

Transition metal vacancy and position engineering enables reversible anionic redox reaction for sodium storage

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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)

In this manuscript, the authors investigated the Mg doping and vacancy effect on the structural evolution and electrochemical property of P2-type $\text{Na}_{0.67}\text{Mg}_x\text{Mn}_{1-x}\text{O}_2$ ($0 \leq x \leq 0.2$). The authors claimed that introducing Mg induces the Mn occupation in the prismatic Na site of $\text{Na}_{0.67}\text{Mg}_x\text{Mn}_{1-x}\text{O}_2$ while the vacancies in the transition metal (TM) oxide layer are preserved keeping the honeycomb superstructure. The incorporation of in-situ x-ray diffraction, in-situ Raman, and scanning transmission electron microscopy demonstrates the improved structural stability of P2- $\text{Na}_{0.67}\text{Mn}_{0.011}[\text{Mg}_{0.1}\text{Mn}_{0.83}]\text{O}_2$ (NMV-M10) compared to the non-doped P2- $\text{Na}_{0.67}[\text{Mn}_{0.9}]\text{O}_2$ (NMV) over the sodiation and desodiation. The electrochemistry, x-ray spectroscopy data, and theoretical study of the materials further support the improved structural stability, and electrochemical performance that involves the oxygen redox derived from the improved structural stability by Mg doping that generates Mn 'rivets' and preserved TM vacancies. Obviously, such P2-structured material and its study can suggest avenues to stabilize the P2-type materials with reversible oxygen redox.

Nevertheless, some of the points described in this manuscript were not convincing to fully support the authors' understanding. For example, the authors claim that Mg doping results in Mn ion occupation in Na sites, but the claim is only based on the observation from STEM images. More investigation into the oxidation state and the coordination environment change of Mn in the Na site should be conducted to support the author's claim.

In addition, the Mg-doped NMVs were synthesized by using a well-known solution-based co-precipitation method for precursors followed by the heat treatment which has also been utilized for many Li or Na cathode materials. However, not like many other Mg-doped P2-type Na cathode papers, the authors claim the Mn occupation in Na sites with preserved TM vacancy sites and ratio in the TM oxide layer. It is hard to understand the reason why the Mg-doped NMV family has the structural difference (Mn occupation in Na sites) compared to previously reported Mg-doped P2- $\text{Na}_{0.67}\text{Mg}_x\text{Mn}_{1-x}\text{O}_2$ papers (e.g. U. Maitra et al., *Nature Chem* 10, 288–295 (2018); J. Qu et al., *ACS Appl. Mater. Interfaces* 2019, 11, 26938, R. Clément et al., *Energy Environ. Sci.*, 2016, 9, 3240).

Furthermore, it is quite unclear whether the $\text{Mn}^{3+/4+}$ redox only occurs in the voltage range of 2.0 – 3.5 V as the lattice shrinkage and expansion along the a axis that is a demonstration of Jahn-Teller distortion by $\text{Mn}^{3+/4+}$ redox, is observable over the entire charge and discharge from the in-situ XRD data ((100) reflection).

Overall, I do not agree that this manuscript delivers sufficient information about the TM vacancy engineering and oxygen redox in battery materials that are expected for publication in *Nature Communication*. Therefore, the publication of this work in the *Nature Communication* is not recommended. I recommend to submit more specialized journal by addressing the several following issues to increase the quality and significance of this paper.

1. Page 5, line 101: According to the manuscript, in NMV-M10, Mg ions occupy the TM-sites and Mn ions of 0.01 mole/f.u. occupies Na sites while preserving the honeycomb structure which possesses vacancy sites of 0.1 mole/f.u. in the TM oxide layer. Previously, C. Zhao et al. first reported the NMV demonstrated the vacancy site of 0.1 mole/f.u. in the TM oxide layer by refining the neutron powder diffraction pattern and no Mn occupation in the Na site. (*Energy Storage Materials*, 2019, 20, 395). This comparison indicates that Mg introduction induces the Mn occupation in Na sites. Then, what is the driving force that makes the Mn ion occupation in Na sites rather than the vacancy sites in the TM oxide layer or triggering Mn-Mg cation site disorder? Considering the ion size of Na^+ (1.02 Å) to Mg^{2+} (0.72 Å), Mn^{3+} (0.645 Å), and Mn^{4+} (0.53 Å) ions, Mg^{2+} is the most likely to occupy the Na sites and Mg^{2+} migration into Na site is well-known by reports from Prof. P. G.

Bruce group and others too (e.g. J. Am. Chem. Soc. 2019, 141, 840–848, Joule, 2021, 5, 1267–1280, J. Mater. Chem. A, 2019, 7, 1491–1498). Therefore, the possibility of Mn occupation in the Na site and its oxidation state should be discussed.

2. Page 7, line 133; The HAADF-STEM and ABF-STEM images of NMV-M10 were used as proof of Mn occupying Na sites. Based on the same logic that HAADF- and ABF-STEM methods can distinguish the Mn and other light cations, there should be a contrast difference in the TM oxide layer demonstrating Mg in TM sites. While the Mn ions only with 0.01 mole/f.u. in the Na layer can show the discernible electron density contrast in many Na sites, Mg ions with 0.1 mole/f.u. don't show evidence of their occupation in TM sites in the TM oxide layer. This result contradicts the previous report that showed Mg ions in the TM sites of Na site in P2-Na_{0.67}Mg_xMn_{1-x}O₂ (ACS Appl. Mater. Interfaces 2019, 11, 26938–26945).

3. Page 8, line 162: the authors divided the voltage range based on the electrochemical reaction centers over the charge and discharge. However, no evidence of electrochemical oxidation center change is provided related to voltage range. As the authors are claiming the newly structured cathode material, showing an ex- or in-situ study on oxidation state change of each element (at least Mn) over the charge and discharge should be demonstrated because it would possibly show different redox chemistry compared to the conventional P2-Na_{0.67}Mn_{1-x}Mg_xO₂ as electrochemistry due to the various redox behavior of metal ion doped P2-type Na_{0.67}TMO₂ cathodes. (Adv. Energy Mater. 2022, 12, 2200702, Angew.Chem.Int.Ed., 2021, 60, 10880–10887). Specifically, C. Zhao et al. showed that Mn^{3+/4+} redox is dominant within the voltage range of 1.5 – 4.1 V in NMV (Energy Storage Materials 20 (2019) 395–400). However, for NMV-M10, the authors claim that the 2.4 – 4.0 V range is only related to the oxygen redox by Na-O-Mg configuration (Figure 2a) without showing the oxidation state change of Mn and O in the corresponding voltage range.

4. Page 11, line 227: There is no description of NMM. But I assume that NMM is P2-Na_{0.67}Mn_{1-x}Mg_xO₂ which doesn't possess vacancy in TM sites. The authors demonstrate that the absence of vacancy from the pristine NMM results in low discharge capacity due to the lack of oxygen redox utilized from the Na-O-□ configuration. However, recent studies show that Mg ion migrates from the TM site to the Na site over the charge and the generation of vacancy site in the TM layer that is related to the Mg-O-□ configuration for oxygen redox (E. Boivin et al., Joule, 2021, 5, 1267–1280). In addition, many other studies regarding the Mg doping on P2-Na_{0.67}MnO₂ have demonstrated the Mg occupation in TM or Na sites (J. Am. Chem. Soc. 2019, 141, 840–848, ACS Appl. Mater. Interfaces 2019, 11, 26938–26945, and etc.) and showed much-improved capacity retention and rate capability compared to the undoped samples. Therefore, the effect of Mg migration in the Mg-doped NMV family should be demonstrated. And if Mg ion migration is confirmed from the Mg-doped NMV family, the “rivet” effect could be reconsidered by involving not only from the Mn ion but also the Mg ion in the Na sites at the high oxidation state of the cathode materials.

5. Page 14, line 301 (Figure 4d and e): the authors claim the oxidized oxygen in the form of peroxo-like species, (O₂)ⁿ⁻ with showing the evolution of O 1s XPS peak at 531.0 eV. However, the XPS data fitting looks problematic for demonstrating the reversible oxygen redox. It seems the authors normalize the XPS peaks based on the most intensive XPS peak from the surface oxygen species. However, this results in the disappearance of the XPS peak from the lattice oxygen and exaggerated XPS peak intensity at 531.0 eV which can be assigned to the peroxo-like species, (O₂)ⁿ⁻. Considering the lattice oxygen should be present at the electrode surface to measure the oxidized oxygen ions, the absence or much suppressed XPS peak of the lattice oxygen from some samples makes the XPS data unreliable. Therefore, the XPS data cannot provide a comparison of the extent of oxygen redox in the samples.

Reviewer #2

(Remarks to the Author)

The manuscript titled "Transition Metal Vacancy and Position Engineering Enables Reversible Anionic Redox Reaction for Sodium Storage" introduces a series of Na_{0.67}Mg_xMn_{1-x}O₂ materials, innovatively developed through a gradient Mg ion and vacancy dual-doping strategy. The dual doping of Mg and vacancy has proven effective in not only improving the anionic redox reversibility but also in enhancing the structural stability by anchoring TM ions within the Na layers. The study offers intriguing results, and the underlying mechanisms are comprehensively elucidated via both experimental characterizations and theoretical calculations. Overall, the work is meticulously crafted. I recommend publishing in Nature Communications after addressing minor revisions.

1. In the manuscript, it's mentioned that anionic redox reactions are initiated by both Mg and vacancy. Could the authors provide a quantitative comparison of the anionic redox capacity contributions from Mg and vacancy, especially considering different Mg concentrations? In addition, the EELS analysis for oxygen redox reactions should be more concrete to indicate the existence of oxygen redox.
2. For NMV, the CV curves with multiple peaks typically suggest Na/vacancy ordering within the sodium transition metal layers. Given this, is it feasible that the vacancies present in the sodium layer initiate the anionic redox reaction? As the electrochemical performance shown, NMV-M10 with Mg and vacancy dual doping not only exhibits increased capacity, but also suppressed voltage decay. The detail reason for that should be further discussed.
3. Why is there a noticeable reduction in the voltage plateau at ~4.1 V, associated with the anionic redox reactions of vacancies, when transitioning from NMV to NMV-M5, yet only a marginal shift from NMV-5 to NMV-M10?
4. As displayed in the ex situ XANES spectra, why does the Mn-O distance become longer when charging to 4.35V? Theoretically, the Mn-O distance should be decreased with the oxidization of Mn³⁺.
5. As the authors mentioned that there is a wide report on the ribbon-ordered superstructure of Mn and Li. Meanwhile, the NMV also shows a superstructure of Mn and vacancy within the TM layers, is there anything in common between them? The concept of Mn ions pinned within the sodium layers is intriguing. However, in LIBs, Li/Ni mixing is typically undesirable, as cation migration often compromises structural stability. Does the presence of Mn ions in the sodium layers here have a similar adverse effect on the material's structural integrity?
6. Characterization on the crack production is meaningful, which reflects the failure mechanism of layered material. It is better to schematically depicted the detailed crack production process from atomic layer to particle.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The manuscript titled "Transition metal vacancy and position engineering enables reversible anionic redox reaction for sodium storage" demonstrates the effect of 1. substitution of vacancies and Mg for transition metal (TM) in TMO₂ layer and 2. Mn occupation in Na layer to the lowering oxygen redox potential and its stabilization together with the improved structural stability of P2-type Na_{0.67}Mg_xMn_{1-x}O₂ ($0 \leq x \leq 0.2$) cathode. The manuscript is well organized delivering the inquired information from the first round of review. I recommend publishing in Nature Communications after addressing minor questions below.

1. Page 5, line 98: The authors demonstrate the Mn²⁺ occupation in Na site (2d) based on the Rietveld refinement result in Table S3. This refinement result is playing a key role for supporting the Mn mis-occupation in Na layer. It would be more supportive if the authors compare and discuss the Rietveld refinement result between when Mn occupied in Na sites and Mg occupied in Na sites.

2. Page 21, line 418: The authors claim that the Mg doping prevents the cluster of vacancies in TM layer. I assume the authors meant that the increased Mn-O bond strength prevent the vacancy clustering by TM migration in TMO₂ layer over the first charge process as Robert A. House et al. suggested (First-cycle voltage hysteresis in Li-rich 3d cathodes associated with molecular O₂ trapped in the bulk, Nature Energy, 2020, 5, 777–785). It would be better to refer this paper and slightly discuss it to compare and emphasize the importance of this work.

Reviewer #2

(Remarks to the Author)

The authors addressed all my concerns carefully, the manuscript, therefore, can be accepted.

Reviewer #3

(Remarks to the Author)

This work provides a thorough characterization of a P2 type NaMnMgO₂ compound. The authors provide concrete explanations as to why its performance both in discharge capacity and stability over numerous charge/discharge cycles exceeds previously studied materials. In doing so they provide a seemingly viable avenue to pursue for designing better sodium based batteries in the future. The most valuable part of this work is relating the structure and engineering of the cathode material (namely vacancy and doping sites) to the oxidation states. This paves a path for significant future study. The identification of Mn 'rivets', while less novel of an idea, is also very useful. Both of these have the potential to be useful not only for this specific compound but to the wider cathode community.

The experimental methodology appears sound, and having both structural and electrochemical characterization in addition to spectroscopy lends additional weight to the work's conclusions. One primary concern is the theoretical calculations. They seemed to be a brief addition without much context in the larger work, but then referenced heavily in the conclusions. A similar concern appeared other times while reading this manuscript. This is a long paper with many results presented, and while some segments were very convincing, in others the conclusions were not readily linked to the data. The stability arguments were the most convincing but the discussion of oxidation states seems more important.

Overall I think the manuscript's main strengths are its detailed nature in the experimental work, and its useful implications for the cathode field. However, it is in need of edits. Greater emphasis on a single, unifying thread throughout the manuscript is needed, to help make sure the reader can see how conclusions were pulled from the work. I will lay out specific comments below.

The paper is well situated amongst previous work in terms of lithium based materials and other Na/Mn based materials with different doping and vacancies, but not other types of structures. For example Kim et al. similarly look at Mg and vacancy doping but in a P3 material in ACS Appl. Energy Mater. 2020, 3, 10423–10434. Please add more context and explain what is different or useful about the P2 structure.

Line 78 - the DFT currently in the paper does not show enhanced structural stability. Fig 6 b-c are used to explain the improved stability seen experimentally but do not, on their own, show it.

Line 126 - explain how you see Jahn-Teller alleviation. Readers aren't seeing a figure here, more words are needed.

Lines 252-254 discuss causes for expansion along the c-axis. Would love to see a longer explanation here - interesting but short.

Line 345 - 356 all discuss information in the supplemental material. This is very common throughout the paper. This is a less necessary edit perhaps, as figures are challenging and not everything can be shown, but for figures heavily discussed in the main text it may be best to include them in the main text as well. If more figures can't be included, then something else is

required so the reader doesn't feel they are missing information.

Theoretical Calculations beginning on line 396 - This section needs the most strengthening over all. A better motivation would be useful as it's not particularly clear why you're doing calculations. The shifting of the O 2p density seems like the most useful thing in this section, please elaborate on how it helps you and why you did it.

For the DFT Methodology, what sized supercells were used? How were locations for vacancies and doping atoms chosen? While basic structures were shown in S25, to make these genuinely convincing more details are needed. Currently I'm concerned that single cell structures, even with a larger number of atoms, aren't fully representative of the material overall but rather of specific doping sites.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have carefully addressed all my concerns and revised the manuscript. I agree with publishing the manuscript in Nature Communications.

Reviewer #3

(Remarks to the Author)

Authors have satisfied all my prior comments with these edits. I recommend publication.

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Response Letter

Manuscript number: NCOMMS-23-44510

Title: Transition metal vacancy and position engineering enables reversible anionic redox reaction for sodium storage

Response to Reviewer-1

General Comment: In this manuscript, the authors investigated the Mg doping and vacancy effect on the structural evolution and electrochemical property of P2-type $\text{Na}_{0.67}\text{Mg}_x\text{Mn}_{1-x}\text{O}_2$ ($0 \leq x \leq 0.2$). The authors claimed that introducing Mg induces the Mn occupation in the prismatic Na site of $\text{Na}_{0.67}\text{Mg}_x\text{Mn}_{1-x}\text{O}_2$ while the vacancies in the transition metal (TM) oxide layer are preserved keeping the honeycomb superstructure. The incorporation of in-situ x-ray diffraction, in-situ Raman, and scanning transmission electron microscopy demonstrates the improved structural stability of P2- $\text{Na}_{0.67}\text{Mn}_{0.011}[\text{Mg}_{0.1} \square_{0.07}\text{Mn}_{0.83}]\text{O}_2$ (NMV-M10) compared to the non-doped P2- $\text{Na}_{0.67}[\square_{0.1}\text{Mn}_{0.9}]\text{O}_2$ (NMV) over the sodiation and desodiation. The electrochemistry, X-ray spectroscopy data, and theoretical study of the materials further support the improved structural stability, and electrochemical performance that involves the oxygen redox derived from the improved structural stability by Mg doping that generates Mn ‘rivets’ and preserved TM vacancies. Obviously, such P2-structured material and its study can suggest avenues to stabilize the P2-type materials with reversible oxygen redox.

Response to General Comment: We deeply appreciate your valuable comments and suggestions on our work. Below, we provide a point-by-point response.

Nevertheless, some of the points described in this manuscript were not convincing to fully support the authors’ understanding. For example, the authors claim that Mg doping results in Mn ion occupation in Na sites, but the claim is only based on the observation from STEM images. More investigation into the oxidation state and the coordination environment change of Mn in the Na site should be conducted to support the author’s

claim.

Response to General Comment: We sincerely thank you for your careful review and valuable comments on our manuscript. We apologize for any confusion caused by certain descriptions, and we have thoroughly considered all of your feedback. We made corresponding changes, and we believe that our revisions have addressed all of your concerns. Thank you once again for your generous comments.

In addition, the Mg-doped NMVs were synthesized by using a well-known solution-based co-precipitation method for precursors followed by the heat treatment which has also been utilized for many Li or Na cathode materials. However, not like many other Mg-doped P2-type Na cathode papers, the authors claim the Mn occupation in Na sites with preserved TM vacancy sites and ratio in the TM oxide layer. It is hard to understand the reason why the Mg-doped NMV family has the structural difference (Mn occupation in Na sites) compared to previously reported Mg-doped P2-Na_{0.67}Mg_xMn_{1-x}O₂ papers (e.g. U. Maitra et al., *Nature Chem* 10, 288–295 (2018).; J. Qu et al., *ACS Appl. Mater. Interfaces* 2019, 11, 26938, R. Clément et al., *Energy Environ. Sci.*, 2016, 9, 3240).

Response to General Comment: The structure of layered oxide cathode materials is intricately linked to their synthesis conditions. Factors such as the choice of precursors, sintering temperature and duration, and ramp rates during heating and cooling can exert significant influence on the resulting structure of the product. Despite employing similar synthesis methods, literature reports often showcase vastly different structures for layered oxides. For instance, Zhou et al. utilized conventional ball milling and sintering to observe Fe atoms occupying sodium layers in Na_{0.67}Mn_{0.5}Co_{0.5-x}Fe_xO₂ materials (*Angew. Chem. Int. Ed.* 2021, 60, 13366–13371), while Zhang et al. employed a sol-gel synthesis approach and noted Zn ions occupying sodium layers (*Adv. Mater.* 2022, 34, 2103210).

Similarly, in the context of Mg-doped oxide materials, Zhou et al. reported Mg potentially occupying sodium layers (*J. Am. Chem. Soc.* 2019, 141, 840–848), whereas Maitra et al. suggested Mg occupying transition metal layers (*Nat. Chem.* 2018, 10,

288–295). Hence, despite employing similar synthesis methodologies for layered oxide materials, significant differences may arise in the actual structures obtained.

In our study, we utilized oxalic acid as an organic acid-assisted precipitation method, coupled with controlled heating and cooling rates, which rationalized the observed structural disparities compared to previous literature reports.

Furthermore, the phenomenon of Mn occupying sodium layers has also been documented in previously reported Mg-doped layered oxide materials. For instance, Huang et al. observed spinel structures at the particle edges in Mg-doped $\text{Na}_{0.83}\text{Li}_{0.25}\text{Mn}_{0.75}\text{O}_2$ materials, indicating the migration of transition metal ions to sodium layers (Adv. Mater. 2022, 34, 2105404). Similarly, Qu et al. observed partial spinel structures in Mg-doped $\text{Na}_{0.6}\text{MnO}_2$ materials (ACS Appl. Mater. Interfaces 2019, 11, 26938). Distinguishing between Na and Mg in high-resolution imaging techniques like HAADF- and ABF-STEM can be challenging due to their close atomic numbers, with the distinct brightness contrast within sodium layers likely representing transition metal Mn atoms. The partial Mn occupation of sodium layers may signify a transitional phase towards spinel formation, indicating the coexistence of MgMn_2O_4 or NaMn_2O_4 spinel structures, with Mn oxidation states existing as Mn^{3+} within the sodium layers (eScience, 1, 2021, 13–27).

Furthermore, it is quite unclear whether the $\text{Mn}^{3+/4+}$ redox only occurs in the voltage range of 2.0 – 3.5 V as the lattice shrinkage and expansion along the a axis that is a demonstration of Jahn-Teller distortion by $\text{Mn}^{3+/4+}$ redox, is observable over the entire charge and discharge from the in-situ XRD data ((100) reflection).

Our response: Thank you for your valuable comments. As reported in several literature sources (Nature Communications, 2021, 12, 4903; Nano Energy, 2020, 69, 104474; Adv. Funct. Mater., 2021, 2106923; Adv. Energy Mater., 2020, 2001346), the redox potential of $\text{Mn}^{3+}/\text{Mn}^{4+}$ in P2-type Na_xMnO_2 cathodes typically occurs at voltages lower than 3.5 V (vs. Na^+/Na). This often manifests as a pair of symmetrical redox peaks in cyclic voltammetry (CV) curves and voltage plateaus in charge/discharge profiles.

As illustrated in Figure 2a and 2c, the CV curves of NMV-M10 and NMV indeed exhibit a pair of sharp peaks at 2.0–2.4 V, along with a flat potential plateau observed at voltages lower than 2.5 V, which aligns with the expected $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox behavior.

In addition, we added the ex-situ Mn 2p XPS test to characterize the valence state changes. As the Mn 2p XPS spectra of NMV (a) and NMV-M10 (b) displayed, NMV and NMV-M10 exhibit similar changes. With charging from pristine state to 4.35 V, the Mn $2p_{3/2}$ peak becomes sharp but with no position shift, suggesting the oxidized of small amounts of Mn^{3+} to Mn^{4+} . After discharging to 3.5V, this peak becomes slightly broadened (the broaden degree is lower than the pristine state), which indicates a very small amounts of Mn^{4+} are reduced to Mn^{3+} and the capacity contribution in this voltage range is mainly provided by anionic (oxygen) redox. When further discharged to 2 V, the Mn 2p peaks exhibits an obvious position change, demonstrating a large amount of Mn^{4+} are reduced and the electrochemical oxidation center changes from anionic redox to cationic redox of $\text{Mn}^{3+}/\text{Mn}^{4+}$. Therefore, it can be concluded that most of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox are proceeded at lower than 3.5 V, and a very small amounts proceed above 3.5 V.

Besides, you may misunderstand the cause of the lattice shrinkage and expansion during Na^+ extraction and intercalation processes. The lattice shrinkage and expansion along the a axis shown in in-situ XRD in layered transition metal oxides is not individually caused by the Jahn-Teller effect of Mn^{3+} . The counter-examples are those of the reported $\text{Na}_{0.72}[\text{Li}_{0.24}\text{Mn}_{0.76}]\text{O}_2$ (*Joule* 2018, 2, 125-140), $\text{Na}_{0.66}\text{Li}_{0.18}\text{Fe}_{0.12}\text{Mn}_{0.7}\text{O}_2$ (*J. Am. Chem. Soc.* 2019, 141, 16, 6680-6689) , $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ and $\text{Na}_{2/3}[\text{Ni}_{1/6}\text{Mn}_{1/2}\text{Fe}_{1/3}]\text{O}_2$ (*Energy Environ. Sci.*, 2019, 12, 2223-2232) cathode materials, where the Mn valence state are +4, but their *in-situ* XRD patterns at initial charge show that the (100) peaks also shift to higher diffractions during the first charge process (Mn^{4+} can't be further oxidized and reduced), which suggest the lattice shrinkage is not caused by the Jahn-Teller effect of Mn^{3+} . Actually, the lattice shrinkage and expansion during Na^+ extraction and intercalation processes in layered oxides are associated with both of cationic and anionic redoxes, the (100) diffraction in NMV-M10 shifts towards higher angle during initial charge process is

induced by $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox, while the following shifting to higher angle is mainly caused by the oxygen redox and a small amounts $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox, the oxygen redox decreased the O-O bond length, which is similar to that of $\text{Na}_{0.72}[\text{Li}_{0.24}\text{Mn}_{0.76}]\text{O}_2$ (Joule 2018, 2, 125-140). The Jahn-Teller distortion by $\text{Mn}^{3+/4+}$ redox generally occurred below ~ 3.5 V, where most of Mn^{4+} are reduced to Mn^{3+} and the (100) peak would split into two diffraction peaks with a new P'2 phase generating.

The following description has been added in the manuscript:" As displayed in Figure S22, the ex-situ Mn XPS spectra of NMV and NMV-M10 exhibit similar changes. With charging from pristine state to 4.35 V, the Mn $2p_{3/2}$ peak becomes sharp but with no position shift, suggesting the oxidized of small amounts of Mn^{3+} to Mn^{4+} . After discharging to 3.5V, this peak becomes slightly broadened (the broaden degree is lower than the pristine state), which indicates a very small amounts of Mn^{4+} are reduced to Mn^{3+} and the capacity contribution in this voltage range is mainly provided by anionic (oxygen) redox. When further discharged to 2 V, the Mn $2p$ peaks exhibits an obvious position change, demonstrating a large amount of Mn^{4+} are reduced and the electrochemical oxidation center changes from anionic redox to cationic redox of $\text{Mn}^{3+}/\text{Mn}^{4+}$. Therefore, it can be concluded that most of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox are proceeded at lower than 3.5 V, and a very small amounts proceed above 3.5 V."

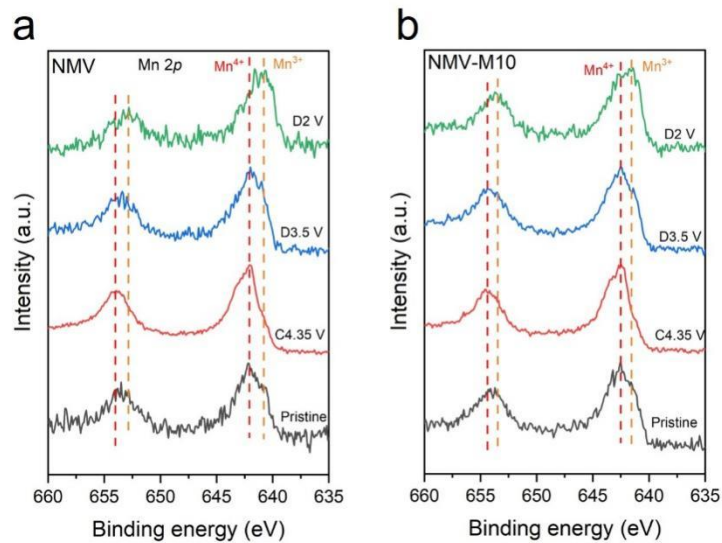


Figure S22. The ex-situ Mn 2p XPS spectra of (a) NMV and (b) NMV-M10 at different charge/discharge states.

To eliminate this confusion, the following description and Figure 2a has been revised in the manuscript: "The expansion along *c* axis is ascribed to the increased electrostatic repulsions between the oxygen layers when Na⁺ ions are extracted, while the shrinkage along *a* axis is related to the oxidation of small amount of Mn³⁺ and oxygen"

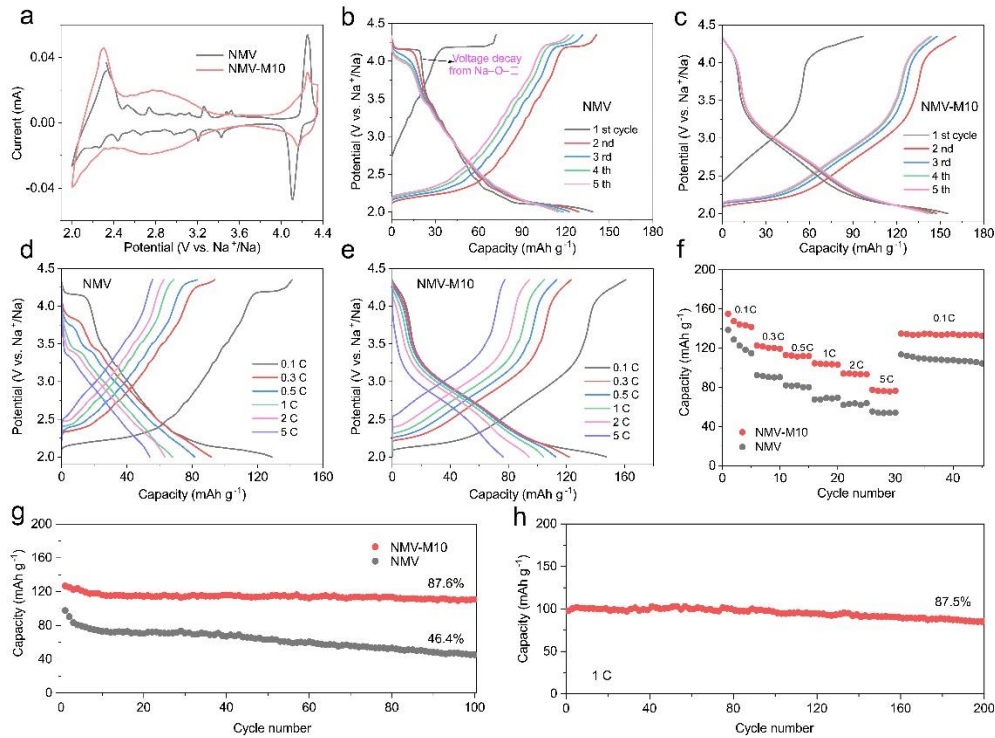


Figure 2. Electrochemical performances of NMV and NMV-M10 in 2.0–4.35 V (vs. Na⁺/Na). (a) CV curves of NMV and NMV-M10; GCD profiles of (b) NMV and (c) NMV-M10 at 0.1 C; representative GCD profiles of (d) NMV and (e) NMV-M10 at different C-rates; (f) rate performances and (g) cycling performances and Coulombic efficiencies of the NMV and NMV-M10 at 0.3 C; (h) cycling performance of NMV-M10 at 1 C.

Overall, I do not agree that this manuscript delivers sufficient information about the TM vacancy engineering and oxygen redox in battery materials that are expected for publication in Nature Communication. Therefore, the publication of this work in the

Nature Communication is not recommended. I recommend to submit more specialized journal by addressing the several following issues to increase the quality and significance of this paper.

Our response: Thank you very much for your thorough review and valuable suggestions. Based on your comments, we have made further revisions and provided additional explanations. We hope these modifications would resolve your concerns.

Comment 1-1. Page 5, line 101: According to the manuscript, in NMV-M10, Mg ions occupy the TM-sites and Mn ions of 0.01 mole/f.u. occupies Nae sites while preserving the honeycomb structure which possesses vacancy sites of 0.1 mole/f.u. in the TM oxide layer. Previously, C. Zhao et al. first reported the NMV demonstrated the vacancy site of 0.1 mole/f.u. in the TM oxide layer by refining the neutron powder diffraction pattern and no Mn occupation in the Na site. (Energy Storage Materials, 2019, 20, 395). This comparison indicates that Mg introduction induces the Mn occupation in Nae sites. Then, what is the driving force that makes the Mn ion occupation in Nae sites rather than the vacancy sites in the TM oxide layer or triggering Mn-Mg cation site disorder? Considering the ion size of Na^+ (1.02 Å) to Mg^{2+} (0.72 Å), Mn^{3+} (0.645 Å), and Mn^{4+} (0.53 Å) ions, Mg^{2+} is the most likely to occupy the Nae sites and Mg^{2+} migration into Na site is well-know by reports from Prof. P. G. Bruce group and others too (e.g. J. Am. Chem. Soc. 2019, 141, 840–848, Joule, 2021, 5, 1267–1280, J. Mater. Chem. A, 2019, 7, 1491–1498). Therefore, the possibility of Mn occupation in the Nae site and its oxidation state should be discussed.

Our response: Thank you for your helpful suggestion. Previous literature has reported the possible formation of more stable spinel structures such as MgMn_2O_4 and NaMn_2O_4 in sodium layered oxides, accompanying by some vacancies existing in the transition metal layer (eScience, 1, 2021, 13–27). This is analogous to our work, indicating that the partial occupation of sodium layers by Mn in our work may be due to the local formation of spinel structures like MgMn_2O_4 or NaMn_2O_4 , resulting in the oxidation state of Mn predominantly being +3 in the sodium layer. Huang et al. also observed that

an obvious spinel structure is formed in Mg-doped $\text{Na}_{0.83}\text{Li}_{0.25}\text{Mn}_{0.75}\text{O}_2$ material, which the authors attributed to the formation of MgMn_2O_4 spinel structure, indicating the migration of transition metal ions to sodium layers (*Adv. Mater.* 2022, 34, 2105404). Thus, the driving force that makes the Mn ion occupation in Nae sites may be caused by the partial formation of the spinel structure, which is more stable than the layered structure. In addition, based on the atomic EDS-mappings, it is evident that the signal of Mg element in the transition metal layer is significantly stronger compared to the weak signal observed in the sodium layer. This indicates that Mg elements are predominantly distributed within the transition metal layer, providing strong evidence that Mg preferentially occupies the positions of transition metals in NMV-M10. Also the occupancy of Mg in sodium layer has been reported by many literatures and in fact the occupation of Mg in the transition metal layer have been more widely reported, the practical position of Mg in different oxides will be different according to the synthesis condition. And according to our characterizations, the Mg elements in NMV-M10 should predominantly distributed within the transition metal layers.

From the perspective of elemental radii, Zhou et al. also observed, through atomic-scale STEM characterization, the phenomenon of partial Fe^{3+} ions occupying sodium layers (*Angew. Chem. Int. Ed.* 2021, 60, 13366 – 13371). As Fe^{3+} shares the same ionic radius as Mn^{3+} (both are 0.645 Å). This suggests that partial occupation of sodium layers by Mn^{3+} can also occur.

The following description has been added in the manuscript:" The HAADF and ABF images demonstrate that a small fraction of Mn ions are located at the Na layers in NMV-M10 with local formation of spinel structures like MgMn_2O_4 or NaMn_2O_4 ."

Comment 1-2: 2. Page 7, line 133; The HAADF-STEM and ABF-STEM images of NMV-M10 were used as proof of Mn occupying Nae sites. Based on the same logic that HAADF- and ABF-STEM methods can distinguish the Mn and other light cations, there should be a contrast difference in the TM oxide layer demonstrating Mg in TM sites. While the Mn ions only with 0.01 mole/f.u. in the Na layer can show the discernible electron density contrast in many Na sites, Mg ions with 0.1 mole/f.u. don't

show evidence of their occupation in TM sites in the TM oxide layer. This result contradicts the previous report that showed Mg ions in the TM sites of Na site in P2-Na_{0.67}Mg_xMn_{1-x}O₂ (ACS Appl. Mater. Interfaces 2019, 11, 26938–26945).

Our response: We are very grateful to your insightful suggestions. For the HAADF characterization in this work, the probe convergence angle was 17.8 mrad, and the camera length was set to be 115 mm. Under such a configuration, the intensity of the HAADF signal is proportional to the atomic number of the elements present in the sample. The highlight we observe is a row of atomic columns rather than individual atoms. Each atomic column consists of both Mg and Mn, with Mn brightness significantly higher than Mg (Mg has a much lower atomic number compared to many other transition metals and heavy elements like Mn). Additionally, the Mg content in each atomic column is relatively uniform and randomly positioned, resulting in consistent atomic brightness without significant differences.

Comment 1-3: Page 8, line 162: the authors divided the voltage range based on the electrochemical reaction centers over the charge and discharge. However, no evidence of electrochemical oxidation center change is provided related to voltage range. As the authors are claiming the newly structured cathode material, showing an ex- or in-situ study on oxidation state change of each element (at least Mn) over the charge and discharge should be demonstrated because it would possibly show different redox chemistry compared to the conventional P2-Na_{0.67}Mn_{1-x}Mg_xO₂ as electrochemistry due to the various redox behavior of metal ion doped P2-type Na_{0.67}TMO₂ cathodes. (Adv. Energy Mater. 2022, 12, 2200702). Specifically, C. Zhao et al. showed that Mn^{3+/4+} redox is dominant within the voltage range of 1.5 – 4.1 V in NMV (Energy Storage Materials 20 (2019) 395–400). However, for NMV-M10, the authors claim that the 2.4 – 4.0 V range is only related to the oxygen redox by Na-O-Mg configuration (Figure 2a) without showing the oxidation state change of Mn and O in the corresponding voltage range.

Our response: We express our gratitude for your valuable suggestions. Similar to most literature reports, we differentiate between the primary redox centers within different

voltage ranges by analyzing the redox peaks in cyclic voltammetry (CV) tests and the corresponding voltage plateaus in charge-discharge curves. Zhao et al.'s description that " $\text{Mn}^{3+/4+}$ redox is dominant within the voltage range of 1.5 – 4.1 V in NMV" is based on the CV test as depicted in the supporting information (Fig. S5), where the $\text{Mn}^{3+/4+}$ redox peaks are broadened. However, their main text illustrates that the voltage plateaus for $\text{Mn}^{3+/4+}$ redox in NMV are consistently below 2.5 V. Moreover, several related studies have reported generally low voltages for $\text{Mn}^{3+/4+}$ redox reactions in such P2-type layered oxides. Additionally, we supplemented our analysis with ex situ Mn 2p XPS tests under different charge-discharge states, revealing that $\text{Mn}^{3+/4+}$ redox primarily occurs at voltages below 3.5 V. Due to the minimal proportion of Mn ions occupying sodium layers (1.1%) in this context, their redox behavior during charge-discharge processes is very difficult to detect. Hence, our focus primarily lies on the redox reactions of Mn within the transition metal layer.

The following description has been added in the manuscript: "As displayed in Figure S22, the ex-situ Mn XPS spectra of NMV and NMV-M10 exhibit similar changes. With charging from pristine state to 4.35 V, the Mn $2p_{3/2}$ peak becomes sharp but with no position shift, suggesting the oxidized of small amounts of Mn^{3+} to Mn^{4+} . After discharging to 3.5V, this peak becomes slightly broadened (the broaden degree is lower than the pristine state), which indicates a very small amounts of Mn^{4+} are reduced to Mn^{3+} and the capacity contribution in this voltage range is mainly provided by anionic (oxygen) redox. When further discharged to 2 V, the Mn 2p peaks exhibits an obvious position change, demonstrating a large amount of Mn^{4+} are reduced and the electrochemical oxidation center changes from anionic redox to cationic redox of $\text{Mn}^{3+}/\text{Mn}^{4+}$. Therefore, it can be concluded that most of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox are proceeded at lower than 3.5 V, and a very small amounts proceed above 3.5 V."

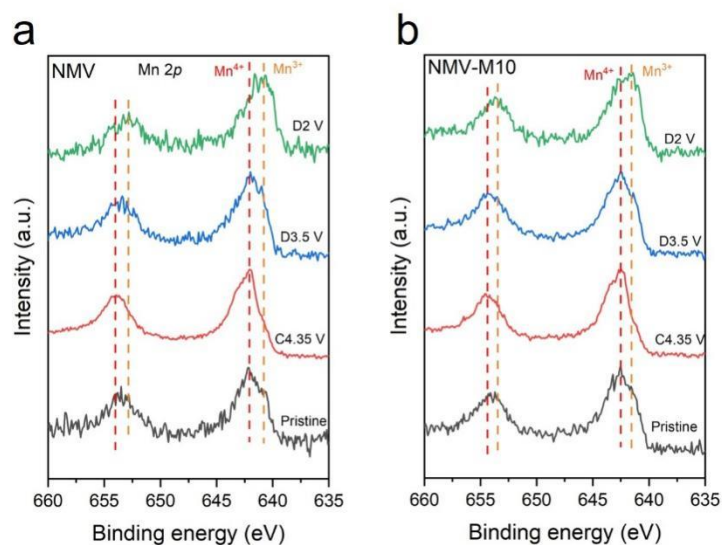


Figure S22. The ex-situ Mn 2p XPS spectra of (a) NMV and (b) NMV-M10 at different charge/discharge states.

To eliminate this confusion, the following description and Figure 2a has been revised in the manuscript: "The expansion along c axis is ascribed to the increased electrostatic repulsions between the oxygen layers when Na^+ ions are extracted, while the shrinkage along a axis is related to the oxidation of small amount of Mn^{3+} and oxygen"

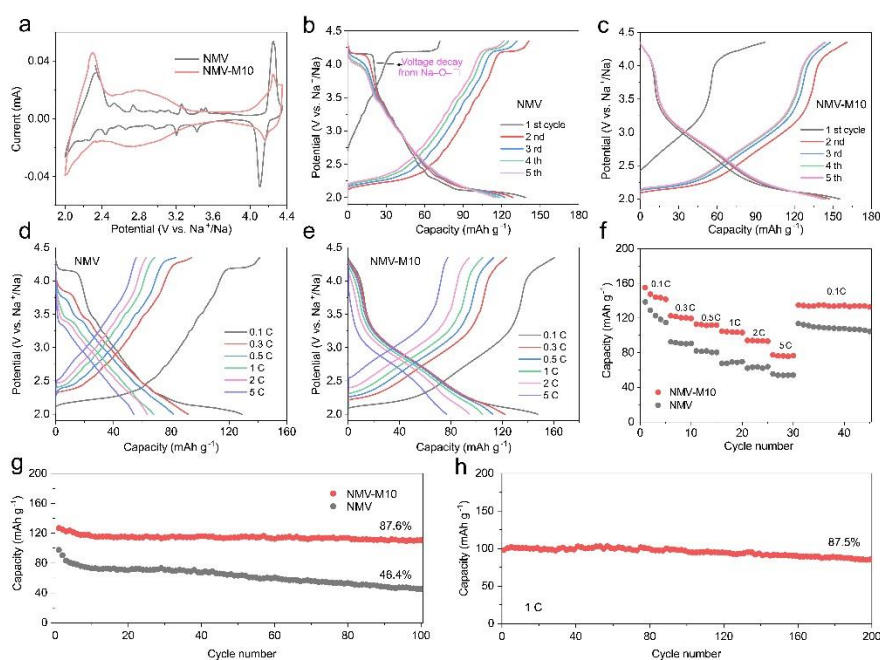


Figure 2. Electrochemical performances of NMV and NMV-M10 in 2.0–4.35 V (vs. Na^+/Na).

Na⁺/Na). (a) CV curves of NMV and NMV-M10; GCD profiles of (b) NMV and (c) NMV-M10 at 0.1 C; representative GCD profiles of (d) NMV and (e) NMV-M10 at different C-rates; (f) rate performances and (g) cycling performances and Coulombic efficiencies of the NMV and NMV-M10 at 0.3 C; (h) cycling performance of NMV-M10 at 1 C.

Comment 1-4: Page 11, line 227: There is no description of NMM. But I assume that NMM is $P2-Na_{0.67}Mn_{1-x}Mg_xO_2$ which doesn't possess vacancy in TM sites. The authors demonstrate that the absence of vacancy from the pristine NMM results in low discharge capacity due to the lack of oxygen redox utilized from the Na-O-□ configuration. However, recent studies show that Mg ion migrates from the TM site to the Na site over the charge and the generation of vacancy site in the TM layer that is related to the Mg-O-□ configuration for oxygen redox (E. Boivin et al., *Joule*, 2021, 5, 1267–1280). In addition, many other studies regarding the Mg doping on $P2-Na_{0.67}MnO_2$ have demonstrated the Mg occupation in TM or Na sites (*ACS Appl. Mater. Interfaces* 2019, 11, 26938–26945, etc.) and showed much-improved capacity retention and rate capability compared to the undoped samples. Therefore, the effect of Mg migration in the Mg-doped NMV family should be demonstrated. And if Mg ion migration is confirmed from the Mg-doped NMV family, the “rivet” effect could be reconsidered by involving not only from the Mn ion but also the Mg ion in the Na sites at the high oxidation state of the cathode materials.

Our response: We deeply appreciate your invaluable insights. As you rightly pointed out in the manuscript, NMM refers to samples lacking initial vacancies, as evidenced by the absence of voltage plateaus related to Na-O-□ during discharge, indicating the presence of only Na-O-Mg configuration to trigger anion redox reactions. Several literature reports suggest that during charging, Mg migrates to sodium layers, forming Mg-O-□ configurations that trigger anion redox reactions, explaining the reason that Na-O-Mg configuration triggers anion redox reactions, which differs from the initial transition metal layer with vacancies forming Na-O-□ configurations. The migrated

Mg Compared to NMV without Mg doping, samples doped only with Mg exhibit improved cycling performance (70.8% vs. 46.4%), indicating that Mg doping indeed stabilizes the structure. On the other hand, for vacancy-doped NMV samples, the presence of vacancies facilitates faster sodium ion diffusion channels, resulting in better rate performance. In addition, it seems the migration of Mg to sodium layers in NMV-M10 doesn't occur, because the migrating of metal ions from TM layers to sodium layer would disrupt the honeycomb-ordered superstructure of Mn and Mg/vacancy, which generally causes an obvious voltage hysteresis in the charge and discharge processes. However, for NMV-M10, the charge voltage plateau is well corresponding to the discharge plateau without voltage hysteresis, thus the Mg migrating doesn't occur in NMV-M10. The Mg doping in TM layers without migration to sodium also has been found in a dual honeycomb-superlattice structured material (*Angew. Chem. Int. Ed.* 2022, 134, 202206625).

Comment 1-5: Page 14, line 301 (Figure 4d and e): the authors claim the oxidized oxide ion in the form of peroxy-like species, $(O_2)^{n-}$ with showing the evolution of O 1s XPS peak at 531.0 eV. However, the XPS data fitting looks problematic for demonstrating the reversible oxygen redox. It seems the authors normalize the XPS peaks based on the most intensive XPS peak from the surface oxygen species. However, this results in the disappearance of the XPS peak from the lattice oxygen and exaggerated XPS peak intensity at 531.0 eV which can be assigned to the peroxy-like species, $(O_2)^{n-}$. Considering the lattice oxygen should be present at the electrode surface to measure the oxidized oxide ions, the absence or much suppressed XPS peak of the lattice oxygen from some samples makes the XPS data unreliable. Therefore, the XPS data cannot provide a comparison of the extent of oxygen redox in the samples.

Our response: Thank you very much for your comments. As you rightly pointed out, our XPS data indeed underwent normalization during processing to intuitively compare and analyze the components change of O 1s band. We also have noticed that the intensive surface oxygen species weaken the lattice oxygen, thus we have removed the O 1s spectra at 3.5 V and the descriptions of the comparison of the extent of oxygen

redox in the samples accordingly. We really thank you for your kind reminding.

Besides, in order to further confirm the existence of oxygen redox in NMV-M10, we performed the ex-situ soft X-ray absorption (SXAS) and EELS characterizations at different charged states. As shown in Figure S21, the SXAS spectra with the total fluorescence yield (TFY) mode at O *K*-edges can be employed to study the O *2p* holes. The dominant pre-edge peaks below 533 eV correspond to the transition of O *1s* electrons to the unoccupied *2p* orbitals, which is hybridized with TM *3d* orbitals. The intensity change of the pre-edge peak area during charge/discharge reflects the covalent intensity of TM *3d*-O *2p* or the generation of oxygen holes. With the charging of NMV-M10 from pristine state to 4.35 V, the obvious increase in the O *K*-edge pre-edge area can be observed, which implies the removal of electrons from oxygen and an increase in the O *2p* holes, indicating the occurrence of oxygen redox. (*Adv. Mater.* **2022**, *34*, 2105404., *J. Am. Chem. Soc.* 2017, *139*, 4835-4845.)

In addition, *Ex-situ* Electron Energy loss spectroscopy (EELS) have also been performed to further demonstrate the oxygen redox in NMV-M10, which gives insight into the electronic structure changes of O-K. The EELS spectra are collected by linear scanning from surface to bulk (Figure S22). As displayed in the bulk (Figure S20g), the pre-edge around 535 eV in the O EELS *K*-edge spectrum is similarly related to the transition of O *1s* electrons to the unoccupied *2p* orbitals, which is hybridized with the TM *3d* orbitals. When charging to 4.35 V, the increase of pre-edge intensity indicates the removal of electrons from oxygen, namely the increase of oxygen holes, which is contributed by the oxygen redox. (*Electrochem. Commun.* 2015, *60*, 70-73., *J. Am. Chem. Soc.* 2017, *139*, 4835-4845., *Adv. Sci.* 2020, *7*, 2001263) This is consistent with the changes in SXAS. After discharging to 2.0 V, intensity decreased, suggesting the good reversibility of oxygen redox.

Therefore, the combined analysis of the O XPS, SXAS and EELS spectra all confirm the existence of oxygen redox reactions in NMV-M10.

The following description has been revised in the manuscript:" To further investigate the anionic redox behavior, *ex-situ* XPS is performed to characterize the electronic structure of oxygen at various charge/discharge states. The *ex-situ* O *1s* XPS

spectra of NMV-M10 and NMV are provided in Figure 4d and 4e. For both NMV-M10 and NMV, the pristine O 1s spectra can be divided into two peaks from the surface oxygen-related species and one peak from lattice oxygen. After charging to 4.35 V, an extra component at 531.0 eV appears, which can be ascribed to the formation of peroxy-like (O₂)ⁿ⁻ species.⁴⁵ This phenomenon evidences that the oxygen redox activity has been triggered to participate in the charge compensation process in both NMV-M10 and NMV."

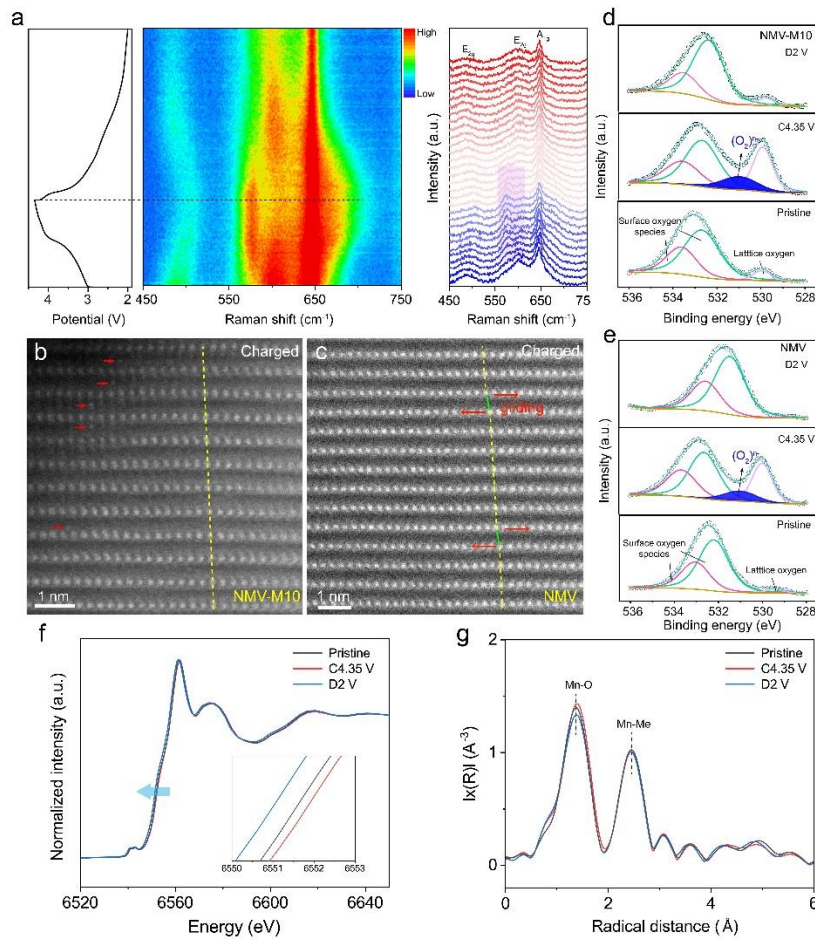


Figure 4. (a) *In-situ* Raman spectra of NMV-M10; atomic-scale HAADF-STEM images of (b) NMV-M10 and (c) NMV; *ex-situ* O 1s XPS spectra of (d) NMV-M10 and (e) NMV; *ex-situ* Mn K-edge (f) XANES and (g) EXAFS spectra of NMV-M10.

The following description has been added in the manuscript:" To further confirm the existence of oxygen redox in NMV-M10, the *ex-situ* soft X-ray absorption spectroscopy (SXAS) at different charged states are collected. As shown in Figure S21,

the SXAS spectra with the total fluorescence yield (TFY) mode at O *K*-edges can be employed to study the O *2p* holes. The dominant pre-edge peaks below 533 eV correspond to the transition of O *1s* electrons to the unoccupied *2p* orbitals, which is hybridized with TM *3d* orbitals. The intensity change of the pre-edge peak area during charge/discharge reflects the covalent intensity of TM *3d*-O *2p* or the generation of oxygen holes. With the charging of NMV-M10 from pristine state to 4.35 V, the obvious increase in the O *K*-edge pre-edge area can be observed, which implies the removal of electrons from oxygen and an increase in the O *2p* holes, indicating the occurrence of oxygen redox."

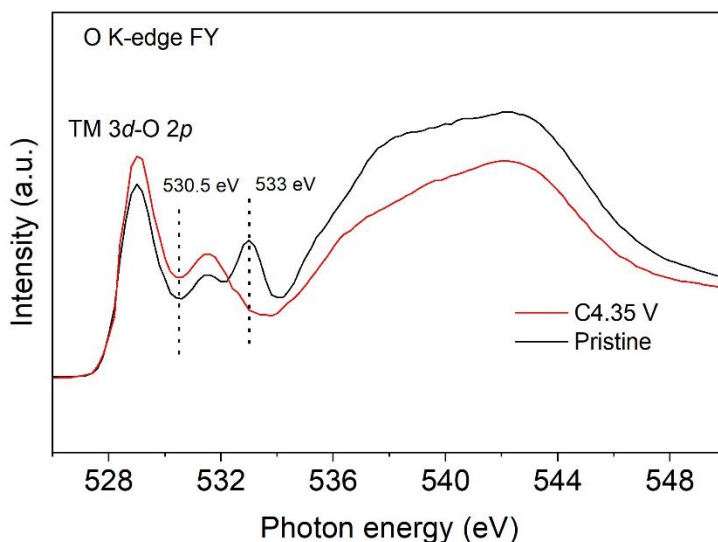


Figure S21. Ex-situ SXAS of the O-K spectra for NMV-M10.

Response to Reviewer-2

General Comment: The manuscript titled "Transition Metal Vacancy and Position Engineering Enables Reversible Anionic Redox Reaction for Sodium Storage" introduces a series of $\text{Na}_{0.67}\text{Mg}_x\text{Mn}_{1-x}\text{O}_2$ materials, innovatively developed through a gradient Mg ion and vacancy dual-doping strategy. The dual doping of Mg and vacancy has proven effective in not only improving the anionic redox reversibility but also in

enhancing the structural stability by anchoring TM ions within the Na layers. The study offers intriguing results, and the underlying mechanisms are comprehensively elucidated via both experimental characterizations and theoretical calculations. Overall, the work is meticulously crafted. I recommend publishing in Nature Communications after addressing minor revisions.

Response to General Comment: We sincerely thank Reviewer-1's careful reviewing and great interest of our work. We have made further revisions on our manuscript based on the Reviewer-2's suggestions.

Comment 2-1: In the manuscript, it's mentioned that anionic redox reactions are initiated by both Mg and vacancy. Could the authors provide a quantitative comparison of the anionic redox capacity contributions from Mg and vacancy, especially considering different Mg concentrations? In addition, the EELS analysis for oxygen redox reactions should be more concrete to indicate the existence of oxygen redox.

Our response: Thanks for your valuable comments. We have provided a quantitative comparison of the anionic redox capacity contributions for different Mg and vacancy doped materials (NMV, NMV-M5, NMV-M10, NMV-M15, NMV-M20, and NMM), respectively. The anionic capacities can be divided into the capacities above 4.0 V and in 2.4–4.0 V, which indicate the anionic contributions of the Na–O–□ and Na–O–Mg. The capacities in 2.0–2.4 V correspond to the cationic redox ($\text{Mn}^{3+}/\text{Mn}^{4+}$) capacity. As displayed in Figure S11, the capacity above 4.0 V gets decreased with the Mg contents increase, which is caused by the partial occupation of vacancies by Mg. The NMV-M10 exhibits the highest capacities in 2.4–4.0 V and slightly decreased capacity above 4.0 V, which suggests the highest overall anionic activity. And NMV-M10 also demonstrates the highest cationic capacities. These results demonstrate the importance of moderate Mg and vacancy co-doping.

The following description has been revised in the manuscript: "As displayed in the bulk (Figure S20g), the pre-edge around 535 eV in the O EELS K-edge spectrum is related to the transition of O 1s electrons to the unoccupied 2p orbitals, which is hybridized with the TM 3d orbitals. When charging to 4.35 V, the increase of pre-edge

intensity indicates the removal of electrons from oxygen, namely the increase of oxygen holes, which is contributed by the oxygen redox. [42-44] After discharging to 2.0 V, intensity decreased, suggesting the good reversibility of oxygen redox."

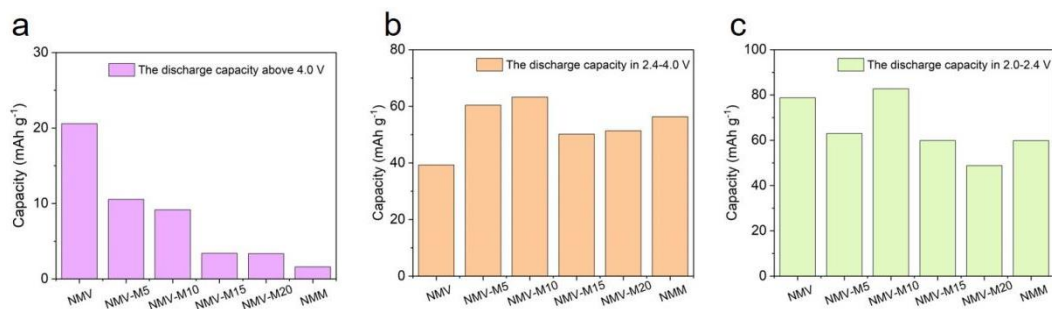


Figure S11. The first discharge capacities of the samples of (a) above 4.0 V; (b) 2.4–4.0 V, and (c) 2.0–2.4 V at 0.1 C.

Comment 2-2: For NMV, the CV curves with multiple peaks typically suggest Na/vacancy ordering within the sodium transition metal layers. Given this, is it feasible that the vacancies present in the sodium layer initiate the anionic redox reaction? As the electrochemical performance shown, NMV-M10 with Mg and vacancy dual doping not only exhibits increased capacity, but also suppressed voltage decay. The detail reason for that should be further discussed.

Our response: Thank you very much for your helpful comments. According to previous reports, only the vacancies existing in the transition metal layers can form the Na–O–□ configuration to trigger the oxygen redox. According to the DFT calculations and previous reports, the Mg and vacancy (□) dual doping has a synergetic effect on creating abundant nonbonding O 2*p* orbitals along the Na–O–Mg, Na–O–□, and Mg–O–□ configurations, which effectively improves the oxygen redox activity. And the COHP calculations (Figure 6d) reflect that the Mn–O bond adjacent to the vacancy exhibits stronger bonding strength in Mg and vacancy dual-doped NMV-M10 than only vacancy-doped NMV, which would suppress the oxygen transforming into irreversible oxygen gas release and improve the oxygen redox reversibility. In addition, the Mg doping is also beneficial for preventing the the clusters of vacancies in TM layer, which

can suppress the formation of molecular O₂ and Mn migrating within the TM plane.

The following description has been revised in the manuscript: "The larger ICOHP value of Mn–O after Mg doping indicates its stronger bond strength, which would suppress the oxygen transforming into irreversible oxygen gas release and improve the oxygen redox reversibility. In addition, the Mg doping is also beneficial for preventing the the clusters of vacancies in TM layer, which can suppress the formation of molecular O₂ and Mn migrating within the TM plane."

Comment 2-3: Why is there a noticeable reduction in the voltage plateau at ~4.1 V, associated with the anionic redox reactions of vacancies, when transitioning from NMV to NMV-M5, yet only a marginal shift from NMV-5 to NMV-M10?

Our response: Thank you very much for your invaluable comments. According to previous reported, this discharge voltage plateau is related to the oxygen redox of Na–O–□, where the Mn atoms and vacancies arrange with ribbon ordering. With the introduction of 5% Mg, on the one hand, the introduced disturb the ribbon-ordered superstructure and transform to a honeycomb-ordered superstructure, which can be observed from the XRD pattern (Figure S3). On the other hand, the introduced Mg ions also occupy some vacancy sites (Table S2). Thus the NMV-M5 exhibit a noticeable reduction in the voltage plateau. However, for NMV-M10, apart from some introduced Mg ions occupy the vacancy sites, a part of Mg ions also occupy Mn sites with a honeycomb ordered superstructure, which enables only a marginal shift of this discharge voltage plateau from NMV-M5 to NMV-M10.

The following description has been revised in the manuscript:"the reduction peaks at ~4.2 V from the oxygen redox of Na–O–□ configuration slightly weaken with the increasing of Mg content, and disappear completely in NMV-M20 (Figure S10). This phenomenon might be caused by the gradual occupation of TM vacancies by Mg²⁺ ions."

Comment 2-4: As displayed in the ex situ XANES spectra, why does the Mn-O distance become longer when charging to 4.35V? Theoretically, the Mn-O distance

should be decreased with the oxidization of Mn^{3+} .

Our response: Thank you very much for your helpful comments. As you claimed, the Mn-O distance should be decreased with the oxidization of Mn^{3+} , however, during the charge process, the oxygen redox can also influence the Mn-O distance, especially at the initial charge process with small amount of Mn^{3+} oxidized. Here, the Mn-O distance in NMV-M10 shows a slightly increase during charge process, possibly due to the oxygen redox reaction that weakens the Mn-O bond, this phenomenon also has been observed in other layered cathode materials with oxygen redox.

The following description has been revised in the manuscript: " The Mn-O distance shows a slightly increase during charge process, possibly due to the oxygen redox reaction that weakens the Mn-O bond."

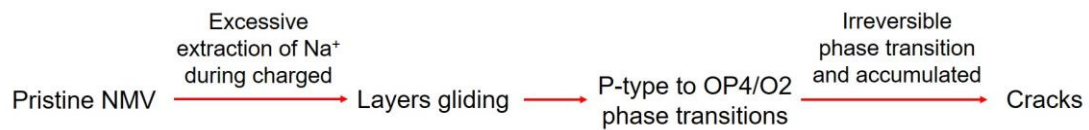
Comment 2-5: As the authors mentioned that there is a wide report on the ribbon-ordered superstructure of Mn and Li. Meanwhile, the NMV also shows a superstructure of Mn and vacancy within the TM layers, is there anything in common between them? The concept of Mn ions pinned within the sodium layers is intriguing. However, in LIBs, Li/Ni mixing is typically undesirable, as cation migration often compromises structural stability. Does the presence of Mn ions in the sodium layers here have a similar adverse effect on the material's structural integrity?

Our response: Thank you very much for your valuable comments. According to the HAADF-STEM image of NMV (Figure S8), a ribbon-ordered superstructure with 4 Mn and 1 vacancy arrangement can be clearly observed, which is similar to the ribbon-ordered superstructure of 4 Mn and 1 Li arrangement illustrated by Peter G. Bruce. This ribbon-ordered superstructure makes the vacancy-contained and Li-contained layered oxides a noticeable discharge voltage plateau at ~ 4.1 V. According to the electrochemical performance comparison of NMV-M10 with NMV and the ex-situ HAADF-STEM characterizations, the Mn ions in the sodium layers are sufficient robust to suppress the layer gliding and thus inhibit the crack formation.

Comment 2-6: Characterization on the crack production is meaningful, which reflects

the failure mechanism of layered material. It is better to schematically depicted the detailed crack production process from atomic layer to particle.

Our response: Thank you very much for your valuable comments. According to the *ex-situ* XRD analysis of NMV, the diffraction peaks from OP4 and O2 phases strengthen progressively after cycling (Figure 5b). Such phase transitions from P-type to O-type phases suggest the occurrence of layer glidings. In constrast, there are no phase transition after cycles for NMV-M10, suggesting the interlayers have been fixed by the "mis-occupied" Mn ions in Na layers. According to the HAADF-STEM of the cracks in NMV, the O-type phases are mainly distributed at the edge of crack. And the EDS elemental mappings show that some obvious Na-deficient regions are generally distributed around the cracks, which suggests that the excessive extraction of Na⁺ causes the oxygen layer gliding. Thus, the formation of the cracks in NMV can be schematically illustrated as following:



For NMV-M10, due to the pinning effect of the "mis-occupied" Mn ions in Na layers, the layers gliding has been effectively suppressed, thus the generation of cracks have been inhibited.

Response Letter

Manuscript number: NCOMMS-23-44510B

Title: Transition metal vacancy and position engineering enables reversible anionic redox reaction for sodium storage

Response to Reviewer-1

General Comment: The manuscript titled “Transition metal vacancy and position engineering enables reversible anionic redox reaction for sodium storage” demonstrates the effect of 1. substitution of vacancies and Mg for transition metal (TM) in TMO₂ layer and 2. Mn occupation in Na layer to the lowering oxygen redox potential and its stabilization together with the improved structural stability of P2-type Na_{0.67}Mg_xMn_{1-x}O₂ ($0 \leq x \leq 0.2$) cathode. The manuscript is well organized delivering the inquired information from the first round of review. I recommend publishing in Nature Communications after addressing minor questions below.

Response to General Comment: We are very grateful to your insightful suggestions. We have modified the description accordingly below.

Comment 1-1. Page 5, line 98: The authors demonstrate the Mn²⁺ occupation in Na site (2d) based on the Rietveld refinement result in Table S3. This refinement result is playing a key role for supporting the Mn mis-occupation in Na layer. It would be more supportive if the authors compare and discuss the Rietveld refinement result between when Mn occupied in Na sites and Mg occupied in Na sites.

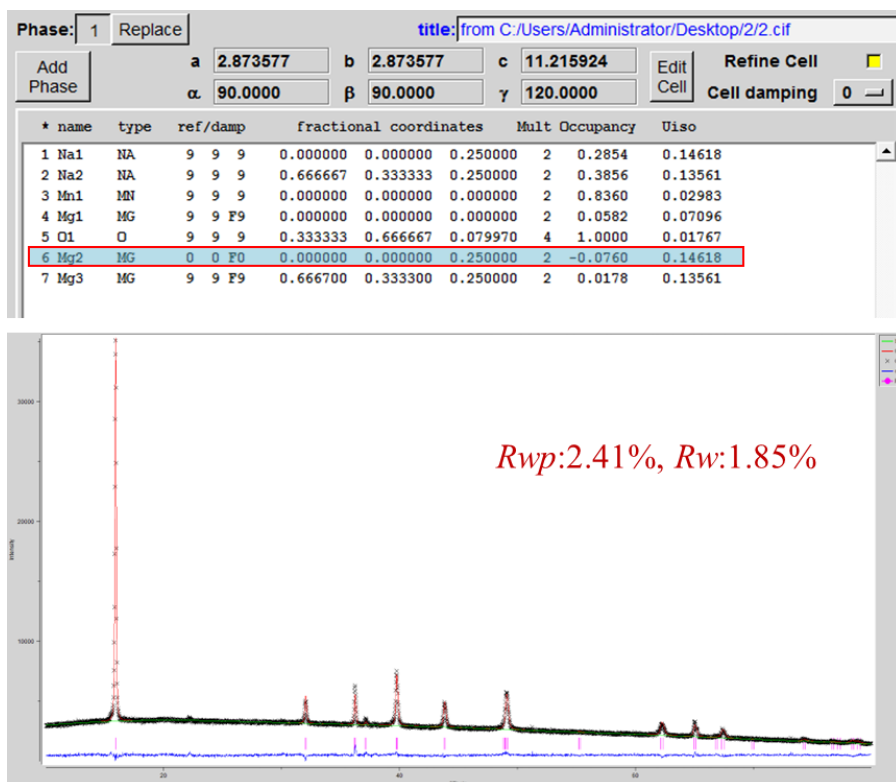
Our response: Thank you for your helpful suggestions. To better illustrate the Mg sites, we have added Rietveld refinement data showing 5% Mg occupying the TM layer and 5% Mg occupying the Na layers. The Na/Mg/Mn elemental ratio of NMV-M10, determined by ICP-OES, is 0.671:0.097:0.836 (Table S1). It is assumed that the chemical composition is Na_{0.67}Mg_{0.05}[Mn_{0.836}Mg_{0.05}]O₂, with 5% Mg occupying both

the Na layers and TM layers.

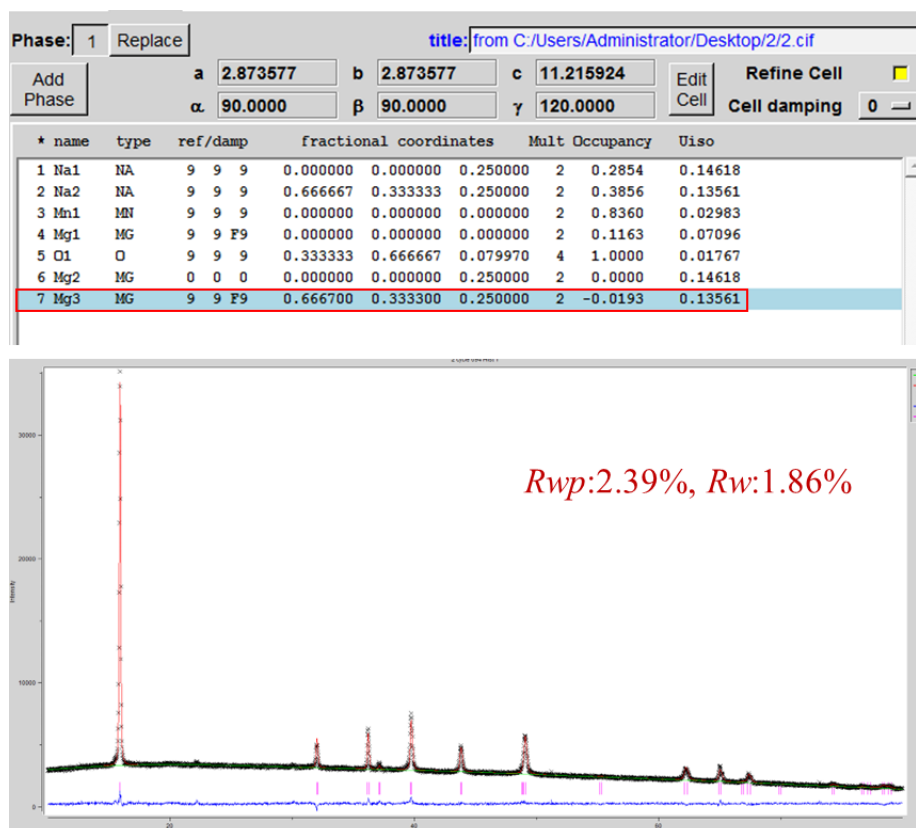
Firstly, considering there are two types of Na sites (Na_f and Na_e) for Mg occupancy, the location of Mg at Na sites was initially unfixed before the Rietveld refinement process. However, after the Rietveld refinement, the Mg occupancy at the Na_f (2b) site became negative, with a sharp decrease in Mg occupancy at the Na_e (2d) site, indicating that Mg cannot be placed at the Na_f site. Secondly, when the Mg occupancy at the Na_f site was set to zero, allowing 5% Mg to occupy the Na_e (2d) site, the Mg occupancy at the Na_e (2d) site also became negative after Rietveld refinement. This indicates that Mg cannot successfully substitute at the Na_e (2d) site either.

Therefore, the Rietveld refinements of NMV-M10 demonstrate that Mg cannot occupy the Na sites, whether at the Na_f (2b) or Na_e (2d) sites. When trace amounts of Mn in the Na sites are taken into account, both R_{wp} and R_w decrease (Table S2), suggesting the possibility of this case.

In addition, according to previous reports (*J. Am. Chem. Soc.* 2019, 141, 840-848), when Mg ions occupy the TM layers, the c parameter increases due to the larger ionic radius of Mg^{2+} ions compared to Mn ions, which increases the TM layer thickness. This increase in the c parameter corresponds to the shift of the (002) plane toward a lower angle. Conversely, when Mg ions occupy the Na layers, the smaller radius of Mg^{2+} compared to Na^+ would reduce the interlayer distance, causing the c -axis to shrink and the (002) plane to shift toward a higher angle.



R1. The first Rietveld refinement process by unfixing the Mg occupancy at Na sites.



R2. The second Rietveld refinement process providing the Mg occupancy at Na_e site.

As displayed in Figure S1b, when the Mg content increases from 0 to 10%, the (002) peak shifts to a lower angle, implying that the Mg^{2+} ions prefer to occupy the TM layers rather than the Na layers. Moreover, comparing the crystal parameters of the P2-phase of NMV and NMV-M10 from the Rietveld refinement results (Tables S2 and S3), the a (b) and c parameters all increase as the Mg content increases from 0 to 10%, suggesting the occupancy of Mg in Mn sites.

Furthermore, the trace amount of Mn ions occupying the sodium layers should not cause a dramatically decreased interlayer distance.

The following description has been added in the manuscript: “When the Mg content increases from 0 to 10%, the (002) peak shifts to a lower position (Figure S1b), indicating an expansion of the unit cell along the c -axis. This shift is due to the larger ionic radius of Mg^{2+} ions compared to Mn ions, which increases the TM layer thickness. If Mg were to occupy the sodium layers, the smaller radius of Mg^{2+} compared to Na^+ would reduce the interlayer distance, causing the c -axis to shrink.⁹ However, this is contrary to the observed results. Therefore, the introduced Mg ions in NMV-M10 are more likely to occupy the transition metal layers. ... With the introduction of 10% Mg, the obtained NMV-M10 adopts a pure P2 phase (Figure 1a). The low agreement factors indicate the reliable refinement results. According to the refinement results (Table S2), the Mg ions occupy the TM-sites, while ~1.1% of Na_c sites are occupied by Mn ions. Such a trace amount of TM ions occupying in sodium layers should not cause the dramatically decreased interlayer distance.”

Comment 1-2: Page 21, line 418: The authors claim that the Mg doping prevents the cluster of vacancies in TM layer. I assume the authors meant that the increased Mn-O bond strength prevent the vacancy clustering by TM migration in TMO_2 layer over the first charge process as Robert A. House et al. suggested (First-cycle voltage hysteresis in Li-rich 3d cathodes associated with molecular O_2 trapped in the bulk, Nature Energy, 2020, 5, 777–785). It would be better to refer this paper and slightly discuss it to compare and emphasize the importance of this work.

Our response: Thanks very much for your valuable suggestions. We also assume that

the increased Mn-O bond strength can restrict TM migration in the TMO₂ layer, thus preventing the formation of vacancy clusters. As revealed by Robert A. House et al., these vacancy clusters serve as sites for trapping O₂ molecules generated during charging, leading to voltage hysteresis and irreversibility of the oxygen redox process in the first cycle. Combing the results of XPS and sXAS, the oxygen redox products of NMV-M10 are mainly (O₂)ⁿ⁻ species instead of O₂ molecules, which inversely proves that the formation of molecular O₂ is suppressed, indicating that TM migration did not occur to form vacancy clusters.

The following content was added accordingly in the revised manuscript: “... The larger ICOHP value of Mn–O after Mg doping indicates its stronger bond strength, which would suppress TM migration in the TMO₂ layer, thus preventing the formation of vacancy clusters. As revealed by Robert A. House et al.,⁵⁴ the formation of O₂ molecules inside the crystal is only possible due to TM migration that creates vacancy clusters. These clusters serve as sites for trapping O₂ molecules generated during charging, leading to voltage hysteresis and irreversibility of the oxygen redox process in the first cycle. Combing the results of XPS and sXAS, the oxygen redox products of NMV-M10 are mainly (O₂)ⁿ⁻ species instead of O₂ molecules, which inversely proves that the irreversible formation of molecular O₂ is suppressed. This indicates that Mg doping does strengthen Mn-O bond and prevent Mn migration to form vacancy cluster, thus enhancing the electrochemical performance with ignorable the irresistibility.”

54. House, R.A., Rees, G.J., Pérez-Osorio, M.A. *et al.* First-Cycle Voltage Hysteresis in Li-Rich 3d Cathodes Associated with Molecular O₂ Trapped in the Bulk. *Nat. Energy* **5**, 777–785 (2020).

Response to Reviewer-2

General Comment: The authors addressed all my concerns carefully, the manuscript, therefore, can be accepted.

Response to General Comment: We sincerely thank you for your thorough review and positive feedback. We are pleased to hear that we have successfully addressed all your concerns. We appreciate your recommendation for acceptance and are grateful for your support and constructive comments throughout the review process.

Response to Reviewer-3

General Comment: This work provides a thorough characterization of a P2 type NaMnMgO₂ compound. The authors provide concrete explanations as to why its performance both in discharge capacity and stability over numerous charge/discharge cycles exceeds previously studied materials. In doing so they provide a seemingly viable avenue to pursue for designing better sodium based batteries in the future. The most valuable part of this work is relating the structure and engineering of the cathode material (namely vacancy and doping sites) to the oxidation states. This paves a path for significant future study. The identification of Mn ‘rivets’, while less novel of an idea, is also very useful. Both of these have the potential to be useful not only for this specific compound but to the wider cathode community. The experimental methodology appears sound, and having both structural and electrochemical characterization in addition to spectroscopy lends additional weight to the work’s conclusions. One primary concern is the theoretical calculations. They seemed to be a brief addition without much context in the larger work, but then referenced heavily in the conclusions. A similar concern appeared other times while reading this manuscript. This is a long paper with many results presented, and while some segments were very convincing, in others the conclusions were not readily linked to the data. The stability arguments were the most convincing but the discussion of oxidation states seems more important.

Overall I think the manuscript’s main strengths are its detailed nature in the experimental work, and its useful implications for the cathode field. However, it is in need of edits. Greater emphasis on a single, unifying thread throughout the manuscript is needed, to help make sure the reader can see how conclusions were pulled from the work. I will lay out specific comments below.

Response to General Comment: We sincerely thank you for your careful review and great interest in our work. We have made further revisions to our manuscript based on your suggestions below.

Comment 3-1: The paper is well situated amongst previous work in terms of lithium-

based materials and other Na/Mn based materials with different doping and vacancies, but not other types of structures. For example, Kim et al. similarly look at Mg and vacancy doping but in a P3 material in ACS Appl. Energy Mater. 2020, 3, 10423–10434. Please add more context and explain what is different or useful about the P2 structure.

Our response: We deeply appreciate your invaluable insights. We have added more discussion to explain the difference between P2 and P3 structures in the revised manuscript as following: “This phenomenon can also be observed in P3-type $\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$, which exhibits a short plateau at ~ 4.2 V but also decays in subsequent cycles.³⁷ In comparison, the P2 structure has demonstrated higher intrinsic ionic conductance and suitable crystal symmetry, which may facilitate the reversibility of Na–O–□ here.³⁸”

37. Kim, E. J., Ma, L. A., Pickup, D. M., Chadwick, A. V., Younesi, R., Maughan, P., Irvine, J. T. S., Armstrong, A. R. Vacancy-Enhanced Oxygen Redox Reversibility in P3-Type Magnesium-Doped Sodium Manganese Oxide $\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$. *ACS Appl. Energy Mater.* **3**, 10423-10434 (2020).

38. Yu, L., Dong, H., Chang, YX. *et al.* Elucidation of the Sodium Kinetics in Layered P-Type Oxide Cathodes. *Sci. China Chem.* **65**, 2005–2014 (2022).

Comment 3-2: Line 78-the DFT currently in the paper does not show enhanced structural stability. Fig 6 b-c are used to explain the improved stability seen experimentally but do not, on their own, show it.

Our response: Thank you very much for your valuable comments. The enhanced structural stability can be reflected in the crystal orbital Hamilton populations (COHP) calculations (Figure 6d). The larger integrated COHP (ICOHP) value of Mn–O with Mg and vacancy dual doping, compared to individual vacancy doping, indicates stronger bond strength. This increased bond strength suppresses the transformation of O^{2-} into irreversible O_2 molecules and improves the oxygen redox reversibility, thereby enhancing the structural stability of these layered oxides.

To eliminate confusion, the following description has been modified in the

manuscript: “The crystal orbital Hamilton populations (COHP) analysis is performed to investigate the chemical bonding information. Especially, the integrated COHP (ICOHP) is calculated to reflect the bonding strength of the Mn–O bond adjacent to the vacancy. The larger ICOHP value of Mn–O after Mg doping indicates its stronger bond strength, which would suppress TM migration in the TMO₂ layer, thus preventing the formation of vacancy clusters.”

Comment 3-3: Line 126 - explain how you see Jahn-Teller alleviation. Readers aren't seeing a figure here, more words are needed.

Our response: Thank you very much for your valuable comments. We have added additional description to explain the Jahn-Teller alleviation as following:

“Six-coordinated Mn³⁺ has an uneven distribution of electrons in its d-orbitals ($t_{2g}^3e_g^1$). Specifically, the single electron in the e_g orbital leads to an uneven electron density distribution, causing the ion to distort to relieve this instability. This distortion, known as the Jahn-Teller distortion, typically results in an elongation or compression of the octahedral coordination environment, which weakens the structural stability of the material. The XPS results indicate that the Mg doping is beneficial for decreasing the amount of Mn³⁺ and alleviating the Jahn-Teller distortion of Mn³⁺.”

Comment 3-4: Lines 252-254 discuss causes for expansion along the *c*-axis. Would love to see a longer explanation here - interesting but short.

Our response: Thank you very much for your comments. We have added a more detailed explanation here as following: “The expansion along *c* axis during charging process is ascribed to the continuous extraction of Na⁺ from the TMO₂ interlayers, which reduces the shielding of positive charges and increases electrostatic repulsions between the oxygen layers, resulting in the increase of interlayer distance, corresponding to the lattice expansion along the *c*-axis.”

Comment 3-5: Line 345 - 356 all discuss information in the supplemental material. This is very common throughout the paper. This is a less necessary edit perhaps, as

figures are challenging and not everything can be shown, but for figures heavily discussed in the main text it may be best to include them in the main text as well. If more figures can't be included, then something else is required so the reader doesn't feel they are missing information.

Our response: Thank you very much for your careful and helpful suggestions. We have simplified the description in the main text for the Supporting Figures.

The following description has been modified in the manuscript: “The ex-situ Mn XPS spectra of NMV and NMV-M10 in Figure S22 demonstrate similar changes. With charging from pristine state to 4.35 V, small amounts of Mn³⁺ are oxidized to Mn⁴⁺. After discharging to 3.5V, Mn 2p_{3/2} peak becomes slightly broadened, which indicates a very small amounts of Mn⁴⁺ are reduced to Mn³⁺ and the capacity contribution in this voltage range is mainly provided by anionic (oxygen) redox. When further discharged to 2 V, a large amount of Mn⁴⁺ are reduced and the electrochemical oxidation center changes from anionic redox to cationic redox of Mn³⁺/Mn⁴⁺. Therefore, it can be concluded that most of the Mn³⁺/Mn⁴⁺ redox are proceeded at lower than 3.5 V, and a very small amounts proceed above 3.5 V.”

Comment 3-6: Theoretical Calculations beginning on line 396 - This section needs the most strengthening over all. A better motivation would be useful as it's not particularly clear why you're doing calculations. The shifting of the O 2p density seems like the most useful thing in this section, please elaborate on how it helps you and why you did it.

Our response: Thank you very much for your insightful comments. According to the experimental results, the oxide with dual Mg and vacancy doping exhibits the highest oxygen redox capacity and reversibility, which are strongly related to the electronic structure of oxygen. Therefore, DFT calculations on individual Mg or vacancy doping, as well as dual Mg and vacancy doping, were performed to study the changes in the O 2p and Mn 3d bands.

To better demonstrate the motivation for DFT calculations, additional description has been added as following: “As discussed above, the NMV-M10 with

dual Mg and vacancy doping features improved oxygen redox activity and reversibility than the individual vacancy and Mg doping, which may suggest the dual Mg and vacancy doping is beneficial for placing the nonbonding O 2*p* band close to the E_f . Therefore, the electronic structures are calculated by DFT calculations to study the effects of Mg and vacancy doping on O 2*p* and Mn 3*d* bands.”

Comment 3-7: For the DFT Methodology, what sized supercells were used? How were locations for vacancies and doping atoms chosen? While basic structures were shown in S25, to make these genuinely convincing more details are needed. Currently I'm concerned that single cell structures, even with a larger number of atoms, aren't fully representative of the material overall but rather of specific doping sites.

Our response: Thank you very much for your comments. The equilibrium lattice constants of NaMnO₂ unit cell were optimized. We then use it to construct a 2×2×2 supercell model with the lattice parameters (a=8.5536Å, b=11.4048Å, c=11.0948Å). The Na₈Mn₁₁O₂₄ or Na₈Mn₁₁MgO₂₄ structures had been established with randomly deleting a Mn atom as a vacancy or doping Mg at Mn position as the Mn-O system is symmetric. Na₈Mn₁₀MgO₂₄ structures had been established doping Mg at Mn position in Na₈Mn₁₁O₂₄ structures.

To eliminate this concern, additional description has been added in the theoretical calculations sections as below: “The equilibrium lattice constants of NaMnO₂ unit cell were optimized. These optimized constants were then used to construct a 2×2×2 supercell model. The Na₈Mn₁₁O₂₄ or Na₈Mn₁₁MgO₂₄ structures were established with randomly deleting a Mn atom as a vacancy or doping Mg at the Mn position, given the symmetric nature of the Mn-O system. Na₈Mn₁₀MgO₂₄ structures were established by doping Mg at the Mn position in Na₈Mn₁₁O₂₄ structures.”

