Minimum Co content limit in layer-structured cathode materials for Li-ion batteries

Yongseon Kim

Department of Materials Science and Engineering, Inha University, Incheon, 22212, Republic of Korea

HIGHLIGHTS

- Structure of layer-structured cathode materials in delithiated state is investigated.
- Interfacial energy acts as energy barrier preventing structural degradation.
- Minimum Co content limit in LiNi_{1-x}Co_xO_2 for the structural stability is proposed.
- Doping can reduce the minimum Co content by inducing uneven Co distribution.

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ABSTRACT

Research to decrease the Co content in layer-structured cathode materials for Li-ion batteries is ongoing to increase the battery capacity and decrease the cost of material by increasing the relative Ni content. However, no clear guidance has yet been provided on the minimum possible Co content. In this study, energetically stable structures of delithiated cathodes are investigated, and a complete crystal structure is modeled as a combination of these structures. By the statistical processing of Co distribution within the model crystal, as well as considering the interfacial energy between differently structured domains induced by stacking faults of the O layers, the lower limit for the Co content is calculated. The result indicates that a minimum of 10.2% Co is necessary to prevent degradation of the crystal structure. For further reduction of the Co content, the Co distribution must be concentrated in certain regions of the crystal, which can be achieved by doping with a small amount of a third element. In this manner, the Co content could be ideally reduced to 4.17%.

1. Introduction

The industry of Li-ion batteries (LIBs) is rapidly growing with their broadening applicability to electric vehicles (EVs) [1-5]; however, LIB technology still falls short of consumer expectations, especially regarding energy storage density and price. LIBs still comprise a significant portion of the total price of EV and even then, the mileage of EVs per charge requires further improvement. The concentration of Li ions is directly related to the energy storage capacity of the LIB, and the Li ions are originally supplied from the cathode materials in current LIB system. Therefore, the capacity of cathode material is directly related to the energy density of LIBs. In addition, the cost of the cathode as a raw material is higher than that of other parts, such as the anode, separator, and electrolyte. Therefore, the development of high-capacity and low-cost cathode materials is pertinent to current LIB technology [3,6,7].

Several candidate materials such as LiFePO_4, LiMn_2O_4, and LiNi_{0.5}Mn_{1.5}O_4 are available as alternatives to LiCoO_2 (LCO) — the most widely used cathode material in current LIBs. However, they have limited utility in high-capacity LIBs because of their small theoretical capacities [8-12]. Therefore, the most realistic short- or mid-term solution for LIB cathodes seems to be Ni-based layer-structured materials. By increasing the Ni content while decreasing the Co content in layer-structured cathodes, the energy capacity could be enhanced in the current commercial charging voltage range of 4.2-4.3 V [3,13-15]. In addition, Ni is cheaper than Co and has a stable supply. Therefore, higher energy storage densities and lower battery costs, which seem to be the most critical issues in the current LIB industry, can be achieved by substituting conventional LCO cathodes with Ni-based materials [16].

However, the problems of inferior durability, thermal instability, high defect concentration, and low structural stability become significant with increase in substitution of Ni in place of Co [3,14,17]; therefore, research efforts are focused on increasing the stability of Ni-based cathodes. Many studies have reportedly improved the structural stability
of Ni-based cathode materials, generally by optimizing the chemical composition and/or the processing conditions for the synthesis [14, 18–22]. Thus, Ni content could gradually increase, with LiNi_{1/3}Co_{1/3}Mn_{1/3}O_{2}, LiNi_{0.8}Co_{0.2}Mn_{0.3}, and LiNi_{0.6}Co_{0.2}Mn_{0.2}O_{2} having been developed and commercialized individually. Efforts to further increase the Ni content to 80% or even 90% are currently in progress [22].

However, few studies have presented the extent to which the Co content can be reduced in layer-structured cathode materials. Although the cathode composition generally involves Mn and various other doping elements in addition to Ni and Co [18,21,23–27], the structural integrity and stability of the crystal are known to be mainly affected by the Co content [14,16,18,28,29]. Therefore, it is necessary to examine the minimum Co content required to maintain structural stability. The results of this examination would reduce unnecessary trial and error in the materials design development of high-Ni-content cathodes. In this context, this study investigates the lower limit of the Co content in Ni-Co-based LIB cathodes, focusing on the crystal stability in their delithiated states; thus, suggesting the ultimate lower limit of Co content as well as methods to reduce the Co content as close as possible to this limit.

2. Methods

Low-energy structures of Layer-structured cathode materials in the 66.7% delithiated state (Li_{0.33}TM_{0.67}O_{2}, where TM = Ni and Co) were explored by an unbiased structure-searching technique based on the particle swarm optimization (PSO) algorithm using Crystal structure AnalYsis by Particle Swarm Optimization (CALYPSO) code [30]. Frame cells of Li_{x}TM_{12}O_{24} were prepared by removing nine Li and five TM atoms from supercells of Li_{12}TM_{12}O_{24}. To this frame cell, one Li and five TM atoms were then added at random places with no limiting rules except the minimum distance between ions in the crystal, which was set to 1.0 Å. Applying only this minimum necessary condition enabled the examination of both the insertion of atoms at vacant lattice sites and the possibility of interstitial site occupation.

The structures generated by the PSO algorithm were optimized by density functional theory (DFT) calculations via the Vienna Ab initio Simulation Package (VASP) [31,32], and the crystal energy obtained from the calculation was fed back to the PSO algorithm (Fig. 1). The most stable structures for Li_{x}TM_{12}O_{24} were derived from 15 total generations of structure-searching, with 50 structures per generation. The DFT calculations were performed using VASP code with a 3 × 3 × 1 k-point grid based on the Perdew–Burke–Ernzerhof generalized-gradient approximation and projector-augmented plane-wave pseudopotentials [33,34], with an energy cutoff of 500 eV. Full relaxation of the atomic positions and lattice vectors was allowed with the energy convergence threshold of 10^{-5}. The energies of the five lowest-energy structures selected from the PSO-DFT method were calculated again more precisely using the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional [35].

3. Results and discussion

3.1. Structures in delithiated state

The two most stable structures determined for the unit supercell of Li_{x}TM_{1/2}O_{24} (TM = Ni and Co) are presented in Fig. 2. These compositions are equivalent to the 66.7% delithiated state of the cathode, denoted as dL-LTMO (delithiated Li–TM oxide). Regarding the two structures, one has no point defects except for the deficiency of Li, while the other structure contains the migration of two transition metal atoms to Li sites and the shift of two Li ions to tetrahedral interstitial sites. The two structures can be expressed in terms of their cationic point defects as [0TM_{2} + 6Li_{tet}] and [2TM_{Li} + 3Li_{tet}]; for simplicity, in this study, they are labeled as P (perfect) and D (defect-containing) structures, respectively.

The P- and D-structure showed lower energies than other structures in the entire x-range of LiNi_{1/12}Co_{1/12}O_{24}, indicating that they are the main components comprising the crystal structure of dL-LTMO. Their energies were far lower than others especially in Ni-rich compositions such as Li_{x}Ni_{11/12}Co_{1/12}O_{24} (dL-LNO) and Li_{x}Ni_{11/12}Co_{1/12}O_{24} (dL-LNi_{11/12}Co_{1/12}O) (Supplementary Information S1). In addition, the stability of P- and D-structure over other structures was maintained in 50–75% of delithiation, and the energy difference between P- and D-structure was similar in this delithiation range (Supplementary Information S2). Therefore, investigation of this study, which will be based mainly on these two structures, seems to hold a reliability especially for delithiated Ni-rich cathodes. (The detailed structural data are shown in Supplementary Information S3).

The D-structure has 50%, 25%, and 25% occupancy of the Li sites in the three Li layers, and the TM ions penetrating the two 25%-Li occupied layers force the shift of two Li ions to tetrahedral interstitial sites. One of the Li-ions in the 50%-Li occupied layer also migrates to a tetrahedral site, thus 75% of the Li-ions (three Li ions in the Li_{x}TM_{12}O_{24} unit supercell) are at tetrahedral sites and 25% of Li ions remain at normal lattice points. Because of the irregular arrangement of the metal ions, O ions also show slight shifts in position along the a- and b-axis from their original lattice sites. The accumulation of these shifts finally generates a stacking fault between the two O layers adjacent to the Li-50% layer. Thus, the D-structure features both point defects (2TM_{Li} and 3Li_{tet}) and planar defects (the stacking fault of the O-layer), while the P-structure has no such defects (Fig. 2).

The energy differences between the P- and D-structures are shown in Fig. 3 as a function of the Co content in dL-LNi_{1-x}Co_{x}O. The Boltzmann factors calculated at room temperature, which should be proportional to the appearance probabilities of the structures, are also depicted in the figure. The graphs show that the P-structure is stable in dL-LCO, while the D-structure is dominant in dL-LNO. The stability of the P-structure is increased as the Co content of TM increases, with a rapid change near 20% Co, showing the Boltzmann factor over 100 times larger than that of the D-structure for Co contents of >25%. Therefore, it is concluded that Co/(Ni + Co) should be 25% at minimum to ensure structural stability by suppressing the formation of the defective D-structure.

3.2. Interfacial energy between structures

In the previous section, the P- and D-structures were established as the most probable structures in dL-LTMO in terms of structural energy. In this section, the possible coexistence of the two structures and the effects of structural coexistence on the stability of dL-LTMO are examined. Because the P- and D-structures have far lower energies than the...
other structures, the entire LTMO structure in the delithiated state may be considered a mixture of these two structures. If the two structures coexist with large domains of each, the interface between them does not affect the proportion of each structure because the interfacial energy is negligible compared to the total crystal energy. However, if they coexist on a very small scale, wherein the domain size is equivalent to the size of the unit supercell, the interfacial area becomes large and the interfacial energy effect may not be negligible.

To examine this consideration, $3 \times 3$ macro-supercells of dL-LNO, comprising nine P and D unit supercells (thus, total 351 atoms, with the composition of $\text{Li}_{27}\text{TM}_{108}\text{O}_{216}$), are designed as presented in Fig. 4 (11 of 20 total cases are presented in the figure), and the structural energies are calculated after the re-optimization of the combined structures by DFT calculation. Differently sized macro-supercells were tested before the calculation, which indicated that the maximum difference in the interfacial energy obtained from $2 \times 3$, $3 \times 3$, and $4 \times 3$ macro-supercells was only 3.6%. Thus, it seemed that the $3 \times 3$ macro-supercells of this study were adequate in size both for the reasonable calculation of energy and for the computational efficiency (Supplementary Information S3).

Fig. 5(a) shows the calculation results of the energies of the macro-
supercells as a function of the number of P-units included in the cells. If the P–D interface has no effect, the total energy is the sum of the P- and D-unit energies, and the summed energy is located on the line connecting the energy points of the two macro-supercells comprising all P-units and all D-units (9P-0D and 0P-9D structures, respectively, in Fig. 5 (a)). However, the energies of the P–D mixed macro-cells deviate from this line, showing far higher energy values and thus indicating that the interfacial energy arising from the coexistence of P- and D-units significantly affects the total crystal energy. This interpretation is supported by a plot of the energies of the macro-supercells as a function of the number of P–D interfaces (Fig. 5(b)), which shows that the supercell energy is strongly proportional to the number of interfaces.

As discussed in the previous section, the D-structure includes a stacking fault due to the positional shift of O ions, as well as the point defects of TM$_\text{Li}$ and Li$_\text{het}$. While the point defects only cause local distortion of the crystal structure, planar defects such as stacking faults cause atomic site mismatches when the defective structure is combined with a perfect structure, thus yielding structural instability at the interface. Therefore, when the D-unit containing a stacking fault is combined with the P-unit, the total energy of the combined structure exceeds the summed energy of the two units because of the generation of interfacial energy. If the domain size of each P- or D-structure is very large, the interfacial area is small and the energy associated with it may become insignificant, but the interfacial area increases as the domain size decreases; thus, the total crystal energy is significantly increased if the P- and D-structures coexist on a unit-supercell level.

When an LNO crystal is delithiated by the charging of the LIB that uses it as the cathode, the delithiated LNO may temporarily have the P-structure. However, the D-structure, which has lower energy in dL-LNO, would nucleate in the P-matrix and the domain would expand, finally causing an increase in the defect concentration and the destruction of the crystal. From the perspective of energy, this procedure is expected to occur like a two-phase reaction: P- and D-structures would coexist with large domain sizes, and the P-to-D transition would proceed with the motion of the domain boundary. This is how the two structures could coexist with the minimum interfacial energy.

However, if it is assumed that a small P-structured area is anchored in the crystal that maintains its defect-free features, the formation and expansion of the D-structure may be hindered by the interfacial energy generated between the expanding D-domain and the anchoring P-domain. In this case, the interfacial energy acts as an energy barrier against the P-to-D structural transition by the nucleation and growth of the D-structured domain in the dL-LNO crystal. Therefore, it is expected that the destruction of the dL-LNO crystal, and the resultant deterioration of performance as the cathode of LIBs, could be prevented if it were possible to retain unit supercell-level P-domains firmly anchored in the crystal.

### 3.3. Calculation of lower limit of Co content

In section 3.2, the possibility of anchoring small P-structured domains to suppress the destruction of layer-structured cathode materials in their delithiated state was proposed. In this section, the actual implementation of this proposal is discussed. As shown in Fig. 3 and the related discussion, substituting some Ni with Co is effective for stabilizing the P-structure; the data showed that the Co content should be ≥ 25% for the P-structured unit supercell to retain sufficient stability over the defective D-structured unit supercell. However, the minimum required Co content can be reduced from this result. All units in the 3 × 3 macro-supercell do not need to be P-structured, because only a partial distribution of P-units is expected to suppress the expansion of the D-domain in the discussion of the previous section. Therefore, the requirement for the Co content can be determined from the following questions:

1. What is the minimum Co content to obtain sufficient stability of the P-structured unit supercell over the D-structured unit?
2. In the macro-supercells combining P- and D-units, how many P-units are necessary to secure sufficient P–D interfacial energy to block the formation and expansion of defective D-domains?
3. In the macro-supercell, how are Co ions distributed over the 3 × 3 sections?

For question (1), section 3.1 noted that the Co content of 25% was necessary to stabilize the P-structure. Question (2) may be answered using Fig. 5(b), which shows that the total energy of the 3 × 3 macro-supercells is increased in proportion to the number of P–D interfaces. Considering that the interfacial energy rapidly increases until six interfaces and then the increasing rate slows from this point, it seems efficient that the required number of interfaces is determined to be six. It may be said that the energy difference between 9D-0D and 1P-8D provides enough energy barrier, which leads to a conclusion that only one P-cell that makes four interfaces would be enough for obstructing the structural degradation. However, it appeared that the P-structure in the 1P-8D macro-supercell suffered severe distortion although it was not converted to the D-structure, while the P-region in 2P-7D sustained the original structure. Therefore, only one P-cell, which provides four interfaces, is not expected to completely prevent the structural degradation, thus the required number of interfaces is determined to be six. Because there are four interfaces in the macro-supercell with 1 P-unit.

![Fig. 5](image-url)

**Fig. 5.** The energies of 3 × 3 macro-supercells calculated after structural optimization by DFT: (a) plot of the supercell energies as a function of the number of P-units in the macro-supercell and (b) plot as a function of the total number of P–D interfaces in the macro-cell.
Combining the discussions for questions (1) and (2), it is concluded that the overall necessary Co content to stabilize the dLi$_{2}$LTMO structure is 4.17% (1.5 P-units of the nine cells (=16.7%) and 25% Co for each P-structured cell, thus 16.7% × 25% = 4.17%). However, this value is correct only when Co ions selectively exist in the 1.5 units, with no Co ions in the other units. This ideal case is unrealistic because Co ions would be randomly distributed over all units. Therefore, a statistical examination is required to determine the distribution of Co ions, as suggested in question (3). This can be performed by calculating the number of cases in which N total Co ions can be divided into nine units.

The calculation result is presented in Fig. 6, which indicates that the expected number of P-units approaches 1.5 when N = 11. That is, 11 out of 108 total Ni ions should be substituted by Co to stabilize the 3 × 3 macro-supercell of the dLi$_{2}$LTMO crystal. Thus, it is concluded that the Co content of 10.2% (≈ 11/108) is necessary to correctly address questions (1)–(3). A perfectly random distribution of Co is assumed in the calculation; this may lead to errors if energy differences arise among the cases of Co distribution. For example, when five Co ions are distributed over two cells, they can be divided into the ratios of 5:0, 4:1, and 3:2; the number of cases is equal if the Co ions are distributed randomly. However, if the summed energy of the two cells differs depending on the division, the Co distribution is not random; instead, one division is energetically preferable. In this case, the Boltzmann factor must be considered to correct the imperfect randomness of the distribution.

To examine whether the Co ions are distributed randomly, the energy of Li$_{12}$Ni$_{1-2x}$Co$_x$O$_{24}$ is calculated as a function of the Co content, as shown in Fig. 7. The calculation is performed not for the delithiated state, but for the stoichiometric composition of the crystal because the distribution of Co is determined during the synthesis of cathode. The result shows that the energy of the supercell changes with an exactly linear proportionality to the Co content, indicating that the 5:0, 4:1, and 3:2 divisions in the above example of five Co ions distributed in two cells would have the same total energy, irrespective of the manner of division.

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Therefore, the calculation based on the assumption of a random distribution seems to be reliable; no correction is necessary for the number of cases by multiplying the Boltzmann factor.

In summary, it is calculated that three Co ions are necessary to stabilize the P-structured Li$_{12}$TM$_{12}$O$_{24}$ unit supercell, and that 1.5 P-units are required to stabilize Li$_{36}$TM$_{108}$O$_{216}$ (≈ 3 × 3-Li$_{12}$TM$_{12}$O$_{24}$). This requirement is found to be satisfied with 11 total Co ions in the 3 × 3 macro-supercell from the statistical examination of a random Co distribution; this is equivalent to the Co content of 10.2% (≈ 11/108). Therefore, it is concluded that the minimum Co content to maintain the crystal stability of a LiNi$_{1-x}$Co$_x$O$_2$ cathode is about 10.2% (i.e., x ≥ 0.102).

### 3.4. Effect of dopants to lower the Co content limit

It was concluded in the previous section that the Co content should be ≥ 10.2% to secure the structural stability of the LiNi$_{1-x}$Co$_x$O$_2$ cathode in the delithiated state. However, further Co content reduction is continuously required in the industry to obtain higher energy capacities and lower material costs. Therefore, the limit to the further decrease of the Co content should be investigated. It was discussed in the previous section that the Co content of 4.17% is sufficient for the structural stability of a 3 × 3 macro-supercell if the Co ions are concentrated in particular units. This calculation result was disregarded because it did not consider the randomness of Co distribution among the units. However, if the distribution could be controlled in certain cells, then the 1.5 P-units required for the structural stability of the 3 × 3 macro-supercell could be achieved with a lower number of Co ions.

For example, if there are six Co ions in the macro-supercell, only two units of the nine must contain Co ions, three per unit, to achieve two P-units (the unit supercells are more stable in the P-structure than in the D-structure when they contain three or more Co ions, as discussed in section 3.1). For this distribution, the Co ions must be divided as 3:3:0:0:0:0:0:0:0 over the nine units, but the probability of achieving this manner of division is only 1.2%, while those for achieving 2:2:1:1:0:0:0:0 and 2:1:1:1:1:0:0:0:0 are much higher. Therefore, to secure two P-units with six Co ions, the selective location of the Co ions in certain units should be induced. Thus, the question of stabilizing the delithiated structure with a smaller amount of Co becomes a question of intentionally unbalancing the Co distribution at the unit supercell level.

Fig. 8 shows the energy change when a Co ion substitutes for a Ni ion in the Li$_{12}$Ni$_{11}$D$_1$O$_{24}$ cell, where D denotes a foreign element doped in LNO. The energy values are normalized to the Co doping energy relative to Ni.
to the case without foreign elements; thus, the relative values of Co doping energy are presented. Because the doping energy depends on the relative positions of Co and D, the energies for the various locations are depicted as box-plots in the figure. It appears that the Co doping energy is affected by the existence of the foreign elements, as well as by the relative positions between Co and D. The doping of Mg, Sc, and Zr increases the Co doping energy, while that of B decreases the energy, indicating that Co doping becomes more difficult with the doping of the former elements, while B doping promotes Co doping. Thus, doping trace amounts of foreign elements may permit the disruption of the randomness of Co distribution, thus inducing preferential locations within the crystal.

If it is assumed that two foreign elements are introduced to the $3 \times 3$ macro-supercell, this is equivalent to the doping concentration of $\approx 2\%$ of 108 total Ni atoms. These dopants would be accommodated by two of the nine units, inducing a difference in the dopability of Co among the units and thus an uneven distribution of Co ions. In this manner, the randomness of the Co distribution can be tuned, and the minimum Co concentration required to retain structural stability can decrease below 10.2%, the result calculated for a random distribution of Co. (In choosing a dopant, the thermodynamic favorability of doping with the selected species should be considered [36,37], as should the possible loss of cathode performance by side effects of the doping.) Thus, we propose the introduction of a small amount of the dopant to control the Co distribution and improve the structural stability of Ni-rich cathodes with lower Co contents than those with randomly distributed Co. In addition, this method is suggested as a mechanism to explain existing experimental results demonstrating improved cathode performance with the addition of dopants.

Thus, the minimum Co content is suggested to be $\approx 4.17\%$ and $\approx 10.2\%$, with and without dopants respectively. Tang et al. [38] previously examined the electrochemical properties of LiNi$_{1-x}$Co$_x$O$_2$ cathode materials (they tested $x = 0.04, 0.08, 0.12,$ and 0.16). In their experiment, the cathodes with $x = 0.16$ and 0.12 showed good cycle performance, but those with $x = 0.08$ and 0.04 showed poor capacity retention of $\approx 60\%$ and $\approx 35\%$ after 100 cycles. The result indicates the minimum Co content to secure the stability of the cathode lies in the range of 8–12%, which is in good agreement with this study’s theoretical expectation of 10.2%. The Co content could be further decreased by doping of other elements: Zhou et al. [39] and Zhang et al. [40] reported stable cathode performance with 7% of Co content, respectively with addition of 3% of Al and Mg. Yoon et al. [41] examined even lower Co content of 2.5%. Their LiNi$_{0.95}$Co$_{0.05}$Mn$_{0.25}$O$_2$ cathode showed better electrochemical performance compared to LiNiO$_2$. However, the cyclic and thermal stability did not seem satisfactory, indicating 2.5% of Co-content is too small to obtain the cathode stability. Therefore, it is expected from the reports that the minimum Co-content would lie in 3–6% range when a dopant is added. This study’s expectation of the lowest possible Co content is $\approx 4.17\%$ when foreign elements are doped, which seems to be a reasonable value compared with those experimental results.

4. Conclusions

The energetically stable structures of layer-structured cathode materials in their delithiated states are investigated by a bottom-up method based on DFT calculations connected with the PSEO algorithm. Two Li$_2$TiM$_2$O$_6$ (TM = Co and Ni) supercells, one with no defects other than a Li vacancy (P-structure) and one including two Ni antisites, two Li at tetrahedral sites, and an O-layer stacking fault (D-structure), are found to be the most stable structures. The D-structure is stable with high proportions of Ni in TM, whereas the P-structure becomes stable as the Co content exceeds 25%. When the two structures coexist in a macro-crystal, an atomic site mismatch arises at the structural interface because of the stacking fault in the D-structure. This induces an interfacial energy, which acts as the energy barrier preventing the formation of the D-structure in a P-matrix. It is calculated that $\geq 16.7\%$ of the P-structure is necessary to ensure a sufficiently high interfacial energy to suppress the expansion of the D-structure and the resultant destruction of the delithiated cathode, if it is assumed that the crystal is a combination of P- and D-structured unit-cells. Based on these calculation results, along with a statistical consideration of the random distribution of Co ions over the P- and D-units, it is concluded that the minimum Co content required for the structural stability of the LiNi$_{1-x}$Co$_x$O$_2$ (LNCO) cathode is 10.2%. For a further reduction of Co, the distribution of the Co ions should be uneven among the supercells, allowing the local Co content to exceed 25% in certain regions and thus maintain the local P-structure. This unit-cell level of unbalance in the Co distribution can be achieved by introducing small amounts of foreign elements as dopants, which induce biases in the distribution of Co. The Co content could be reduced to 4.17% with an ideally uneven distribution of Co ions, which may be the lowest possible limit of Co in an LNCO crystal.

Declaration of competing interest

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

CRediT authorship contribution statement

Yongsun Kim: Conceptualization, Investigation, Writing - original draft, Funding acquisition.

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Appendix A. Supplementary data

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