Thermodynamically Revealing the Essence of Order and Disorder Structures in Layered Cathode Materials①

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ABSTRACT Layered transition metal (TM) oxides are one of the most widely used cathode materials in lithium-ion batteries. The atomic configuration in TM layer of these materials is often known to be random when multiple TM elements co-exist in the layer (e.g. Ni, Co and Mn). By contrast, the configuration tends to be ordered if the elements are Li and Mn. Here, by using special quasi-random structures (SQS) algorithm, the essential reasons of the ordering in a promising Li-rich Mn-based cathode material Li_2MnO_3 are investigated. The difference of internal energy and entropy between ordered and disordered materials is calculated. As a result, based on the Gibbs free energy, it is found that Li_2MnO_3 should have an ordered structure in TM layer. In comparison, structures with Ni-Mn ratio of 2:1 are predicted to have a disordered TM layer, because the entropy terms have larger impact on the structural ordering than internal energy terms.

Keywords: entropy, special quasi-random structures (SQS), layered cathode materials, Gibbs free energy; DOI: 10.14102/j.cnki.0254–5861.2011–2680

1 INTRODUCTION

The Nobel Prize in Chemistry 2019 was awarded jointly to John B. Goodenough, M. Stanly Whittingham and Akira Yoshino due to their distinguished contributions to the development of lithium-ion batteries (LIBs), which have fundamentally changed the world by powering portable devices and electronic vehicles over the recent decades[1]. Among different kinds of cathode materials, such as lithium ion phosphate, spinel Lithium manganese oxide, and layered transition metal oxide, structures with extra lithium are the most expected high capacity cathode materials. For example, $Li_3Ni_xMn_yC_{3-x-y}O_6$ (NMC)[2, 3] is one of the most common layered transition metal oxide materials. To further expand the theoretical capacity of cathode materials, many efforts have been made to combine Li_2MnO_3 with NMC to obtain Li-rich cathode materials, which enables extra-Li storage in transition metal layer. Li_2MnO_3 exists in Li-rich materials as domains, which is evidenced by a 'supercell' peak in X-ray diffraction (XRD) patterns due to the ordered transition metal layer in Li_2MnO_3[4], which does not exist in NMC. Many theoretic works have proposed various explanations for the ordered transition metal layer. For instance, transition metal atoms can have direct electrons exchanges with each

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other to form an inorganic aromatic structure[5]. An atom without spin electron is likely to form a stable super-structure with six atoms with spin electrons in transition metal layer to avoid magnetic frustration[6]. And six transition metal can form a 90-degree super-exchange interaction ring[7, 8] in transition metal layer to stabilize the structure, but these theories are proposed under estimations or simulations in an ideal condition (0 K). To fully understand the origins of the ordered transition metal layer, a method to predict the atomic configuration in transition metal in high temperature is needed to guide the synthesis of new materials.

Here, we focus on the high temperature of 1000 K, which is around the sintering temperature of Li_2MnO_3. By using a method to predict the effect of entropy in Gibbs free energy and an algorithm to simulate the internal energy of disordered structure[9], we compared the energy level between the atomic interactions (which promote ordered structure) and the temperature disturbance (entropy) (which forms disordered structure)[10]. It is found Li_2MnO_3 tends to form an ordered structure because the atomic interactions to build ordered structure are much stronger than the disturbance of temperature. In comparison, NMC materials have much weaker interactions so as to form disordered structures.

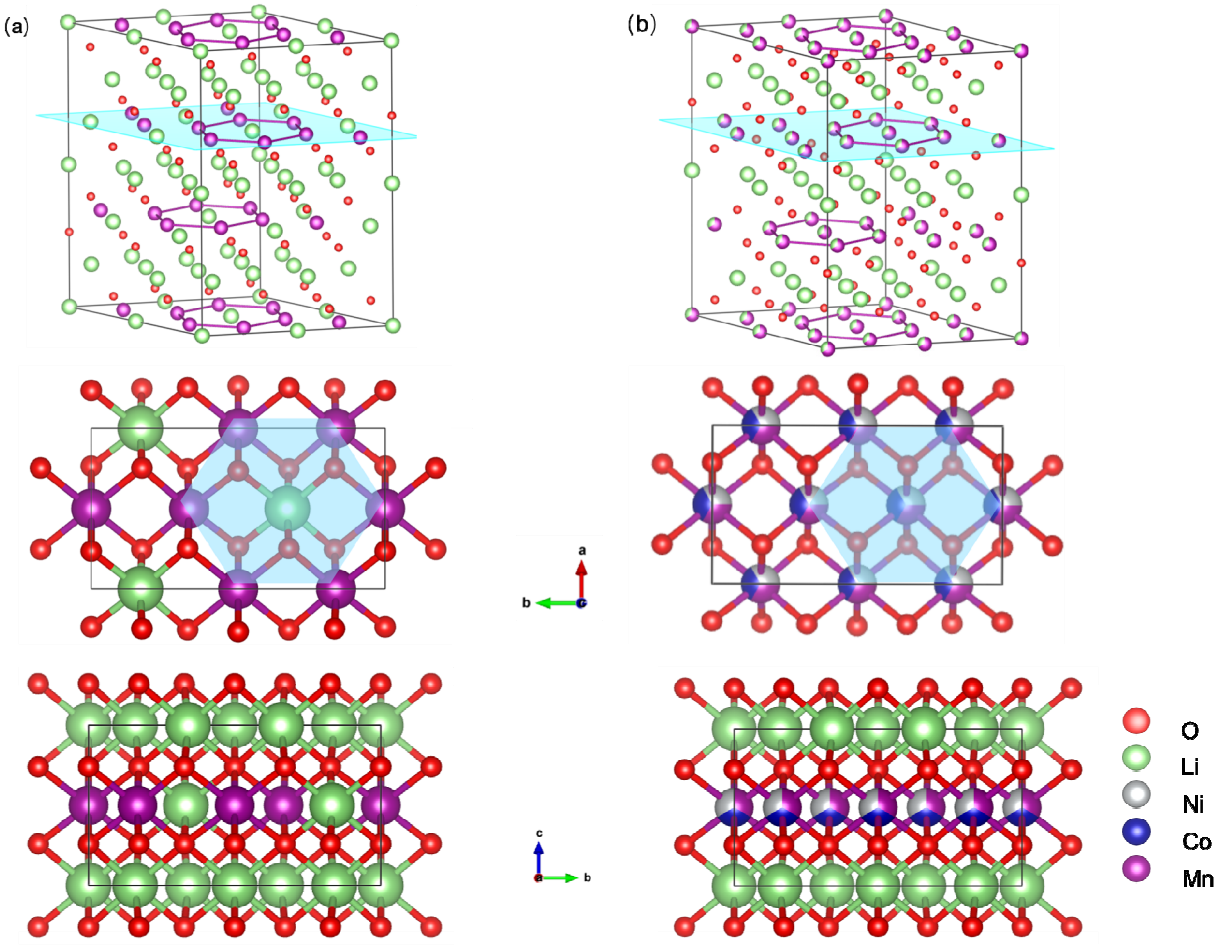

Fig. 1. (a) The ordered TM layer in the structure of Li_2MnO_3 (b) The disordered TM layers in the structure of $Li_3Ni_xMn_yCo_{3-x-y}O_6$

2 CALCULATION METHOD

To calculate the actual structure in different temperature, Gibbs free energy is represented in the following form,

$$G = U + PV - TS \quad (1)$$

where G represents Gibbs free energy, U represents the internal energy of structure, P represents the external pressure, V represents the volume of structure, T represents the temperature of the structure and S represents the entropy of structure.

As the layered lithium cathode materials are all in the form of solid, they should have little change in volume. The thermal expansion coefficient[11] is around 24.4×10^{-6} K^{-1}. The total Gibbs free energy change in the PV term from 0 to 1000 K is calculated around the scale of 1×10^{-4} meV/atom, which will be found to be much smaller than the changes of entropy and the changes of internal energy at least four orders of magnitude (see Table 1). Thus, the term of PV is neglected in our calculations.

Based on the formula (1), to calculate the difference of Gibbs free energy between ordered structure and disordered structure, the following equation is applied.

$$G_{disordered} - G_{ordered} = \Delta G = \Delta U - T\Delta S = U_{disordered} - U_{ordered} - T(S_{disordered} - S_{ordered}) \quad (2)$$

By calculating the terms of $U_{\text{disordered}}$, U_{ordered}, $S_{\text{disordered}}$ and S_{ordered}, the temperature-dependent difference of Gibbs free energy between ordered and disordered structure can be obtained. Then, we will express our method below to calculate the entropy terms and internal energy term.

The calculation of entropy

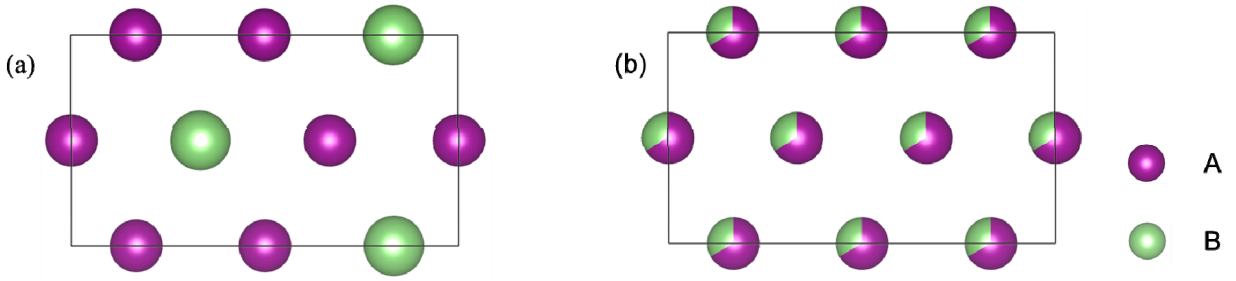

Fig. 2. (a) Unit cell of ordered structure (b) Unit cell of disordered structure. The purple circles indicate the centered atoms A and the green circles indicate the circled atoms B

Here, what we calculated is mainly the configuration entropy[8]. Since the two kinds of crystal structures are almost uniform, the effect of thermal entropy is very small, so the entropy is mostly caused by the configuration of structure. We take Boltzmann's entropic equation as the following expression:

$$S = k\, ln\Omega \quad (3)$$

Here, S is the entropy, k is Boltzmann constant,and Ω is the number of microstates. There are 9 atoms in transition metal layer in a unit cell of Li_2MnO_3. As the only difference between ordered and disordered structure happens in transition metal layer as Fig. 2, we can express our term of ΔS as the following formula[12] :

$$S_{disordered} - S_{ordered} = k\, ln\frac{(9n)!}{(6n)!\,(3n)!} \quad (4)$$

Here, n is the number of unit cell, which has 36 atoms. If we take a real particle which has a huge amount of unit cell, n should be large enough so that we can take an approximation of a formula below:

$\ln(N!) \approx N\ln N - N$.

By taking this approximation into the equation above, we can obtain

$$S_{disordered} - S_{ordered} \approx nk[9ln3 - 6ln2] = n \times 0.494meV/K \quad (5)$$

The calculation of internal energy

DFT is employed to calculate our total energy. In addition, PWmat code[13, 14] which is implemented in graphic process unit (GPU), Perdew-Burke-Ernzerhof[15] exchange-correlation functional and Hubbard U model[16] were also used in our calculation. The U values of 4.4 eV on the *d*-orbital of Mn and 3.4 eV on the *d*-orbital of Ni were adopted[17]. K point was set to make the product of atomic number and *k*-point number is larger than 1000. Both cell and atomic position can be fully relaxed with a residual force less than 0.01 eV/Å. The spin polarization was used in all our calculations.

By using the DFT calculation, we can easily calculate the total energy, i.e. the internal energy of ordered layered materials. To calculate the total energy of disordered structure, SQS (Special quasi-random structures) method[9] is used to create a structure, which has the atomic neighbor environment similar to that of random structure. We used a 4×2×1 super cell to build the quasi-random structure. The environment of the first and second nearest neighbors were considered in the structure manufacturing. Two types of elements are demonstrated in the TM layer, a centered element A (1/3) and a circled element B (2/3). 10000 steps of Monte-Carlo random search were performed to obtain a final structure[18]. The neighbor environment was shown in Fig. 3. The expected values (pink bars) indicate the probability of real random structures whereas the actual values (blue bars) indicate the neighbor environment of supercell quasi-random structures.

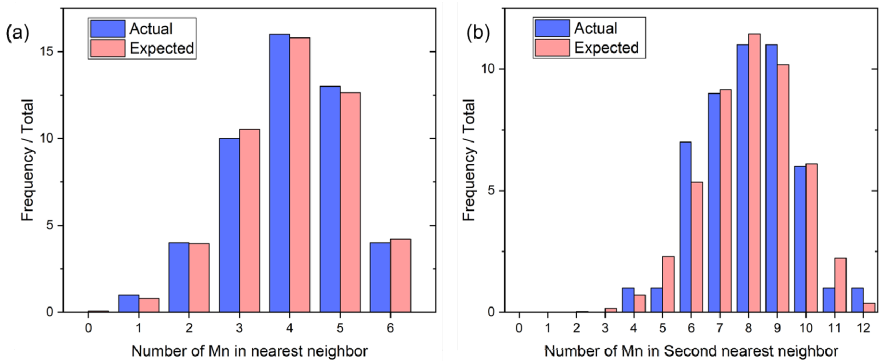

Fig. 3. (a) Statistics for the coordination environment of B element in the nearest neighbor with comparison with the statistical prediction value. (b) Statistics for the coordination environment of B element in the Second nearest neighbor with comparison with the statistical prediction value

3 RESULTS AND DISCUSSION

The structures searched in our SQS and Mont-Carlo process are shown in Fig. 4. In this figure, A atoms (purple) indicate centered atoms which have 1/3 portion in TM layer, and B atoms (green) indicate circles atoms which have 2/3 portion in TM layer. We calculated these structures of (a) A = Li, B = Mn, with chemical formula of Li_2MnO_3; (b) A = Ni, B = Mn, with chemical formula of $Li_3Ni_2MnO_6$.

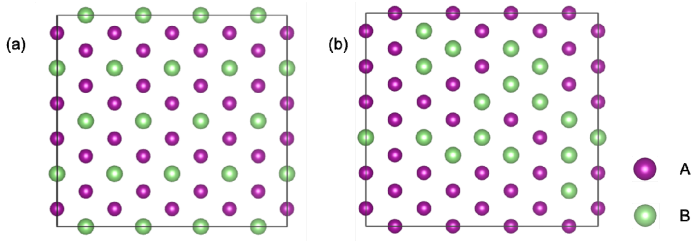

Fig. 4. (a) The ordered transition metal layer and (b) the disordered transition metal layer. Purple circle indicates the centered A type atoms, and green circle indicates the circled B type atoms

Table 1. Total Energy Calculation of Different Structure by Using DFT

Structure	E (eV)	$\triangle E$ (eV)	$\triangle E$/n (meV/atom)
Li_2MnO_3	–140737.8811		
Li_2MnO_3 quasi-random	–140712.0345	25.8446	134.62
$Li_3Ni_2MnO_6$	–227994.4701		
$Li_3Ni_2MnO_6$ quasi-random	–227993.7498	0.72	3.75

The total energy results are listed in Table 1. For Li_2MnO_3, the internal energy difference between ordered and disordered structures is 134.62 meV/atom. If we set T=1000 K, the term of T Δ S is 13.7 meV/atom, which is much smaller than that of internal differences. Thus, Li_2MnO_3 stays in an ordered transition metal layer. In comparison, for $Li_3Ni_2MnO_6$, the internal energy difference is 3.57 meV/atom, which is smaller than the entropy term (13.7 meV) at 1000 K. Moreover, it is also calculated that T = 273 K when T△S = △E (3.27 meV/atom) energy at 273 K, which is much lower than its sintering temperature (700 K). Thus, the structures of $Li_3Ni_2MnO_6$ exhibit disordered transition metal layer under room temperature. These calculated results are fully consistent with experimental ones[16].

In Li_2MnO_3 and $Li_3Ni_2MnO_6$, the number of atoms contributing to the structural entropy only accounts for one sixth of the total number of atoms, where there are only two kinds of atoms. It is expected that doping, anti-position, defect, and even more kinds of atoms participating in disordering arrangement will increase the entropy from ordered to disordered structures. In extreme cases, this increment of free energy at 1000 K could be almost an order of magnitude larger than 13.7 meV/atom and therefore the impact of entropy will be too high to be ignored.

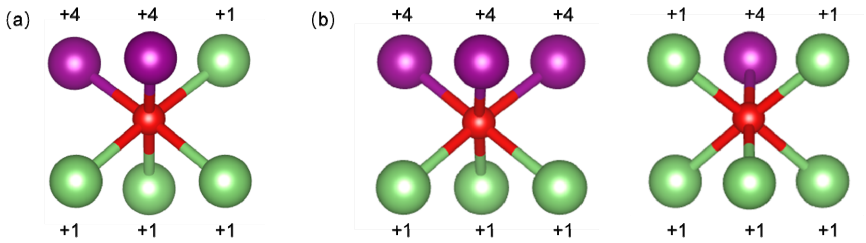

Fig. 5. (a) In ordered Li_2MnO_3 materials, all of oxygen belongs to this coordination environment. (b) In disordered Li_2MnO_3 materials, some oxygen will have such coordination environment.

Reasons for the ordered transition metal layer in Li_2MnO_3 can be fitted by Pauling's charge balance rules in 1927.

According to Pauling's rule[20], the coordination environment of anions must meet local electrical neutrality (show in Fig. 5a). The strength of the cationic electrostatic bond is represented by S, and its size is the ratio of the valence (w_+) to the coordination number (n_+) of the cation paired with it. For the oxygen atom in Fig. 5a:

$$\sum_i S_i = \sum_i \frac{(w_+)_i}{(n_+)_i} = 4 \times \frac{1}{6} + 2 \times \frac{4}{6} = 2 \qquad (6)$$

The result is the same as the anionic valence state (-2) of oxygen, which means this structure is stable.

As for the disorder in the transition metal layer, structures are changed. There must be oxygen atoms bonded with more Mn atoms, for example three Mn and three Li atoms, shown in Fig. 5(b). And there must be oxygen atoms bonded with less Mn atoms, saying one Mn and 5 Li atoms, as shown in Fig. 5(c). At this time, their ΣS are:

$$\sum_i S_i = \sum_i \frac{(w_+)_i}{(n_+)_i} = 3 \times \frac{1}{6} + 3 \times \frac{4}{6} = 2.5 \qquad (7)$$

$$\sum_i S_i = \sum_i \frac{(w_+)_i}{(n_+)_i} = 5 \times \frac{1}{6} + 1 \times \frac{4}{6} = 1.5 \qquad (8)$$

respectively, which both have a large deviation from the valence state of oxygen. Therefore, this structure is unstable

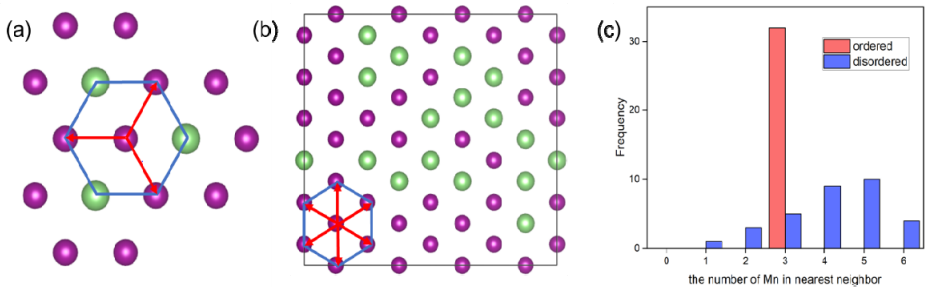

Fig. 6. (a) The nearest neighbor of Mn in ordered Li_2MnO_3. (b) The nearest neighbor of Mn in ordered Li2MnO3. (c) The statistics of the number of Mn in the nearest neighbor of Mn

Moreover, according to another Pauling's rule[20], the distance between highly charged cations tends to be large, in order to reduce the electrostatic repulsion between them. In Li_2MnO_3, Mn atoms with very large valences (+4) should be scattered as far as possible and cannot be clustered together. In the ordered Li_2MnO_3 structure, for each Mn atom, there are only 3 adjacent Mn among its 6 nearest neighbors (shown in Fig.6a). This is an optimal arrangement for reducing the connection between Mn and Mn. But in the disordered Li_2MnO_3 structure, some Mn atoms could have four, five or even six Mn as neighbors (shown in Fig. 6b and 6c). Therefore, in order to minimize stress from the total electrostatic energy, Li_2MnO_3 has a strong tendency to form an ordered ring structure; whereas in $Li_3Ni_2MnO_6$, the valence state of Mn is +4, half of Ni is +3, and the other half of Ni is +2, which is type of $LiTMO_2$ (average valence of TM is +3) with an average of Ni and Mn valence state of +3, in which the strength of cationic electrostatic bond is equal to the anionic valence state (-2) of oxygen to fit Pauling's charge balance rules. In addition, this TM cationic valence difference is not large, so the stress from electrostatic interactions caused by this difference is small, resulting in that the effect on the structure order and disorder can be tuned by other interactions, such as reluctance rubbing, entropy, and super-exchange.

In addition, in Li_2MnO_3, the manganese ring structure with Li (nonmagnetic ion) in centers of the hexagons relieves the degeneracy of the frustrated magnetic lattice, which enhances two adjacent Mn atoms to undergo 90-degree super-exchange interaction through O atoms, thereby making the ring structure stable to form an inorganic aromatic structure[5]. For $Li_3Ni_2MnO_6$, there is also a mechanism of the existence of strongly frustrated magnetic interactions between spins with TM magnetic ions in the centers of hexagons to reduce super-exchange interaction[5]. Thus, the super-exchange interaction between Ni and Mn in $Li_3Ni_2MnO_6$ has few effects.

4 CONCLUSION

By doing a calculation in entropy in 1000 K and building a quasi-random structure of layered materials, our calculations provide theoretical explanations to experimental results where Li_2MnO_3 has an ordered transition metal layer and NMC has a disordered transition metal layer. In Li_2MnO_3, atomic interaction including electrostatic force, super-exchange interaction, inorganic aromatic interaction and the elimination of magnetic frustration is much stronger than the effect of temperature. However, in NMC materials, although the ordered structure has a lower energy than the disordered

one at 0 K, the temperature takes effects above 200 K, which leads to a disordered structure at room temperature. This result suggests that the impact of temperature is not neglectable in calculations, because the nature of the thermodynamics determines that a more disordered structure at high temperature. This affection is around 13.5 meV/atom at 1000 K for any structures with two different types of elements with the ratio of 1:2. In order to experimentally build an ordered transition metal layer, stronger tendency to ordered structure or lower synthesis temperature are needed. It is also revealed that greater differences in atomic covalence state could promote to minimize stress from electrostatic interaction for ordered structures.

Overall, this work proposed a possible way to estimate the magnitude of the entropy at high temperature. Intrinsic origins of ordered structures in Li_2MnO_3 and disordered structures in NMC materials are explained. Possible pathways and strategies (e.g. promoting 90-degree super-exchange interaction and eliminating magnetic frustration) to experimentally obtain ordered structures. More structures can be simulated by this method and ordered transition metal layer at high temperature can be predicted in the future.

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