901915 (2019), therefore, I hope the authors can further highlight their innovative points. The following concerns need to be addressed before the manuscript can be accepted.

Response: Thank you for your great summary of the novelty and comments to improve our manuscript. As you will see in our response letter, we have discussed the differences between our work and the existing literature. The Adv. Energy Mater. paper has been discussed and cited in our manuscript as [25].

1. What is the accurate/approximate cooling rate of the NMC-S in oxygen flow and NMC-Q quenched in the air? What are some other environmental conditions (such as the humidity of the air)? Since the thermal processing parameters and environmental conditions have a significant impact on the properties of the prepared materials, it is recommended to enrich the relevant details of the experiment.

Response: The authors appreciate the reviewer's insightful comments.

We totally agree with the reviewer's opinion that both cooling rate and humidity have a significant impact on the properties of the NMC cathode materials during synthesis. In our work, the approximate cooling rate for NMC-S and NMC-Q is 3 °C/min and 140 °C/min, respectively, by the calculation from total cooling time to room temperature. The air in quenching process has about 38% relative humidity. We added above information in the *Materials synthesis* section in the main text to clarify it more clearly.

2. Fig. 1c describes that NMC-Q has a lower Ni oxidation state than NMC-S at ~10nm depth in TEY mode, while the Ni oxidation state remains virtually the same for NMC-S and NMC-Q at the ~50 nm probing depth based on the FY mode. If the author discusses the conclusion, it may be nice.

Response: Thank you very much for the reviewer's suggestion.

The soft XAS results in TEY mode show that NMC-Q exhibits a lower Ni oxidation state than NMC-S at ~10 nm depth from the particle surface in Figure 1c, showing a reduction of Ni oxidation state at the particle surface by quenching. The Ni oxidation state remains virtually the same for NMC-S and NMC-Q at the ~50 nm probing depth in the FY mode, showing a high similarity of Ni oxidation state in the bulk between

NMC-Q and NMC-S samples. One can conclude that quenching has a negligible effect on the bulk Ni oxidation state of NMC materials. To further validate our conclusion, we performed STEM-EELS measurements on NMC-Q and NMC-S along the c directions (Figure S1). The Ni L-edge EELS spectra for both NMC-Q and NMC-S show a peak shift to higher energy from the surface to bulk, showing surface Ni reduction. It appears that Ni reduction is deeper in NMC-Q. We also analyzed the O K-edge spectra where the appearance of pre-peak (here marked by '*', sensitive to the TM oxidation state) can be seen from 5 nm from the surface for NMC-Q and 2 nm for NMC-S. Thereby we can confirm that NMC-Q shows a thicker Ni reduction surface layer than NMC-S. Combining soft XAS and STEM-EELS results, it can be concluded that (1) NMC-Q shows a lower Ni oxidation state than NMC-S on the surface; and (2) NMC-Q and NMC-S display a high similarity of Ni oxidation state in the bulk, showing the negligible effect of quenching on the Ni oxidation state in the bulk. We added discussion on this aspect in Page 6 in the main text.

At a ~10 nm probing depth by the TEY mode, the quenched sample NMC-Q shows a lower L_{3high}/L_{3low} ratio and thereby a lower Ni oxidation state than NMC-S on the particle surface (Figure 1c). The Ni oxidation state remains virtually the same for NMC-S and NMC-Q at the ~50 nm probing depth based on the FY mode, showing a high similarity of Ni oxidation state in the bulk between NMC-Q and NMC-S samples. One can conclude that quenching has a negligible effect on the bulk Ni oxidation state of NMC materials. To further validate our conclusion, we performed STEM-EELS measurements on NMC-Q and NMC-S (Figure S1). The Ni L-edge EELS spectra for both NMC-Q and NMC-S show a peak shift to higher energy from the surface to bulk, showing surface Ni reduction. It appears that Ni reduction is deeper in NMC-Q. We also analyzed the O K-edge spectra where the appearance of pre-peak (here marked by '*', sensitive to the TM oxidation state) can be seen from 5 nm from the surface for NMC-Q and 2 nm for NMC-S. Thereby we can confirm that NMC-Q shows a thicker Ni reduction surface layer than NMC-S. Combining soft XAS and STEM-EELS results, it can be concluded that (1) NMC-Q shows a lower Ni oxidation state than NMC-S on the surface; and (2) NMC-Q and NMC-S display a high similarity of Ni oxidation state in the bulk, showing the negligible effect of quenching on the Ni oxidation state in the bulk.

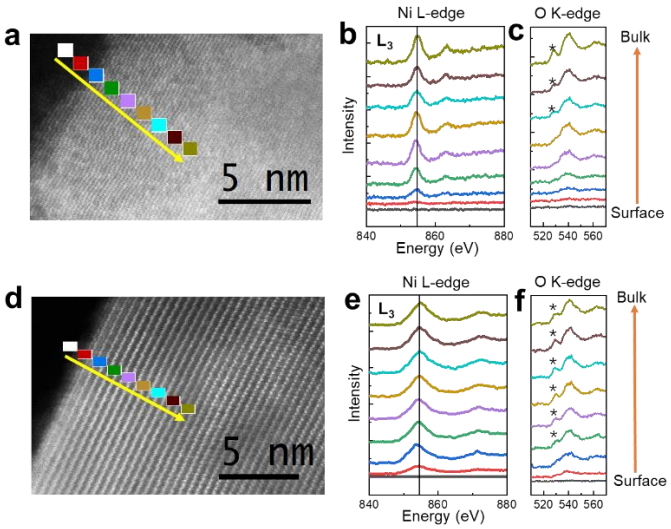

Figure S1. STEM images to show the selected regions for EELS acquisition for (a) NMC-Q and (d) NMC-S. EELS Ni L-edge spectra (b,e) and O K-edge spectra (c,f) for NMC-Q and NMC-S corresponding to the regions in a and d.

3. Please explain the decrease in first turn capacity after heat treatment.

Response: Thank you very much for the reviewer's comment.

In the first cycle, the discharge specific capacity of NMC-Q is 195 mAh/g, slightly lower than that of NMC-S (198 mAh/g) in Figure 3a,b and Figure S8. It could be attributed to the Li diffusion from the bulk to the surface during quenching, shown in the XPS, STEM-EELS and soft XAS results, leading to some Li inventory loss for initial cycling. The corresponding changes have been added in Page 12 in the main text.

The initial specific discharge capacity of NMC-Q and NMC-S at 0.5C is 195 mAh/g and 198 mAh/g, respectively (Figure 3a,b and Figure S8). NMC-Q shows a slightly lower initial capacity than NMC-S at 0.5C. It could be attributed to the Li diffusion from the bulk to the surface during quenching, shown in the XPS, STEM-EELS and soft XAS results, leading to some Li inventory loss for initial cycling.

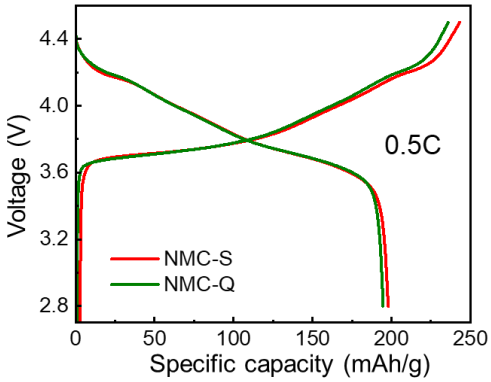

Figure S8. The charge/discharge profiles of NMC-Q and NMC-S for the first cycle at 0.5C with a voltage range of 2.8-4.5 V.

4. It is recommended to add TEM characterization to further investigate the recrystallization process of the particles during quenching.

Response: The authors appreciate the reviewer's insightful comments.

From the BF-STEM images, we can see the thickness of the Li_2CO_3 formation on the quenched (NMC-Q) samples (Figure S2a) is almost 3-5 nm whereas it is only 1-2 nm for NMC-S samples (Figure S2b), confirming more Li_2CO_3 existence on the surface of NMC-Q than that of NMC-S. Combining XPS, soft XAS, TXM and STEM-EELS results, the extra Li_2CO_3 on the surface of NMC-Q originates from the bulk Li diffusion during quenching, indicating the recrystallization process of surface structure of NMC-Q. The corresponding results of STEM have added in Page 7 in the main text.

From the BF-STEM images, we can see the thickness of the Li_2CO_3 formation on the quenched (NMC-Q) sample (Figure S2a) is 3-5 nm, whereas it is only 1-2 nm for the NMC-S sample (Figure S2b), confirming more Li_2CO_3 existence on the surface of NMC-Q than that on NMC-S.

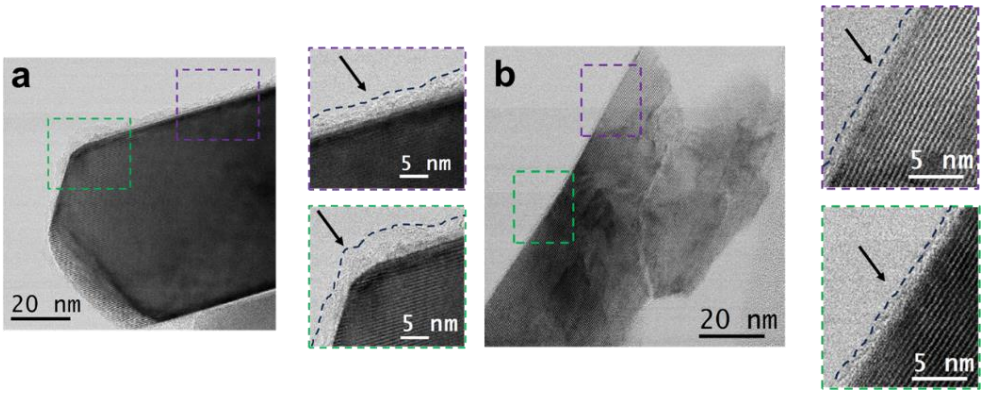

Figure S2. BF-STEM images of (a) NMC-Q and (b) NMC-S with magnified regions.

5. The rise in capacity during cycling in Fig. 3c,d. Why? Please explain.

Response: Thank you very much for the reviewer's comment.

In Figure 3c and d, the specific capacity and specific energy correspond to discharging process or lithiation of Li ions into the NMC crystal structure. The capacity delivery highly depends on Li ion transport in NMC lattice and electrolyte penetration in the electrode. So, the rise of capacity during the first several cycles is likely associated with the improving penetration of electrolyte into the electrode and improvement of Li ion transport in the NMC lattice during lithiation. Note that the slight capacity increase exists in both NMC-Q and NMC-S samples, and it is common in the literature.[1, 2] It is more significant for the NMC-Q sample, because it takes more cycles to overcome the initial kinetic barrier created by the surface reduced layer,[3] shown in Figure R1. We believe the comparison of battery performance between NMC-Q and NMC-S is reliable

and compelling with the identical cell system and test conditions here. The above explanation has been added into Page 12 in the main text.

The cells show increasing specific capacity and energy during the first several cycles in Figure 3c,d, which is associated with the increasing Li ion transport kinetics due to factors such as improved electrolyte wetting. The increase is more obvious for the NMC-Q because it takes more cycles to overcome the initial kinetic barrier created by the surface reduced layer.[3] When cycled at a higher C rate (1C in Figure 3c,d), the kinetic barrier plays a larger role than when cycled at a lower C rate (0.5C in Figure 3a,b).

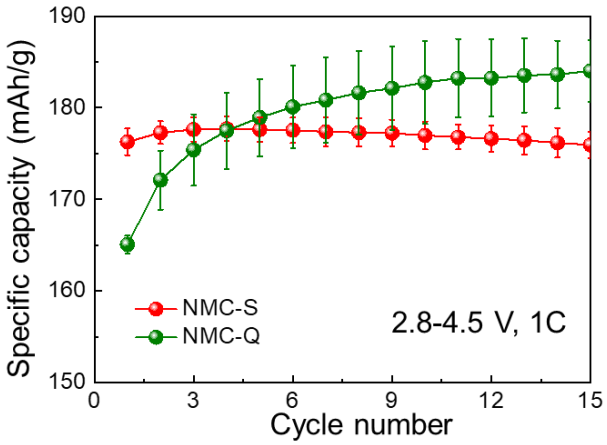

Figure R1. Zoom in Figure 3c in the range of the first 15 cycles.

6. The inconsistency between the initial segment capacity rise in Fig. 3a, b and Fig. 3c.t. Why?

Response: Figure 3a,b and Figure 3c,d show battery data cycled at different C rates. When cycled at a higher C rate (1C in Figure 3c,d), the kinetic barrier plays a larger role than when cycled at a lower C rate (0.5C in Figure 3a,b).

7. The experimental results showed that the distribution of Li in NCM-S and NCM-Q prepared in two ways is different. According to Figure 2e, quenching could enrich lithium on the surface of the NCM particles, while slower cooling appeared to reduce the lithium content of the surface with an increase in the valence state of nickel. Figure S5c supports the above result, and the Li-deficient layer (ca. 20~400 nm) can also be observed in Figure S5c. What is the mechanism of regulating Li distribution by quenching?

Response: We appreciate the reviewer's comment about the Li distribution mechanism. According to Figure 2e, we can directly observe that similar Ni K-edge energy level and overall uniform distribution in the bulk of NMC-Q and NMC-S particles, indicating similar Ni oxidation state and distribution inside the particles at the pristine state. Moreover, the Ni K-edge level of NMC-Q on the surface is lower than that of NMC-S,

showing a lower Ni oxidation state on the surface of NMC-Q than that of NMC-S, consistent with soft XAS results in Figure 1c,d. Combining with XPS, soft XAS and STEM-EELS results, one can conclude that more Li_2CO_3 exists on the surface of NMC-Q than that of NMC-S. More Li_2CO_3 on the surface of NMC-Q originates from the Li diffusion from the bulk of NMC crystal structure to the surface, which is driven by the rapid decrease of temperature on the surface during quenching. The rapid temperature decrease reduces the solubility of Li ion in the lattice. The Li diffusion from the bulk to the surface can also be regarded as Li loss, which happens together with O loss. Then, Li_2O forms on the surface of NMC-Q, which is later changed to Li_2CO_3 by reacting with the CO_2 in the air. Ultimately, NMC-Q shows a reconstructed surface layer with a lower Ni oxidation state, or named as the Li-deficient layer, and accompanied with more Li_2CO_3 formation on the particle surface during quenching. The above explanation has been added into Page 10 in the main text.

More Li_2CO_3 on the surface of NMC-Q originates from the Li diffusion from the bulk of NMC crystal structure to the surface, which is driven by the rapid decrease of temperature on the surface during quenching. The rapid temperature decrease reduces the solubility of Li ion in the lattice. The Li diffusion from the bulk to the surface can also be regarded as Li loss, which happens together with O loss. Then, Li_2O forms on the surface of NMC-Q, which is later changed to Li_2CO_3 by reacting with the CO_2 in the air. Ultimately, NMC-Q shows a reconstructed surface layer with a lower Ni oxidation state and more Li_2CO_3 formation on the particle surface.

8. It is proposed to add the cross-sectional primary particle morphology (Fig. 2e) and elemental distributions to verify the effect of air quenching on the internal structure of particles as well as the migration trend of Li to the outer surface of particles.

Response: Thank you very much for the reviewer's comments.

We carried out the cross-sectional SEM measurements of NMC-Q and NMC-S particles, as shown in Figure R2. Both NMC-Q and NMC-S present a spherical polycrystalline secondary particle morphology and are composed of nanoscale primary particles (Figure R2a,c and Figure R2g,h), indicating quenching does not change internal primary grains arrays of NMCs. The primary particles show a rod-type arrangement, which can create less tortuous lithium ions pathways, thus improving the charge homogeneity and lower cell polarization of NMCs in our previous work.[4] Herein, the rod-type arrangement of primary particles facilitates lithium diffusion from the bulk to the surface during quenching. For the elemental distribution, it is hard to differentiate Li and/or C distribution in NMC-S and NMC-Q particles internal structure by EDS mapping in Figure R2c,i due to their low atomic mass. In addition, carbon contamination is inevitable due to FIB sample preparation. Nevertheless, all elements

including Ni, Co and Mn exhibit uniform distribution across the whole particles in both samples in Figure R2d-f and Figure R2j-l, showing the negligible impact of quenching on the elemental distribution.

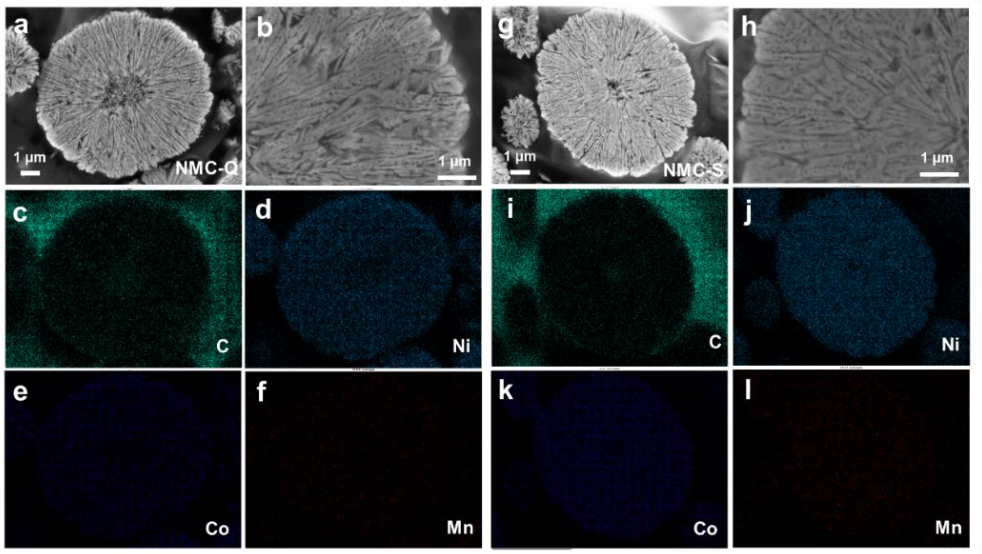

Figure R2. Cross-sectional SEM images of (a,b) NMC-Q particles and corresponding cross-sectional EDS mapping of (c) C, (d) Ni, (e) Co and (f) Mn. Cross-sectional SEM images of (g,h) NMC-S particles and corresponding cross-sectional EDS mapping of (i) C, (j) Ni, (k) Co and (l) Mn.

9. For NCM811 high nickel positive electrode air quenching, quenching at different humidity may affect the surface Li_2CO_3 content, please give a description about the quenching environmental condition control.

Response: We thank the reviewer for this suggestion.

The air in quenching process to prepare NMC-Q sample has about 38% relative humidity, which has been added in Page 18 in the main text.

The approximate cooling rate for NMC-S and NMC-Q is approximately 3 °C/min and 140 °C/min, respectively, by the calculation from total cooling time to room temperature. The air in the quenching process has about 38% relative humidity.

10. The quenching of NCM-Q is carried out in air. According to the XPS result, there is more Li_2CO_3 on the surface of NCM-Q. Does this mean that besides high cooling-rate, the air (especially CO_2 and H_2O in the air) also plays a nonnegligible role in promoting the enrichment of lithium on the surface and enhancing the surface stability?

Response: Thank you very much for pointing out the issue.

Indeed, the Li_2CO_3 formation has a direct relationship with CO_2 and H_2O in the air, and its content varies with the storage conditions such as humidity and time due to a time-consuming reaction process as following:[5, 6, 7, 8]

$LiTMO_2 + xH_2O \rightarrow Li_{1-x}H_xTMO_2 + xLiOH$

$2LiTMO_2 + xH_2O + xCO_2 \rightarrow 2Li_{1-x}H_xTMO_2 + xLi_2CO_3$

For example, the Li_2CO_3 forms on the NCA particle surface during exposure to laboratory atmosphere for 2 years.[5] The nearly identical results are achieved among NMC523 and NMC701515 materials, which are stored at 55 °C and 80% relative humidity for 4 weeks and at 60 °C and 80% relative humidity for 30 days, respectively.[6, 7] Even for NMC811, Li_2CO_3 formation on the surface requires10 days of storage at 25 °C and 40% relative humidity.[8] To study the Li_2CO_3 formation mechanism and its effect on NMC performance, most researchers stored NMC materials for a relatively long time and high humidity.

However, Li_2CO_3 on the surface of NMC particles originated from two sources: (1) an excess amount of LiOH introduced in synthesis, and (2) the reactions with H_2O and CO_2 in the air during storage. In our work, we prepared NMC-Q materials by quenching for a short time, and then transferred them into an argon-filled glovebox for storage immediately. Similarly, NMC-S materials were also transferred into the argon-filled glovebox for storage when cooled down to below 100 °C immediately. So, more Li_2CO_3 formed on the surface of NMC-Q is conjectured to be caused by the Li diffusion from the bulk to the surface and then reacts with CO_2 and H_2O in a short time.

11. Li_2CO_3 is often regarded as a surface residue which is unfavorable to the performance due to its low conductivity. Ref 24 (Advanced Energy Materials 9, 1901915 (2019)) compared samples cooled at different rates in the air and it was found that there was less Li_2CO_3 on the surface of the quenched sample, so the quenched NCM had a lower impedance. In this manuscript, the NCM-S was cooled in oxygen air flow, and the content of Li_2CO_3 on its surface is less than that of the quenched NCM-Q, but the impedance of NCM-S is higher. It seems to be contrary to the conclusion of Ref 24. How to understand this phenomenon?

Response: Thank you for pointing out these differences.

The mechanism of Li_2CO_3 formation on the surface is a complicated question, involving synthesis process (atmosphere, cooling rate, et al.) and storage conditions (exposure time, temperature, CO_2/H_2O partial pressures, et al.). In our work, we transferred NMC-S and NMC-Q samples immediately into an argon-filled glovebox (O_2 < 0.5 ppm, H_2O < 0.5 ppm) after cooling to circumvent Li_2CO_3 formation within a long-time storage. Therefore, we think that the difference of Li_2CO_3 contents between NMC-S and NMC-Q mainly originates from the cooling rate here. As for the effect of the Li_2CO_3 on the electrochemical performance and/or the impedance, it is still controversial[9] because some researchers reckon that an Li_2CO_3 layer on the surface can release stress and provide a stable interface, thus resulting in decreased interface resistance for charge transfer.[10] And Faenza et al. thought that the Li_2CO_3 on the surface

without other impurities could result in excellent cycling stability, comparable to the initial pristine NCA.[11] In our opinion, the impedance measurements involves the surface chemistry and bulk properties of NMC polycrystalline secondary particles.[12] Combining more detailed surface and bulk properties analysis after cycling, however, it can conclude that both improved interfacial stability and homogeneous charge distribution of NMC-Q after quenching could result in a lower impedance and a better electrochemical performance than that of NMC-S in our work.

12. The increased content of Li_2CO_3 on the surface does not affect the cycling performance of the material, but rather enhances the cycling performance. Why? Please elucidate the mechanism.

Response: We are thankful for the reviewer's comments.

For the effect of Li_2CO_3 on electrochemical performance of NMC cathodes, it is still a debatable question. Some researchers reported that Li_2CO_3 on the surface will result in a degradation of electrochemical performance with an increase of impedance due to their low electronic conductivity and decomposition by reacting with electrolyte during cycling. However, some reports found that Li_2CO_3 on the surface of layered compounds can release anisotropic stress to alleviate crack formation and provide a stable interface with electrolyte, then improving cycling stability of layered cathodes.[10, 11] In this work, we found that more Li_2CO_3 exists on the surface of NMC-Q than that of NMC-S during quenching. Meanwhile, a reduction of Ni oxidation state accordingly occurs on the surface of NMC-Q, meaning the change of surface structure of NMC-Q due to a rapid temperature decrease. More importantly, the above change of surface structure can lead to an increase of bulk charge homogeneity during cycling, which jointly enhance the battery performance. Both surface and bulk properties could impact battery performance. Our results show that the surface properties can impact the bulk reactions and thus the battery performance of NMC polycrystalline particles.

13. It seems that poly(vinylidene difluoride) is abbreviated to PVDF in most literature. It is suggested to amend "poly(vinylidene difluoride, as the binder) (PVdF)" to "poly(vinylidene difluoride) (PVDF, the binder)" in the section "Electrochemical measurements.

Response: Thanks for pointing these out. Changes are made.

14. It is recommended that the full name of all abbreviations should be given when they first appear, such as TXM.

Response: Thanks for pointing these out. Changes are made.

15. If the author adds dQ/dV, CV, rate, Gitt, lithium ion diffusion coefficient, etc., it will be better for supporting the electrochemical performance.

Response: We thank the reviewer for the suggestion.

NMC-Q shows better rate capability and cycling stability at 0.5C than that of NMC-S cathodes with the change of surface structure by quenching in Figure S9a and b. From the dQ/dV curves in Figure S9c and d, we observed that the curves of NMC-Q exhibit insignificant changes than that of NMC-S from 10^{th} to 300^{th} cycle, therefore we can say the cell polarization is mitigated in the quenched samples, contributing to better cycle life for NMC-Q. The corresponding changes have been added in the Page 12 in the main text.

We further compare the rate capability and phase transition during cycling of NMC-Q and NMC-S. Comparing to NMC-S, NMC-Q shows improved rate capability, especially at high current rate. For instance, the NMC-Q maintains a reversible specific capacity of 164 mAh/g at 2C, while the NMC-S delivers a specific capacity of only 136 mAh/g in Figure S9a. The cycling stability of NMC-Q is also better than that of NMC-S at 0.5C (Figure S9b). From the dQ/dV curves at 0.5C in FigureS9c and d, it can be observed that the curve of NMC-Q exhibits less significant changes than that of NMC-S, contributing to better cycle life for NMC-Q. Figure S10 show that the charge transfer resistances of NMC-Q after 1 cycle and 50 cycles are both lower than those of NMC-S.

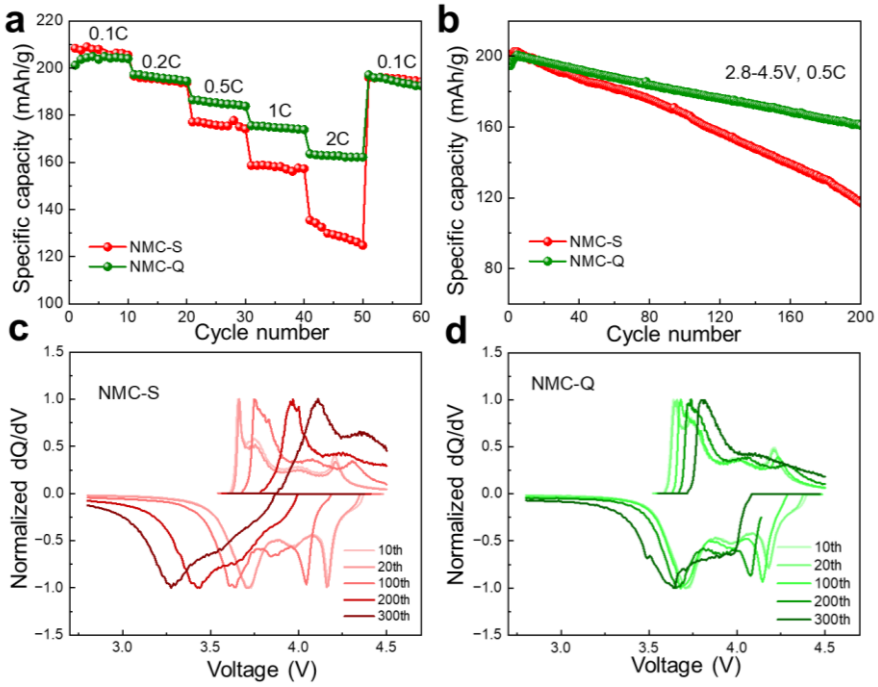

Figure S9. (a) Rate capability and (b) cycling performance at 0.5C of NMC-S and NMC-Q cathodes in Li metal cells with a voltage range 2.8-4.5 V. dQ/dV curves of 10^{th}, 20^{th}, 100^{th}, 200^{th} and 300^{th} cycle at 0.5C for (c) NMC-S and (d) NMC-Q.

16. Please elucidate the mechanism of uniform distribution of charge in secondary particles for enhancing material properties.

Response: We are thankful for the reviewer's comments.

The cycle life of NMC gets better with an increase of charge homogeneity, as a positive effect of uniform charge distribution on NMC performances.[4, 13] The reason is that the uniform charge distribution in the bulk of NMC secondary particles can alleviate stress hotspots and improve chemo-mechanical properties. For chemo-mechanical properties, their breakdown can significantly increase the specific surface area and accelerate the electrode-electrolyte side reactions, result in the surface oxygen loss, electrolyte decomposition, impedance buildup, and capacity fading.[4, 14] So, the increase of charge homogeneity in the bulk of NMC is of importance to improve their chemo-mechanical properties, and thus enhance cycling stability of NMC cathodes. The bulk charge distribution is highly correlated to the surface properties of polycrystalline cathode particles.[13] In our work, we found that both bulk charge homogeneity and surface structure stability of NMC materials increased by quenching, which further improve their performance together.

Reviewer #2 (Remarks to the Author):
This work reported the use of a thermal processing technique to improve the quality of layered cathode materials. NMC811 is used as a platform to validate the process. The study is also supported by several synchrotron techniques, including transmission x-ray microscopy. The work also shows elemental distribution in NMC polycrystalline particles can be manipulated by regulating the cooling rate. The process creates a surface Ni reduction layer to decrease the surface reactivity. It is also demonstrated that the process allows the redox reactions to proceed more homogeneously throughout polycrystalline particles, leading to more favorable capacity retention cycled to high voltages. The reported technique is innovative and the underlying mechanism has been fully revealed in the work. The study has a great combination of phenomenon-mechanism demonstrations. It can be accepted in publication in NC after addressing the following aspects:

1. The complete parameters of the Rietveld refinement should be included as a table in SI.
Response: We appreciate the reviewer's suggestion. The parameters of the Rietveld refinement have been added in SI.

2. More discussion on how the surface residue Li carbonate may impact full cell performance would be great.
Response: The authors appreciate the reviewer's suggestion.
The impact of residual Li carbonate on the full cell performance should be studied from both cathode and anode perspectives. In general, we found the literature has been quite controversial on this topic. In terms of the cathode, some studies have investigated the issues: (1) increased resistance of the electrode-electrolyte interface due to the low conductivity Li_2CO_3, (2) limited Li ion diffusion if the Li carbonate layer becomes too

thick, and (3) slurry gelation in the cathode coating process and battery swelling during cycling. In contrast, some other reports found that the residue Li carbonate can (1) inhibit the parasitic reactions and reduce cathode degradation by preventing the direct contact between the electrolyte and the cathode surface, (2) enhance cycling stability by passivating the cathode surface and mitigating side reactions, and (3) release anisotropic stress to alleviate crack formation and provide a stable interface with electrolyte. When it comes to the anode, the impact of residue Li carbonates can also vary. Li_2CO_3 can be converted to Li_3PO_4 and LiF by reacting with the electrolyte as following equation: $4Li_2CO_3 + LiPF_6 \rightarrow Li_3PO_4 + 6LiF + 4CO_2$,[15] which are two favorable components for constructing a robust solid electrolyte interphase (SEI). Therefore, the Li_2CO_3 facilitates SEI formation and growth on the anode surface, thus decreasing the consumption of cyclable Li ion inventory. However, the residue Li carbonate would induce severe electrolyte decomposition at the same time, which are hostile for the full cell performance. Overall, the role of Li_2CO_3 in full cells is quite complicated. We have added to the discussion of the manuscript the following content:

While we observe a positive impact of quenching experiments on cycling the NMC cathode, we have to note that the Li_2CO_3 residue on the NMC surface could influence the full cell performance when paring NMC with a graphite anode. Properly regulating the decomposition path of Li_2CO_3 in the full cell would be needed.

3. Since surface reduction can also happen during electrolyte soaking of Ni-rich materials, will it have similar impacts on the charge distribution and performance discussed in this work?

Response: The authors appreciate the reviewer's insightful comments.

Indeed, the change of surface structure can be caused during electrolyte soaking for Ni-rich cathodes, which we have experienced in our past experiments as well.[16, 17] Per the reviewer's suggestion, we soaked our NMC-S electrodes in the electrolyte (1 M $LiPF_6$ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with 2 wt % vinylene carbonate (VC)) for 10 days and cycled it under the same condition of as synthesized NMC-S. Figure R3 shows reduced discharge capacity during the formation cycle for the electrolyte soaked NMC-S. The electrolyte soaking affected the layered structure. The electrolyte soaked NMC811 would not be the same as quenched NMC811, which demonstrates the unique advantage of the thermal quenching technique.

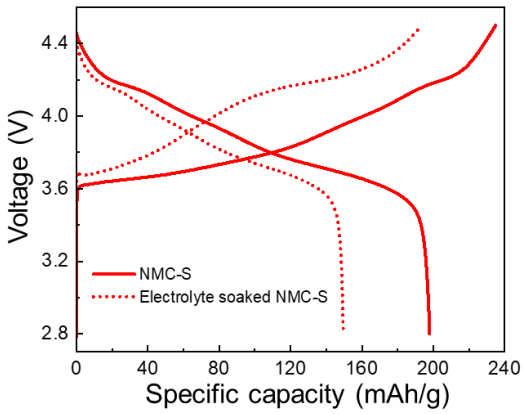

Figure R3. The charge/discharge curve for electrolyte (1 M $LiPF_6$ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with 2 wt % vinylene carbonate (VC)) soaked (NMC-S and as-synthesized NMC-S at 0.1C (2.8-4.5V).

4. Adding more discussion on how the processing technique may impact the manufacturing facility would be good. Will the proposed technique save energy?

Response: Thank you very much for the suggestion.

Since we have not applied the method in real production, we analyze the potential benefit based on our small-scale synthesis and the literature. The NMC-Q materials were prepared by transferring the cathode powder out of the tube furnace at 750 °C and poured onto a copper plate to quench in a few minutes, which is so far below the time required for the NMC-S materials to cool down. The shortened time could save about 470 L oxygen gas in our current synthesis process. In the literature, the cooling rate has been regulated to control meso-structure and oxygen and cation vacancies to enhance alkali ions mobility, structural stability and capacity cyclability of battery materials.[18, 19, 20, 21, 22, 23] Furthermore, quenching has been commonly used to maintain the unique high-temperature phases, especially for sodium ion batteries.[24] The proposed quenching technique can save energy in the manufacturing battery materials with some caveats. We have added to the discussion of the manuscript the following statement:

Applying the quenching technique to real production of battery materials could potentially save time and energy for manufacturing. When the thermal processing strategy is integrated with other strategies such as doping and coating, higher quality cathode materials are on the horizon. Several emerging battery chemistries, especially sodium ion battery cathode materials, need thermal quenching to synthesize materials with desired phases for good battery performance.[25] Therefore, some efforts in designing thermal treatment apparatus at the manufacturing line are recommended to garner the manufacturing benefit of quenching.

Reviewer #3 (Remarks to the Author):

This manuscript reports on a quenching treatment for NCM811 cathodes during calcination to generate Li_2CO_3 and reduce Ni oxidation states near the particle surface. The cathodes exhibit few side reactions and charge distribution homogeneity, and show a more stable cycling retention at 4.5 V. However, there have been many reports on the fast-cooling treatment for Ni-rich cathode (Electrochimica Acta 2017, 227, 225; Advanced Energy Materials 2019, 9, 1901915), and the author does not clearly illustrate the surface-bulk interactions. This work is not recommended for publication in Nature Communications, and several questions are desirable to be addressed as follows:

Response: We are thankful for the reviewer's comments.

We agreed with the reviewer that other reports (Electrochimica Acta 2017, 227, 225; Advanced Energy Materials 2019, 9, 1901915) adopted similar fast-cooling treatment for Ni-rich cathode materials. These works found that Ni-rich cathodes could deliver enhanced electrochemical performance after fast-cooling treatment, which is supportive for our results that NMC-Q shows higher capacity and better cycling stability than that of NMC-S. For the mechanism of performance improvement, one work attributed to an increase of interfacial stability and bulk interslab distances for fast Li ions transport and less loss of lattice oxygen during cycling. (Electrochimica Acta 2017, 227, 225). Another work found that the surface change can be suppressed by quenching, and thus improving the surface stability and rate performance of NMC cathodes. (Advanced Energy Materials 2019, 9, 1901915). Overall, the benefit to battery performance is consistent with our discovery. Our study here provides new insights into how quenching can benefit bulk properties in terms of the homogeneous charge distribution. In recent years, charge distribution in secondary particles has been shown to affect battery performance.[4, 13, 14] Some previous studies have shown the interaction between surface and bulk indeed exists.[13, 14] However, it has not been clear shown that how the cooling rate affects the surface structure and thus bulk charge distribution homogeneity. It is significant to study the degradation mechanism taking into consideration surface chemistry and charge distribution homogeneity in the bulk at the same time, because the capacity delivery of NMCs involves redox reactions and kinetics throughout the whole polycrystalline particles. Our results provided unambiguous evidence by comprehensive synchrotron characterizations about the effect of surface structure on the charge distribution in the bulk and elucidated the correlation between surface structure, bulk properties and electrochemical performance of NMC cathode materials. We are confident that the insights delivered in the work are critical and complementary to the arguments made in the existing literature that thermal processing could be a strong tuning knob to improve battery performance, beyond the conventional compositional changes.

1. Please provide more experimental details about the quenching method. Was it in ambient environment or dry air? Were the treatments and the results controllable?

Response: We appreciate the reviewer's suggestion.

NMC-Q was quenched by transferring cathode powder out of the tube furnace at the peak temperature of 750 °C after calcination immediately and poured onto a copper plate to quench within about 5 minutes in the ambient environment with about 38% relative humidity. More details about quenching have been added in the *Materials synthesis* section in the main text. The experiments have been repeated, so the results are reliable. However, more high-precision facilities and instruments are needed for large manufacturing. We have added in the discussion of the manuscript:

Applying the quenching technique to real production of battery materials could potentially save time and energy for manufacturing. When the thermal processing strategy is integrated with other strategies such as doping and coating, higher quality cathode materials are on the horizon. Several emerging battery chemistries, especially sodium ion battery cathode materials, need thermal quenching to synthesize materials with desired phases for good battery performance.[25] Therefore, some efforts in designing thermal treatment apparatus at the manufacturing line are recommended to garner the manufacturing benefit of quenching.

2. It is unreasonable to compare the Ni-rich cathodes that slowly cooled in O_2 and that quenched in the air. It is known that Ni-rich cathodes are vulnerable in the ambient environment with residual lithium species generated on the surface, leading to inferior performance.

Response: Thank you very much for the comment.

We agree with the reviewer that Ni-rich cathodes are vulnerable in the ambient environment and have been carefully studied in previous papers.[26, 27, 28] When conducting the current research, we managed to use that knowledge to limited the unnecessary ambient exposure time. As reported in the literature, the residual lithium species on the surface is enormously dependent on the exposure time, temperature, and CO_2/H_2O partial pressures.[3, 5, 6, 7, 8] However, the generation process needs to expose cathode materials in an environment with a relatively long time and high humidity, such as 55 °C and 80% relative humidity for 4 weeks,[6] or at 60 °C and 80% relative humidity for 30 days.[7] In this work, we transferred both powders and electrodes into an argon-filled glovebox immediately for storage. The materials transferring process is too short to complete residual lithium species generation, so the comparison of NMC-Q and NMC-S is reasonable to study the underlying mechanism of thermal processing on layered cathodes.

3. Does the surface lithium species here contain only Li_2CO_3? Why would it benefit to the performance? The author claims that the Li ions diffuse out of the lattice, then would the lack of Li ions in the bulk influence the electrochemical performance?

Response: Thank you very much for the reviewer's comments.

As known, the residual lithium species on the surface are usually composed of Li_2CO_3, $LiHCO_3$, and LiOH. Based on the XPS results, we think the peak in XPS Li1s spectra at ~55 eV mainly belongs to Li_2CO_3, similar to the previous report.[29] Our soft XAS results also support such an assignment. For the mechanism of performance improvement of NMC-Q, it should be taking surface structure and bulk properties into account at the same time. In our work, we found that the surface change occurs in a narrow region near the surface of NMC-Q, as shown by soft XAS, TXM, and STEM-EELS. The surface change involves more Li_2CO_3 formation and lower Ni oxidation state on the surface of NMC-Q than that of NMC-S. Firstly, more Li_2CO_3 formation on the surface of NMC-Q originates from Li diffusion from the bulk to the surface, but the quantity of Li diffusion is minor and only from the 10-20 nm depth of NMC secondary particles. It can be verified by a slightly lower initial capacity of NMC-Q (195 mAh/g) than that of NMC-S (198 mAh/g) in Figure S8. Secondly, some reports found that Li_2CO_3 layer on the surface can release stress and provide a stable interface, thus suppressing interface resistance increase for charge transfer and resulting in excellent cycling stability.[10, 11] So, we think that small amount of Li_2CO_3 exists on the surface of NMC-Q may not be detrimental for the performance. Thirdly, it has been reported that the surface change can suppress the structural changes and minimize the oxygen evolution, further improving structural and cycling stability of NMC cathodes.[30] Last but not the least, our study shows that the surface chemistry after quenching could facilitate the enhancement of charge distribution homogeneity in the bulk during electrochemical cycling, further improving performance of NMC-Q during extended cycling. Therefore, it can conclude that the nanoscale surface change on NMC-Q induced by quenching can modify NMC cathode materials with an improvement of interfacial stability and charge distribution homogeneity.

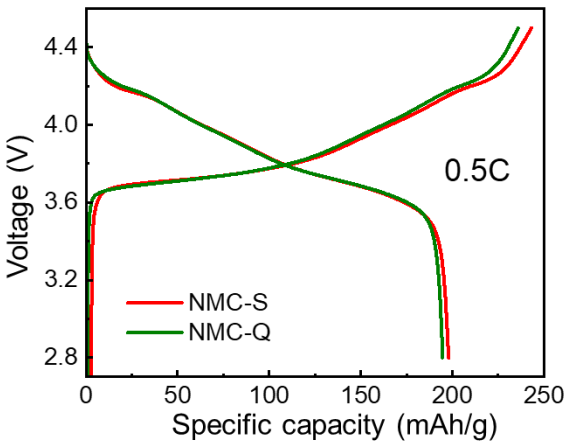

Figure S8. The charge/discharge profiles of NMC-Q and NMC-S for the first cycle at 0.5C with a voltage range of 2.8-4.5 V.

Other reports (Electrochimica Acta 2017, 227, 225; Advanced Energy Materials 2019, 9, 1901915) adopted similar fast-cooling treatment for Ni-rich cathode materials. These works found that Ni-rich cathodes could deliver enhanced electrochemical performance after fast-cooling treatment, which is supportive for our results that NMC-Q shows higher capacity and better cycling stability than that of NMC-S. For the mechanism of performance improvement, one work attributed to an increase of interfacial stability and bulk interslab distances for fast Li ions transport and less loss of lattice oxygen during cycling. (Electrochimica Acta 2017, 227, 225). Another work found that the surface change can be suppressed by quenching, and thus improving the surface stability and rate performance of NMC cathodes. (Advanced Energy Materials 2019, 9, 1901915). Overall, the benefit to battery performance is consistent with our discovery. Our study here provides new insights into how quenching can benefit bulk properties in terms of the homogeneous charge distribution. Cho and coworkers used a different strategy to create surface reduction,[31] which also led to improve battery performance, similar to our study here.

4. The surface difference between the two cathodes needs more characterization. Do the Li-containing species cover the particle surface evenly? Why the surface Ni ions are reduced after quenching. The surface of Ni-rich cathodes tends to be reduced with oxygen loss and form an inactive rock-salt phase. What about the surface situation here? Finally, how do the above two features induce charge homogeneity?

Response: We are thankful for the reviewer's comment.

We performed STEM-EELS measurements on NMC-Q and NMC-S as shown in Figure S1. The Ni L-edge EELS spectra for both NMC-Q and NMC-S show a peak shift to higher energy from the surface to bulk. For NMC-Q the peak shift can be seen at 5 nm from the surface while for the NMC-S the peak shift can be seen at 2 nm. We also analyzed the O K-edge spectra where the appearance of pre-peak (here marked by '*',

sensitive to the TM oxidation state) can be seen from 5 nm from the surface for NMC-Q and 2 nm for NMC-S. Thereby we can confirm that NMC-Q shows a high gradient of Ni-oxidation state from surface to bulk while very minimal oxidation state gradient for NMC-S. We analyzed the Ni oxidation state of NMC-Q and NMC-S samples after 200 cycles by XPS in Figure 4a,b, showing that Ni undergoes more reduction on NMC-S after 200 cycles than that on NMC-Q. Combining TXM results after cycling in Figure 4c-e, one can conclude that the pre-passivated surface helps maintain the surface stability and ensure the charge homogeneity. Cho and coworkers used a different strategy to create surface reduction,[31] which also led to improve battery performance, similar to our study here.

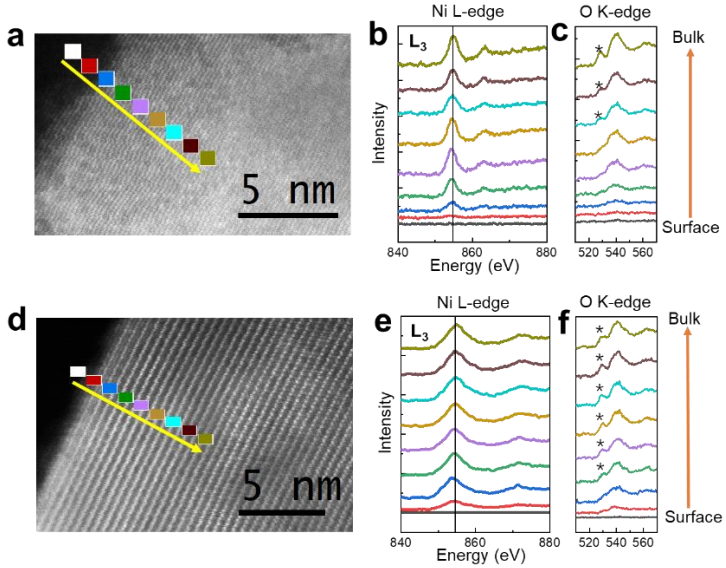

Figure S1. STEM images to show the selected regions for EELS acquisition for (a) NMC-Q and (d) NMC-S. EELS Ni L-edge spectra (b,e) and O K-edge spectra (c,f) for NMC-Q and NMC-S corresponding to the regions in a and d.

5. On Page 17, Line 340, the author states that the charge homogeneity may promote higher chemo-mechanical stability, which is indeed a critical factor influencing the cathode performance. What about the chemo-mechanical performance of the two cathodes in this work? Please provide related evidence.

Response: The authors appreciate the reviewer's insightful comments.

As shown in Figure S9c and d, NMC-Q shows less evolution than NMC-S in the dQ/dV curves, showing that the cell polarization is mitigated in this sample. In our previous report,[4] we comprehensively investigated the effect of charge homogeneity for chemo-mechanical and electrochemical performance, showing that less stress generation in the lithiation/delithiation process corresponds to a smaller charge heterogeneity. So, we believe that the improvement of charge homogeneity can contribute to higher chemo-mechanical stability, enhancing the cycling stability of NMC-Q cathodes.

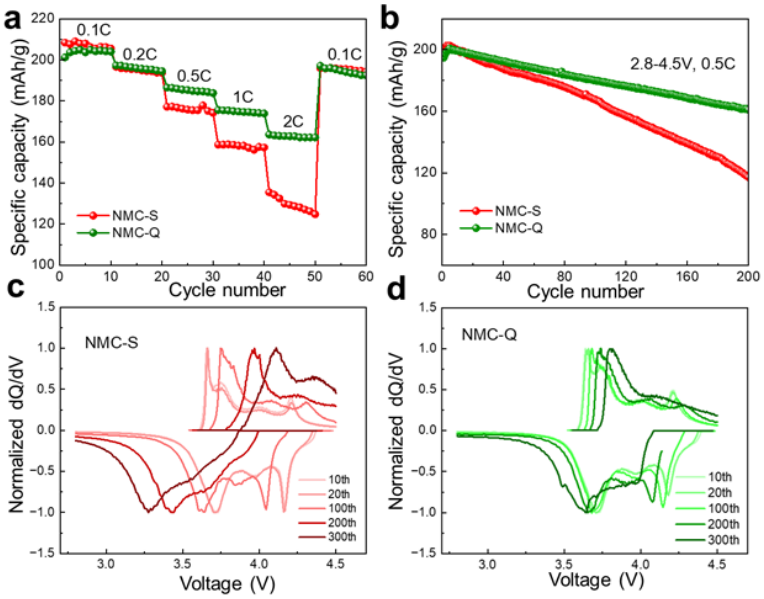

Figure S9. (a) Rate capability and (b) cycling performance at 0.5C of NMC-S and NMC-Q cathodes in Li metal cells with a voltage range 2.8-4.5 V. dQ/dV curves of 10th, 20th, 100th, 200th and 300th cycle at 0.5C for (c) NMC-S and (d) NMC-Q.

6. Why does the capacity of NMC-Q increase in the first few cycles?

Response: Thank you very much for the reviewer's comment.

In Figure 3c and d, the specific capacity and specific energy correspond to discharging process or lithiation of Li ions into the NMC crystal structure. The capacity delivery highly depends on Li ion transport in NMC lattice and electrolyte penetration in the electrode. So, the rise of capacity during the first several cycles is likely associated with the improving penetration of electrolyte into the electrode and improvement of Li ion transport in the NMC lattice during lithiation. Note that the slight capacity increase exists in both NMC-Q and NMC-S samples in Figure R1, and it is common in the literature.[1, 2] It is more significant for the NMC-Q sample, because it takes more cycles to overcome the initial kinetic barrier created by the surface reduced layer. We believe the comparison of battery performance between NMC-Q and NMC-S is reliable and compelling with the identical cell system and test conditions here. The above explanation has been added onto Page 12 in the main text.

The cells show increasing specific capacity and energy during the first several cycles in Figure 3c,d, which is associated with the increasing Li ion transport kinetics due to factors such as improved electrolyte wetting. The increase is more obvious for the NMC-Q because it takes more cycles to overcome the initial kinetic barrier created by the surface reduced layer.[3] When cycled at a higher C rate (1C in Figure 3c,d), the kinetic barrier plays a larger role than when cycled at a lower C rate (0.5C in Figure 3a,b).

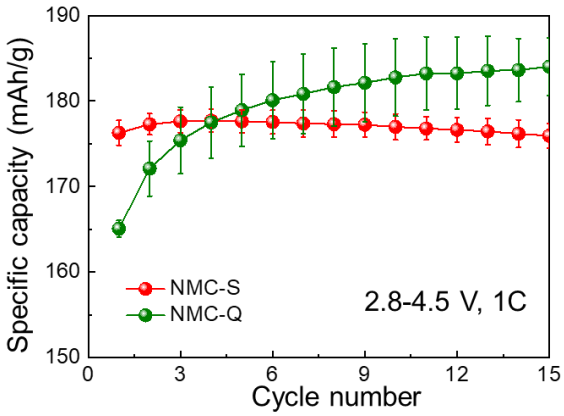

Figure R1. Zoom in Figure 3c in the range of the first 15 cycles.

7. The author states that this thermal processing is a simple and scalable step and could be a promising CAM manufacturing path forward. Did the author attempt to perform a scalable application and validation in pouch cells?

Response: We acknowledge the reviewer's comment about the scalable application. In our work, we prepared NMC cathode materials by a specific cooling method (quenching), which can shorten the cooling time, reduce the consumption of oxygen gas, and decrease the energy consumption to some degree. Fundamentally, we found the surface change occurs on the surface of NMC-Q during quenching. The surface change of NMC-Q displays as more Li_2CO_3 formation and lower Ni oxidation state on the surface than that of NMC-S, as shown by XPS, STEM-EELS, soft XAS and TXM results. Ultimately, these changes have led to a positive impact on battery performance. Our fundamental study reported here provides a refined example of how a simple thermal processing step can engineer surface chemistry to eventually regulate the redox reactions and charge distribution in the bulk. In summary, we engineered the very top surface of NMC secondary particles using the non-equilibrium quenching method. This method can be applied in addition to other materials stabilization strategies. Nevertheless, we agree that more high-precision facilities and instruments are needed for large manufacturing. We have added the following content to the discussion of the manuscript:

Applying the quenching technique to real production of battery materials could potentially save time and energy for manufacturing. When the thermal processing strategy is integrated with other strategies such as doping and coating, higher quality cathode materials are on the horizon. Several emerging battery chemistries, especially sodium ion battery cathode materials, need thermal quenching to synthesize materials with desired phases for good battery performance.[25] Therefore, some efforts in designing thermal treatment apparatus at the manufacturing line are recommended to garner the manufacturing benefit of quenching.

Reference

1. Chen J*, et al.* Constructing a thin disordered self-protective layer on the $LiNiO_2$ primary particles against oxygen release. *Advanced Functional Materials* **33**, 2211515 (2023).
2. Wu F*, et al.* Dual-anion ionic liquid electrolyte enables stable Ni-rich cathodes in lithium-metal batteries. *Joule* **5**, 2177 (2021).
3. Mu L*, et al.* Surface transformation by a "cocktail" solvent enables stable cathode materials for sodium ion batteries. *Journal of Materials Chemistry A* **6**, 2758 (2018).
4. Xu Z*, et al.* Charge distribution guided by grain crystallographic orientations in polycrystalline battery materials. *Nature Communications* **11**, 83 (2020).
5. Grenier A*, et al.* Reaction heterogeneity in $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ induced by surface layer. *Chemistry of Materials* **29**, 7345 (2017).
6. Kazutoshi M*, et al.* Effects of CO_2 in air on Li deintercalation from $LiNi_{1-x-y}Co_xAl_yO_2$. *Journal of Power Sources* **81-82**, 558 (1999).
7. Cho DH*, et al.* Effect of residual lithium compounds on layer Ni-rich $Li[Ni_{0.7}Mn_{0.3}]O_2$. *Journal of The Electrochemical Society* **161**, A920 (2014).
8. Oh P*, et al.* Overcoming the chemical instability on exposure to air of Ni-rich layered oxide cathodes by coating with spinel $LiMn_{1.9}Al_{0.1}O_4$. *Journal of Materials Chemistry A* **4**, 5839 (2016).
9. Liang L*, et al.* Surface/interface structure degradation of Ni-rich layered oxide cathodes toward lithium-ion batteries: fundamental mechanisms and remedying strategies. *Advanced Materials Interfaces* **7**, 1901749 (2019).
10. Li H*, et al.* Combination effect of bulk structure change and surface rearrangement on the electrochemical kinetics of $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ during initial charging processes. *ACS Applied Materials & Interfaces* **10**, 41370 (2018).
11. Faenza NV*, et al.* Growth of ambient induced aurface impurity apecies on layered positive electrode materials and impact on electrochemical performance. *Journal of The Electrochemical Society* **164**, A3727 (2017).
12. Trevisanello E*, et al.* Polycrystalline and single crystalline NCM cathode materials-quantifying particle cracking, active surface area, and lithium diffusion. *Advanced Energy Materials* **11**, 2003400 (2021).
13. Hou D*, et al.* Surface coating by mechanofusion modulates bulk charging pathways and battery performance of Ni-rich layered cathodes. *Proceedings of the National Academy of Sciences* **119**, e2212802119 (2022).
14. Li S*, et al.* Mutual modulation between surface chemistry and bulk microstructure within secondary particles of nickel-rich layered oxides. *Nature Communications* **11**, 4433 (2020).
15. Zhang SS*, et al.* Enhanced electrochemical performance of Ni-rich layered cathode materials by using $LiPF_6$ as a cathode additive. *ChemElectroChem* **6**, 1536 (2019).
16. Lin F*, et al.* Surface reconstruction and chemical evolution of stoichiometric layered cathode materials for lithium-ion batteries. *Nature Communications* **5**, 3529 (2014).
17. Lin F*, et al.* Profiling the nanoscale gradient in stoichiometric layered cathode particles for lithium-ion batteries. *Energy & Environmental Science* **7**, 3077 (2014).
18. Liu X*, et al.* Al and Fe-containing Mn-based layered cathode with controlled vacancies for high-rate sodium ion batteries. *Nano Energy* **76**, 104997 (2020).
19. Yao K*, et al.* Bundled defect-rich MoS_2 for a high-rate and long-life sodium-ion battery: achieving 3D diffusion of sodium ion by vacancies to improve kinetics. *Small* **15**, 1805405 (2019).

20. Zheng L*, et al.* Hexagonal and monoclinic $NaNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Na-NCA) for sodium ion batteries. *Journal of Power Sources* **433**, 226698 (2019).
21. Hirsh H*, et al.* Meso-structure controlled synthesis of sodium iron-manganese oxides cathode for low-cost Na-ion batteries. *Journal of The Electrochemical Society* **166**, A2528 (2019).
22. Su Z*, et al.* Quenching-induced defects liberate the latent reversible capacity of lithium titanate anode. *Advanced Materials* **35**, 2208573 (2023).
23. Jo S*, et al.* Solid-state reaction heterogeneity during calcination of lithium-ion battery cathode. *Advanced Materials* **35**, 2207076 (2023).
24. Kim JC*, et al.* Direct observation of alternating octahedral and prismatic sodium layers in O3-type transition metal oxides. *Advanced Energy Materials* **10**, 2001151 (2020).
25. Rahman MM*, et al.* Chemical modulation of local transition metal environment enables reversible oxygen redox in Mn-based layered cathodes. *ACS Energy Letters* **6**, 2882 (2021).
26. Mu L*, et al.* The sensitive surface chemistry of Co-free, Ni-rich layered oxides: identifying experimental conditions that influence characterization results. *Journal of Materials Chemistry A* **8**, 17487 (2020).
27. Shkrob IA*, et al.* Chemical weathering of layered Ni-rich oxide electrode materials: evidence for cation exchange. *Journal of The Electrochemical Society* **164**, A1489 (2017).
28. Pritzl D*, et al.* Washing of nickel-rich cathode materials for lithium-ion batteries: towards a mechanistic understanding. *Journal of The Electrochemical Society* **166**, A4056 (2019).
29. Im J*, et al.* Fluorinated carbonate-based electrolyte for high-voltage $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$/graphite lithium-ion battery. *Journal of The Electrochemical Society* **164**, A6381 (2017).
30. Kim H*, et al.* A new coating method for alleviating surface degradation of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode material: nanoscale surface treatment of primary particles. *Nano Letters* **15**, 2111 (2015).
31. Cho Y*, et al.* A new type of protective surface layer for high-capacity Ni-based cathode materials: nanoscaled surface pillaring layer. *Nano Letters* **13**, 1145 (2013).

Response letter

Dear Reviewers,

Thank you for reviewing our manuscript (***NCOMMS-23-48088A***) entitled "***Thermal processing to modulate surface chemistry and bulk charge distribution in layered cathodes for lithium batteries***". We sincerely appreciate all the insightful comments and valuable suggestions, which we believe have helped us greatly improve the manuscript. We have carefully considered these comments and thoroughly revised our manuscript.

In this revised manuscript, we addressed review comments point by point and annotated the changes in the revised manuscript. For ease of reference, our response is in blue, and all changes in the revised manuscript are highlighted in yellow.

We appreciate your attentiveness and earnestness and thank you once again for your consideration and support.

With our best regards,

Feng Lin
On behalf of all coauthors

Reviewer #1 (Remarks to the Author):

The authors have well addressed all the concerns raised by the reviewers. The manuscript will be ready for publication after revising the following question:
1. In Figure 4c, there is a problem with the format of "Ni L3high/L3low". Please modify it.
Response: Thank you for reviewing our manuscript. Changes are made.

Reviewer #2 (Remarks to the Author):

The author has revised the manuscript point-to-point. The innovation and quality of the manuscript have met the requirements of Nat.Commun. journal, and we recommend it for publication.
Response: Thank you for reviewing our manuscript.

Reviewer #3 (Remarks to the Author):

The authors have extended their manuscript and improved the quality to a certain extent. The reviewer has also carefully read through the comments from other reviewers and the responses from the authors. However, the major concern of the reviewers remains unsolved. In particular, the mechanism how the surface properties can impact the bulk reactions is not clarified, which is one of the core concepts of this work. It is unreasonable to directly build an interaction relationship between the surface and the bulk simply via the individual experimental consequences. Does the NMC-S and NMC-Q only have the difference in surface? For example, it is likely that the quenching induces the change of strain or defects distribution in the crystal bulk, which can cause the more homogenous charge distribution. Besides, there are still several issues listed below. Therefore, this work cannot be accepted at the current state.
Response: The authors appreciate the reviewer's insightful comments.
In our pervious report, we found that the surface coating can regulate the crack initiation and propagation pattern during delithiation and can reduce the overall mechanical fracture. (*PANS. 2022, 119, e2212802119).* Other report found that the regions with higher porosity in the bulk of NMCs are associated with more severe surface lattice reconstructions and thus cell performance degradation. (*Nat. Commun. 2020, 11, 4433*) All these studies have shown the interaction between surface and bulk indeed exists. In this work, we innovatively proposed that the cooling rate can affect the surface structure, which shows quenching can induce more Li_2CO_3 formation and Ni reduction on the surface of NMC-Q with a thickness of about 5 nm. However, the cooling rate has negligible effect on the bulk structure and morphology of NMCs, including the change

of strain and defects distributions (Figure 2). The changes of surface structure of NMC-Q can facilitate the improvement of charge distribution homogeneity in the bulk of NMC-Q during delithiation and lithiation. The coupling effect between the surface and the bulk collectively enhance chemo-mechanical robustness and thus cell performance with NMC-Q cathodes.

1. From the Li 1s XPS spectra, compared with the 81.0% proportion of NMC-Q, there is 68.0% Li_2CO_3 of NMC-S, which should be derived from residual lithium. Does the left 13.0% Li_2CO_3 come from the Li diffusion in the lattice and induce the improved performance of NMC-Q?

Response: We appreciate the reviewer's comment.

The residual lithium on the surface of NMC secondary particles with natural cooling rate is thought to come from two aspects: (1) using an excess amount lithium precursor (e.g. LiOH in our work), and (2) reacting with H_2O and CO_2 in the ambient environment. In this work, we prepared NMC-S and NMC-Q materials with same 5% excess LiOH addition. Then we transferred both NMC-S and NMC-Q powders and electrodes into an argon-filled glovebox immediately for storage within same procedures and subequal processing time. Therefore, it can be speculated that the difference of 13.0% Li_2CO_3 on the surface of NMC-Q and NMC-S is mainly originated from the Li diffusion from the bulk of secondary particles during quenching. Due to the Li loss from the lattice, the surface TM (mostly Ni) gets reduced, as shown in our soft XAS data. We provided extensive discussion on this topic during our last revision, where we also cited references that reported similar performance observations for NMC materials (with surface reduction) synthesized by other means.

2. The composition of the surface Li layer remains elusive. Chemical titration can be useful technique to distinguish the Li_2CO_3 and LiOH.

Response: We are thankful for the reviewer's insightful suggestion.

We have carried out chemical titration to investigate the composition of residual lithium compound on the surface of NMC-S and NMC-Q cathode materials. NMC-Q and NMC-S (0.8 g) powder were magnetically stirred in 150 mL deionized water, then were titrated by a solution of HCl of 0.4687 M to quantify the Li_2CO_3 and LiOH by means of an automatic titrimeter equipped with pH electrode (905 Titrando, Metrohm). The corresponding results are as following Table R1. The Li compound ratio in total including Li_2CO_3 and LiOH on the surface of NMC-Q is 2.29%, which is higher than NMC-S with 2.13%, consistent with XPS, STEM, soft XAS and TXM results. It further confirms that more Li compound on the surface of NMC-Q derives from Li diffusion from the bulk to the surface during quenching.

Table R1. The Li Li_2CO_3 and LiOH ratio of NMC-Q and NMC-S samples.

Sample ID	Li compound in total	Li_2CO_3	LiOH
NMC-Q	2.29%	1.91%	0.38%
NMC-S	2.13%	1.73%	0.40%

3. The author states that Li and O loss and the subsequent Li_2O formation contribute to the surface Li_2CO_3 layer. However, it is known that Li/O loss is accompanies with the formation of inert rock-salt NiO-like phase, which deteriorates the cathode performance. What about the NMC-Q here?

Response: The authors appreciate the reviewer's insightful comments.

Combining XPS, soft XAS, TXM and STEM-EELS results, we can confirm that NMC-Q shows a high gradient of Ni-oxidation state from surface to bulk while very minimal oxidation state gradient for NMC-S. We analyzed the Ni oxidation state of NMC-Q and NMC-S samples after 200 cycles by soft XAS in Figure 4a,b, showing that Ni undergoes more reduction on NMC-S after 200 cycles than that on NMC-Q. Combining TXM results after cycling in Figure 4c-e, one can conclude that the pre-passivated surface helps maintain the surface stability and ensure the charge homogeneity. Cho and coworkers used a different strategy to create surface reduction, (*Nano Letters 2013, 13, 1145*) which also led to improve battery performance, similar to our study here. More importantly, we found that the change of surface structure can lead to an increase of bulk charge homogeneity during cycling, which jointly enhance the battery performance. Both surface and bulk properties could impact battery performance. Our results show that the surface properties can impact the bulk reactions and thus the battery performance of NMC polycrystalline particles.

4. To clearly clarify the difference of the two cathodes, STEM images showing surface crystal structures should be provided.

Response: We thank the reviewer for this suggestion. We have added STEM images for NMC-Q and NMC-S in Figure R1. We can clearly see that there presents a reconstruction layer forming on the surface of both NMC-Q and NMC-S particles, but the reconstruction layer on the surface of NMC-Q is thicker than that of NMC-S, which is consistent with the soft XAS results in Figure 1c, d. Meanwhile, from the O K-edge SETM-EELS spectra in Figure S1b, e, NMC-Q and NMC-S show apparent pre-edge peak marked by '*'. This pre-edge peak is associated with the transition from O1*s* to O2*p*-TM3*d* hybridized state and is sensitive to the transition metal's oxidation state. (*Nat. Commun. 2014, 5, 3529, Energy Environ. Sci., 2014, 7, 3077, J. Am. Chem. Soc.*

2005, 127(49), 17479). For NMC-Q, the pre-edge peak of O K-edge is absence at the subsurface region but is distinct and sharp in the bulk of particles in Figure S1b. For NMC-S, the pre-edge peak of O K-edge can be seen at both subsurface and bulk regions in Figure S1e. Similarly, from Figure S1c and f, we can see a peak shift of Ni L-edge for NMC-Q, whereas insignificant peak shift for NMC-S from the subsurface to the bulk. Thus, combining STEM images and EELS spectra results, it can confirm that NMC-Q indeed has a thicker surface reconstruction layer than that of NMC-S.

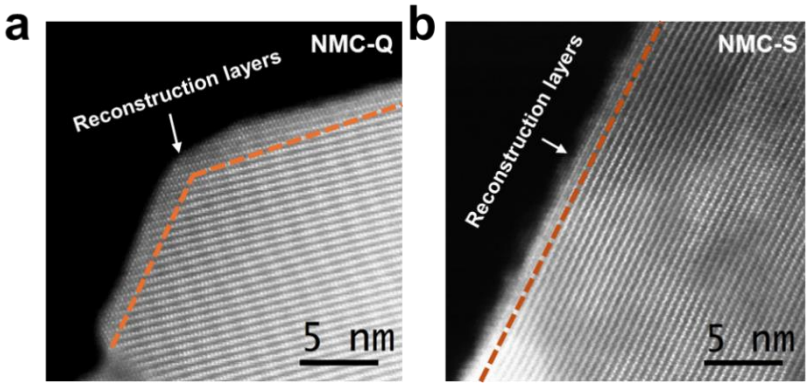

Figure R1. High-resolution STEM images of (a) NMC-Q and (b)NMC-S materials.

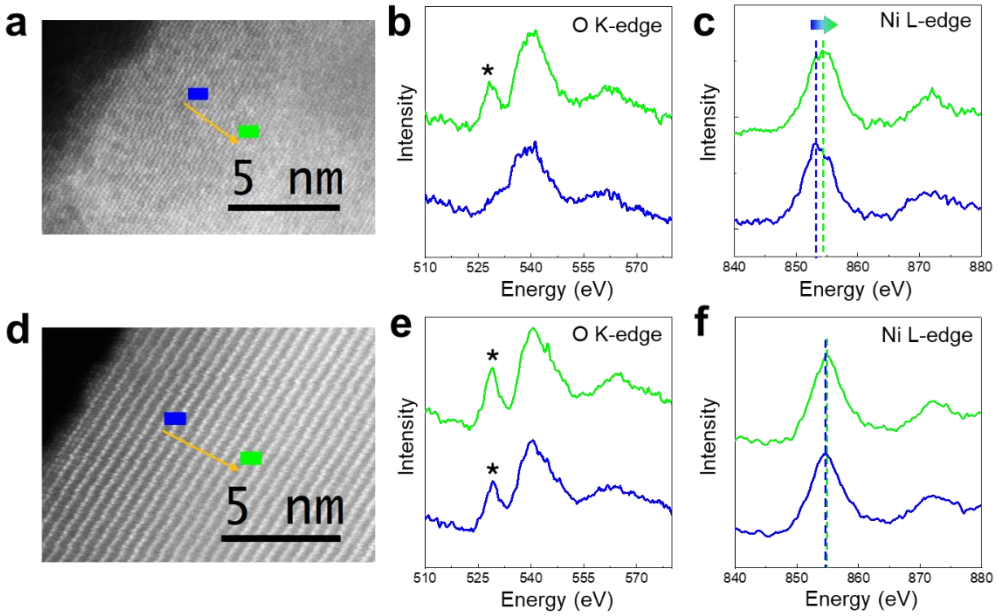

Figure S1. STEM images to show the selected regions for EELS acquisition for (a) NMC-Q and (d) NMC-S. EELS O K-edge spectra (b,e) and Ni L-edge spectra (c,f) for NMC-Q and NMC-S corresponding to the regions in a and d.

5. Typically, the Ni reduction corresponds to the Ni L edge EELS peak shifting to low energy loss. However, there is no peak shift in the supplemented Figure S1.

Response: We thank the reviewer for this suggestion.

We have replotted the STEM-EELS as shown in Figure S1. The energy resolution of

the measurement is not high enough at the surface, so we have not considered the surface acquisition for both NMC-Q and NMC-S. From the O K-edge SETM-EELS spectra in Figure S1b, e, NMC-Q and NMC-S show apparent pre-edge peak marked by '*'. This pre-edge peak is associated with the transition from O1*s* to O2*p*-TM3*d* hybridized state and is sensitive to the transition metal's oxidation state. (*Nat. Commun. 2014, 5, 3529, Energy Environ. Sci., 2014, 7, 3077, J. Am. Chem. Soc. 2005, 127(49), 17479*) For NMC-Q, the pre-edge peak of O K-edge is absence at the subsurface region but is distinct and sharp in the bulk of particles in Figure S1b. For NMC-S, the pre-edge peak of O K-edge can be seen at both subsurface and bulk regions in Figure S1e. Similarly, from Figure S1c and f, we can see a peak shift of Ni L-edge for NMC-Q, whereas insignificant peak shift for NMC-S from the subsurface to the bulk. Thus, combining STEM images and EELS spectra results, it can confirm that NMC-Q indeed has a thicker surface reconstruction layer than that of NMC-S.

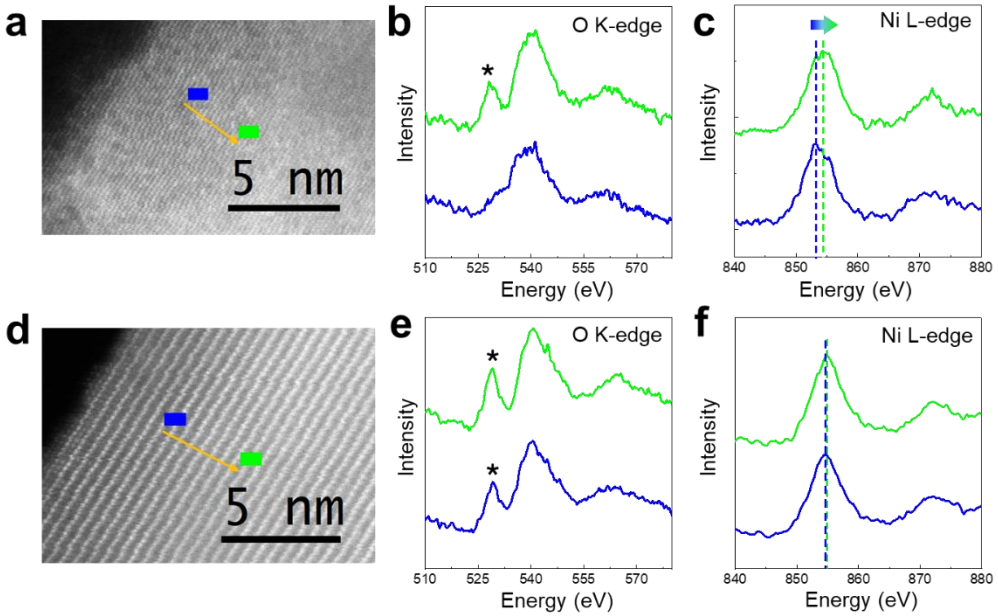

Figure S1. STEM images to show the selected regions for EELS acquisition for (a) NMC-Q and (d) NMC-S. EELS O K-edge spectra (b,e) and Ni L-edge spectra (c,f) for NMC-Q and NMC-S corresponding to the regions in a and d.

6. Please explain the mechanism of the reduced valence of surface Ni in the quenching process.

Response: We are thankful for the reviewer's comments.

The reduction of Ni oxidation state and more Li_2CO_3 on the surface of NMC-Q originates from the Li diffusion from the bulk of NMC crystal structure to the surface, which is driven by the rapid decrease of temperature on the surface during quenching. The rapid temperature decrease reduces the solubility of Li ion in the lattice. The Li diffusion from the bulk to the surface can also be regarded as Li loss, which happens

together with O loss. Then, Li_2O forms on the surface of NMC-Q, which is later changed to Li_2CO_3 by reacting with the CO_2 in the air. Ultimately, NMC-Q shows a reconstructed surface layer with a lower Ni oxidation state, or named as the Li-deficient layer, and accompanied with more Li_2CO_3 formation on the particle surface during quenching. Ni reduction and Li_2CO_3 are discussed in our above responses and in our manuscript.

7. To elucidate the chemo-mechanical stability, cross-section SEM images of the cycled cathode particles should be provided to observe the evolution of cracks.

Response: We thank the reviewer for this suggestion.

We have added cross-sectional SEM images of cycled cathodes in Figure R2. The cross-sectional SEM images were performed on the cycled NMC-Q and NMC-S after 100 cycles at 1C to being comparable with TXM results. The bulk of NMC-Q secondary particles is intact without cracks in Figure R2a,b, but NMC-S undergoes noticeable cracking after cycling in Figure 2c,d. Combining with TXM results (Figure 5), it can confirm that the NMC-Q undergoes less microstructural changes in the particles and shows less crack in the bulk than that of NMC-S, indicating that better chemo-mechanical stability and more homogeneous charge distribution of NMC-Q during long-term cycling.

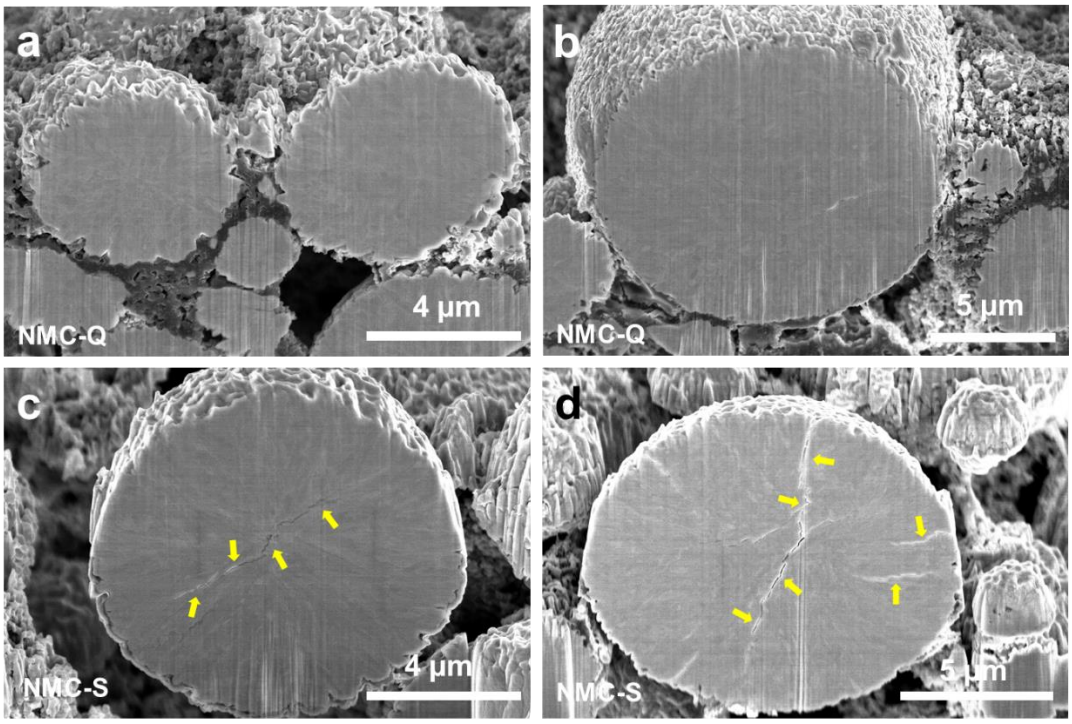

Figure R2. Cross-sectional SEM images of (a,b) NMC-Q and (c,d) NMC-S cycled cathodes after 100 cycles at 1C (2.8-4.5V).