Charge Compensation Mechanisms and Oxygen Vacancy Formations in LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$: First-Principles Calculations

Xiao-Hong Shi, Ya-Ping Wang, Xinrui Cao, Shunqing Wu, Zhufeng Hou, and Zizhong Zhu*

ABSTRACT: Charge compensation mechanisms in the delithiation processes of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (NCM111) are compared in detail by the first-principles calculations with GGA and GGA+U methods under different $U$ values reported in the literature. The calculations suggested that different sets of $U$ values lead to different charge compensation mechanisms in the delithiation process. Co$^{3+}$/Co$^{4+}$ couples were shown to dominate the redox reaction for $1 \geq x \geq 2/3$ by using the GGA+U$_1$ method ($U_1 = 6.0$ 3.4 3.9 for Ni, Co, and Mn, respectively). However, by using the GGA+U$_2$ ($U_2 = 6.0$ 5.5 4.2) method, the results indicated that the redox reaction of Ni$^{2+}$/Ni$^{3+}$ took place in the range of $1 \geq x \geq 2/3$. Therefore, according to our study, experimental charge compensation processes during delithiation are of great importance to evaluate the theoretical calculations. The results also indicated that all the GGA+U$_i$ ($i = 1, 2, 3$) schemes predicted better voltage platforms than the GGA method. The oxygen anionic redox reactions during delithiation are also compared with GGA+U calculations under different $U$ values. The electronic density of states and magnetic moments of transition metals have been employed to illustrate the redox reactions during the lithium extractions in NCM111. We have also investigated the formation energies of an oxygen vacancy in NCM111 under different values of $U$, which is important in understanding the possible occurrence of oxygen release. The formation energy of an O vacancy is essentially dependent on the experimental conditions. As expected, the decreased temperature and increased oxygen partial pressure can suppress the formation of the oxygen vacancy. The calculations can help improve the stability of the lattice oxygen.

1. INTRODUCTION

Rechargeable lithium-ion batteries have entered the electrical vehicle market and plug-in hybrid vehicles because of their high energy density, high working voltage, long cycle life, outstanding safety characteristics, and environmental friendliness. Although lithium transition metal (TM) oxides such as layered structured material LiCoO$_2$, olivine structured materials LiFePO$_4$, and layered structures LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (NCM111) are good cathode materials for lithium-ion batteries, cobalt is relatively costly while LiFePO$_4$ has a low energy storage capability. Hence, great efforts have been made to reduce the Co content in LiCoO$_2$ material; therefore, the layered LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (NCM111) is one of the most studied systems. Although NCM111 has been studied extensively, the available results are not considered to be sufficient to regard the problem as completely solved. For example, the electrochemical properties dependent on $U$ are not well understood, as the GGA+U method is very necessary to describe the strong electron correlations of d-orbitals of the transition metal elements. In this work, the electrochemical properties and the formation energy of an oxygen vacancy in NCM111 cathode material have been investigated by first-principles calculations. In particular, charge compensation mechanisms during delithiation in NCM111 are compared in detail with GGA and GGA+U calculations under different $U$ values reported in the literature. The calculations suggest that different sets of $U$ values lead to different charge compensation mechanisms in the delithiation process. Therefore, experimental charge compensation processes during delithiation are then of great importance to evaluate the theoretical calculations, although theoretical calculations are declared as ab initio. The oxygen anionic redox reactions during delithiation are also compared by using GGA+U calculations under different $U$ values. Furthermore, the results also indicated that all the GGA+U$_i$ ($i = 1, 2, 3$) schemes predicted better voltage platforms than the GGA method.

The formation of oxygen vacancies could affect various properties of the host oxide cathode materials, such as the cycling stability in the batteries. The understanding of the behavior of oxygen vacancies in oxides becomes important and
can help lay the foundation for the anion defect engineering to boost the electrochemical performance of cathode materials. In this paper, we have also investigated the formation energies of an oxygen vacancy in the bulk phase of NCM111, which could help understand the possible occurrence of the oxygen vacancy. These calculations can also provide guidelines for reducing the oxygen release and improving the stability of the lattice oxygen in the cathode materials of the lithium-ion batteries. The formation energy of an O vacancy is essentially dependent on the experimental conditions. As expected, the increased temperature and decreased oxygen partial pressure decrease the formation energy of the O vacancy; that is, the lower temperature and higher oxygen partial pressure can suppress the formation of the oxygen vacancy.

### 2. CALCULATION METHODS

All the calculations have been performed by using the Vienna *ab initio* simulation package (VASP), which is based on the density functional theory (DFT), the plane wave basis, and the projector augmented wave (PAW) representation. The Perdew–Burke–Ernzerhof (PBE) functional for the generalized gradient approximation (GGA) is used to process the electron exchange correlation energy. The cutoff for the plane wave kinetic energy is set to 600 eV. The Monkhorst–Pack method is used to determine k-points grid for the Brillouin zone integration, which is $3 \times 3 \times 1$ in the present supercell calculations. The atomic positions and lattice parameters were fully optimized, where the convergence criteria for the Hellmann–Feynman force for each atom was set to be 0.01 eV/Å. The electrochemical properties and the oxygen vacancy formation of NCM111 were calculated by a $2 \times 2 \times 2$ supercell. For calculating the oxygen vacancy in the NCM111, one oxygen atom is extracted from the supercell. The minimum distance between two oxygen vacancies is 9.97 Å, and the concentration for the oxygen vacancy in the NCM111, one oxygen atom is extracted from the supercell. The minimum distance between two oxygen vacancies is 9.97 Å, and the concentration for the oxygen vacancy in the material is 0.69%. All calculations were performed under a spin-polarization scheme, including ferromagnetic and antiferromagnetic configurations.

In order to describe the strong electron correlation interactions in the $d$-orbitals of the transition metal elements, the GGA$+U$ method is adopted. Because different sets of $U$ values had been reported for Ni, Co, and Mn elements in the literature, we examined in detail the effects of three different sets of effective $U$ values (i.e., $U_{	ext{eff}} = U - J$; hereafter denoted $U_1$, $U_2$, and $U_3$) on the electrochemical properties of Li$_{x}$Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ ($x = 1, 2/3, 1/3, 0$) (hereafter denoted Li$_{x}$NCM111). The $U$ values employed in our calculations were $U_1 = 6.0$ 3.4 3.9 $^{34}$ (for Ni, Co, and Mn, respectively), $U_2 = 6.0$ 5.5 4.2 $^{34}$, and $U_3 = 5.0$ 5.0 5.0. Wang et al. also reported first-principles estimations of the $U$ parameters for several transition metals. They reported $U$ values to be 6.4 eV for Ni; 3.3 eV for Co; and 3.5, 3.8, or 4.0 eV for Mn. Because this set of $U$ values was very close to $U_2 = 6.0$ 3.4 3.9, only the $U_2$ was then calculated. The van der Waals interactions are not included in the calculations because the bonding in this material of NCM111 is mainly ionic mixed with covalent although it is a layered material.

### 3. RESULTS AND DISCUSSION

#### 3.1. Structural Evolution and Voltage Profiles during Li-Ion Extractions

The structure of the perfect NCM111 calculated in this paper is based on the one with a space group of $P_{3_1}2_1$ shown in Figure 1a, which comes from Ohzuku. This structure has also been employed in other theoretical calculations. For the crystal structures of delithiated phases, we adopt here an approximate scheme to obtain the structures of Li$_{x}$Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ ($x = 1, 2/3, 1/3, 0$) in the process of Li extraction. For $x = 1$, the material is simply NCM111. For $x = 2/3$ where one-third of the lithium ions are deintercalated in NCM111 (i.e., for Li$_{2/3}$NCM111), the corresponding crystal structure of the Li-layer is shown in Figure 1b, which is the same for all the Li layers. The dotted circles represent the extracted lithium ions. When two-thirds of the lithium ions are extracted in NCM111 (i.e., $x = 1/3$ and for Li$_{1/3}$NCM111), more lithium ions at the three vertices of the hexagons in Figure 1b are removed, as shown in Figure 1c. In all these cases, Li ions are extracted uniformly. For $x = 0$, all the lithium ions are deintercalated from NCM111. Then, all the lithium layers disappear.

We first calculate the cohesive energies of NCM111 by using GGA ($U = 0$), GGA+$U_1$, GGA+$U_2$, and GGA+$U_3$ methods (with $U_1 = 6.0$ 3.4 3.9 for Ni, Co, Mn, respectively, $U_2 = 6.0$ 5.5 4.2, $U_3 = 5.0$ 5.0 5.0), as well as under the spin-polarized scheme for both the ferromagnetic (FM) and antiferromagnetic (AFM) configurations. In this paper, we calculated the cohesive energies of NCM111 in three kinds of antiferromagnetic configurations. Case 1: all the spins of adjacent transition metal ions are in opposite directions (where the magnetic moments of Co are 0 $\mu_B$). The cohesive energy (taken always to be positive) of such an AFM magnetic ordering is smaller (around 0.02 eV/supercell for all the $U$ employed) than that of FM ordering. This means that FM should be favored by the system under such a magnetic ordering. Case 2: the spins in the Ni sublattice are in opposite directions to the Mn sublattice (again, magnetic moments of Co are 0 $\mu_B$), while the spins in all the transition metal layers are parallel. Such a magnetic ordering had been described as AFM by Ceder et al. (it should be noted that the antiferromagnetism mentioned here is actually ferrimagnetism, because the atomic magnetic moments of Ni, Co, Mn ions are all different). The calculations show that the cohesive energy of this AFM is larger than that of FM by about 0.30 eV/supercell.
for all the \( U \) employed, implying that the system should favor this AFM, as compared with FM. Case 3: based on the AFM ordering in case 2, however, spins of transition metal ions are in different directions in the adjacent layers of the transition metals. The calculated cohesive energy is almost indistinguishable with that of AFM ordering in case 2. This is because there is one layer of lithium ions existing in between the transition metal layers, leading to a very weak superexchange interaction between the transition metal layers. The results show that the cohesive energy of this AFM is larger than that of FM (between 0.36 and 0.41 eV/supercell; see Table 1 below).

**Table 1. Calculated Lattice Parameters and Cohesive Energy Differences \( \Delta E_f \) between FM and AFM Configurations (72 f.u./supercell), by Using the GGA and GGA+U Methods**

| U   | FM-GGA+U  | AFM-GGA+U  | \( \Delta E_f \) (eV) |
|-----|-----------|------------|------------------------|
| \( a = b \) | \( a = c \) | \( a = b \) | \( a = c \) |
| \( U = 0 \)  | 2.88 14.30 | 2.88 14.30 | −0.38          |
| \( U_1 = 6.0 3.4 3.9 \) | 2.88 14.30 | 2.88 14.30 | −0.37          |
| \( U_2 = 6.0 5.5 4.2 \) | 2.88 14.37 | 2.88 14.35 | −0.36          |
| \( U_3 = 5.0 5.0 5.0 \) | 2.89 14.37 | 2.89 14.36 | −0.41          |

Lattice parameters of NCM111 (exptl37,39): \( a = b = 2.867 \text{ Å} \), \( c = 14.246 \text{ Å} \)

Table 1 presents the calculated lattice parameters and the cohesive energy differences between FM and AFM configurations for NCM111 (72 f.u. per supercell). As shown in Table 1, the computational lattice parameters of NCM111 agree rather well with experimental values. Because it is meaningless to compare directly the cohesive energies with different values of \( U \), because of different Hamiltonian employed, only the cohesive energy difference \( \Delta E_f = E(\text{FM-GGA}+U) - E(\text{AFM-GGA}+U) \) are presented.

We notice that the working temperature of the battery is usually much higher than the Curie temperature \( T_C \), therefore, the electrochemical properties of NCM111 are insensitive to the magnetic ordering of the material. Furthermore, the cohesive energies of different magnetic orderings are rather close. In the discussions below, all the results are then based on the antiferromagnetic ordering of case 3 (unless otherwise indicated), which has the largest cohesive energy.

We now calculate the formation energies of \( \text{Li}_x \text{NCM111} \) in each delithiated concentration \( (x = 1, 2/3, 1/3, 0) \) by the GGA + \( U \) method under different \( U \) values. The formation energy formula employed is as follows:

\[
E_f(x) = E(\text{Li}_x \text{NCM111}) - [xE(\text{NCM111}) + (1 - x)E(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2)]
\] (1)

that is, the formation energy is calculated relative to the fully lithiated NCM111 and fully delithiated \( \text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2 \) phases. Figure 2a demonstrates the convex hull plots for the calculated formation energies of \( \text{Li}_{x} \text{NCM111} \) by using the GGA \( (U = 0) \) and GGA+\( U \) methods, as a function of Li concentration \( x \). Results for different effective \( U \) values, i.e., \( (U_1 = 6.0 3.4 3.9, U_2 = 6.0 5.5 4.2, U_3 = 5.0 5.0 5.0) \), are presented. For GGA \( (U = 0) \) and GGA+\( U_1 \) calculations, two stable intermediate phases (i.e., \( \text{Li}_{2/3} \text{NCM111} \) and \( \text{Li}_{1/3} \text{NCM111} \)) can be observed in the charging process. However, for GGA+\( U_2 \) and GGA+\( U_3 \) calculations, only one intermediate phase (i.e., \( \text{Li}_{1/3} \text{NCM111} \)) can be observed in the charging process. Also in Figure 2a, the formation energies for the GGA+\( U_1 \) and GGA+\( U_3 \) schemes are very close at Li concentration \( x = 2/3 \). In addition, the formation energies for the GGA+\( U_1 \) and GGA+\( U_2 \) methods are very close at Li concentration \( x = 1/3 \). The formation energies by the GGA method are always the largest (the absolute value) during the delithiation.

We then calculate the averaged voltages of \( \text{Li}_x \text{NCM111} \) in the charging process. The averaged voltage formula employed is as follows:

\[
\text{V}_{\text{avg}}(x) = \frac{xV(\text{NCM111}) + (1 - x)V(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2))}{x + (1 - x)}
\] (2)

Figure 2. (a) The convex hull plots for the calculated formation energies and (b) the calculated averaged voltage curves of \( \text{Li}_x \text{NCM111} \), as a function of Li concentration \( x \), by using the GGA \( (U = 0) \) and GGA+\( U \) methods with different effective \( U \) values (i.e., \( U_1 = 6.0 3.4 3.9, U_2 = 6.0 5.5 4.2, \) and \( U_3 = 5.0 5.0 5.0) \).
where $E(Li_{x_1}NCM111)$ and $E(Li_{x_2}NCM111)$ are the cohesive energies of the material at Li concentrations of $x_1$ and $x_2$, respectively. $E[Li]$ is the cohesive energy of a single Li atom in bulk lithium. As shown in Figure 2b, the first voltage plateau by using GGA ($U = 0$) method is around 2.74 V, while the second voltage plateau is 2.95 V. Such voltage plateaus are in basic agreement with those (e.g., 2.99 and 3.30 V) shown by Ozuku et al. The third average voltage plateau is about 3.99 V. The calculated first voltage platform by the GGA scheme is generally lower than the experimental value. Generally speaking, the calculated voltage platforms by the GGA+U ($i = 1, 2, 3$) methods are all significantly higher than those of the GGA method. For the GGA+U$_1$ method, the three voltage plateaus are visibly different. However, for GGA+U$_2$ and GGA+U$_3$ calculations, there are only two voltage platforms that are very different. The maximum averaged voltage is achieved by the GGA+U$_2$ and GGA+U$_3$ scheme, which is about 4.24 V. Under the GGA+U$_i$ ($i = 1, 2, 3$) methods, the calculated first voltage platform is between 3.65 and 3.83 V, which agrees well with the experimental value of 3.8 V. In other words, the GGA ($U = 0$) scheme underestimates the first voltage plateau significantly, while GGA+U methods predict reasonably good values of the first voltage platform, as compared with the experimental value.

3.2. Electronic Structures and Redox Reactions during Li-Ion Extractions. The valence states of the isolated TM atoms in the NCM111, together with their electronic configurations and the magnetic moments, are shown in Table 2. The schematic plots of the 3d-orbital electron arrangements in the octahedral TM-O$_6$ ligand field and the corresponding Atomic Valence States in NCM111.

| Electron configuration (isolated atoms) | Number of atoms (in supercell) | Atomic magnetic moment/μ$_B$ | 3d-orbital electron arrangement (in NCM111) | Valence state |
|----------------------------------------|-----------------------------|-----------------------------|---------------------------------|-------------|
| Ni 3d$^8$4s$^2$                        | 24                          | 2                           | $s_{0}^{+}+s_{0}^{-}$           | Ni$^{4+}$   |
| Co 3d$^7$4s$^2$                        | 24                          | 0                           | $s_{0}^{+}+s_{0}^{-}$           | Co$^{3+}$   |
| Mn 3d$^5$4s$^2$                        | 24                          | 3                           | $s_{0}^{+}+s_{0}^{-}$           | Mn$^{4+}$   |

The magnetic moments of Li$_x$NCM111 ($x = 1, 2/3, 1/3, 0$) during the delithiation process of NCM111 are also presented in the table. Considering Table 2, it would be helpful to understand the electrochemical properties (e.g., redox reactions) during the delithiation process of NCM111.

First, the magnetic moments of the Li$_x$NCM111 ($x = 1, 2/3, 1/3, 0$) during the delithiation are calculated by the GGA ($U = 0$) method, and the results are presented in Table 3. It is helpful to perform GGA calculations, in order to compare the GGA+U$_i$ calculations with different values of $U$. Here, the changes in the magnetic moments are analyzed to help characterize the charge compensation mechanisms during the delithiation (for $U = 0$). For $1 \geq x \geq 2/3$, where in total 24 Li ions are extracted from the supercell, the results show that there are correspondingly 24 Ni$^{2+}$ ions oxidized, changing their magnetic moments from 2 $μ_B$ to 1 $μ_B$ and their valence from Ni$^{2+}$ to Ni$^{3+}$. Actually, 12 of the 24 Ni$^{2+}$ ions lose one spin-up electron in the eg band (see Table 2), and the other 12 Ni$^{2+}$ ions lose one spin-down electrons in the eg band, leading to magnetic moment change from 2 $μ_B$ to 1 $μ_B$. For $2/3 \geq x \geq 1/3$, when 24 Li ions are further extracted, again, there are 24 Ni$^{3+}$ ions oxidized, changing their magnetic moments from 1 $μ_B$ to 0 $μ_B$ and their valence states from Ni$^{3+}$ to Ni$^{4+}$. When the NCM111 are fully delithiated (i.e., $1/3 \geq x \geq 0$), that is, the remaining 24 Li ions are deintercalated, the results suggest that 24 Co$^{3+}$ ions are now oxidized, transforming their magnetic moments from 0 $μ_B$ to 1 $μ_B$ and their valences from Co$^{3+}$ to Co$^{4+}$ (see Table 2, where one electron is lost in the t$_{2g}$ band for each Co$^{3+}$). In this region, i.e., $1/3 \geq x \geq 0$, Ni ions do not participate in the redox reaction because all the Ni ions are now Ni$^{4+}$. During the whole delithiation process, all 24 Mn ions are not involved in the redox reactions, keeping Mn$^{4+}$ and magnetic moment of 3 $μ_B$ unchanged. Summarizing, for $1 \geq x \geq 2/3$ and $2/3 \geq x \geq 1/3$, it is the Ni ions who are in charge of the compensation of electrons, while for $1/3 \geq x \geq 0$, it is the Co ions who participate in the redox reaction. These results on the redox reactions are consistent with those of Cedar et al. at every delithiated concentration and the experimental results as well.

The magnetic moments of the Li$_2$NCM111 ($x = 1, 2/3, 1/3, 0$) during the delithiation process are also calculated by using the GGA+U$_i$ methods (with $U_i = 6.0, 3.4, 1.9, 1.1$, and $U_i = 5.0, 5.0, 5.0$), and results are shown in Table 4. The changes of magnetic moments of TM ions during the delithiation by using the GGA+U$_1$ calculations are visibly different from those using the GGA+U$_2$ and GGA+U$_3$ calculations (it is worth noting that the changes of magnetic moments of TM ions for GGA+U$_2$ and GGA+U$_3$ schemes are very close). In the following discussion, only the results from GGA+U$_1$ and GGA+U$_2$ calculations are to be compared.
Table 4. Magnetic Moments of Li$_x$NCM111 ($x = 1, 2/3, 1/3, 0$), Calculated by Using the GGA$+$U Method with Three Sets of different $U_x$ (i.e., $U_1 = 6.0$ $3.4$ $3.9$, $U_2 = 6.0$ $5.5$ $4.2$, $U_3 = 5.0$ $5.0$ $5.0$).

| Li$_x$NCM111 | magnetic moments ($\mu_B$) | GGA$+$U$_1$ ($U_1 = 6.0$ $3.4$ $3.9$) | GGA$+$U$_2$ ($U_2 = 6.0$ $5.5$ $4.2$) | GGA$+$U$_3$ ($U_3 = 5.0$ $5.0$ $5.0$) |
|-------------|---------------------|------------------|------------------|------------------|
| $x$         | Ni      | Co    | Mn     | Ni      | Co    | Mn     | Ni      | Co    | Mn     |
| 1           | 1.74(12) | 0 (24) | 3.16(12) | 1.74(12) | 0 (24) | 3.16(12) | 1.74(12) | 0 (24) | 3.16(12) |
| 2/3         | 1.73(12) | 1.09(12) | 3.16(12) | 1.73(12) | 1.09(12) | 3.16(12) | 1.73(12) | 1.09(12) | 3.16(12) |
| 1/3         | 0.99(12) | 1.12(12) | 3.17(12) | 0.99(12) | 1.12(12) | 3.17(12) | 0.99(12) | 1.12(12) | 3.17(12) |
| 0           | 0.13(12) | 1.02(12) | 3.20(12) | 0.13(12) | 1.02(12) | 3.20(12) | 0.13(12) | 1.02(12) | 3.20(12) |

In these calculations, where 24 Li$^+$ ions are extracted from the supercell, we can clearly see from Figure 4a,b that only the blue peaks of Co-3d electrons cross the Fermi level, indicating the valence electron loss of Ni-3$d$ orbitals; see Figure 3a,b). That is, the Ni$^{2+}$ ions are oxidized into Ni$^{3+}$ ones, and the redox reaction is Ni$^{2+}$/Ni$^{3+}$. For 2/3 $\geq x \geq 1/3$, where another 24 Li$^+$ ions are now participating in the redox process, with Co$^{3+}$ ions oxidized to Co$^{4+}$ ones. During the whole delithiation process, the purple peaks of Mn-3$d$ electrons do not cross the Fermi level, keeping Mn$^{4+}$ valence unchanged. That is, Mn$^{4+}$ ions are not involved in the redox reactions. All the charge compensation mechanisms of TM ions discussed based on the PDOS here are consistent with the analysis of the changes of the magnetic moments of TM ions during delithiation.

For 1 $\geq x \geq 2/3$, where 24 Li$^+$ ions are extracted from the supercell, the results of GGA$+$U$_1$ in Table 4 show that there are correspondingly 24 Co$^{3+}$ ions now oxidized, transforming their magnetic moments from 0 $\mu_B$ to 1 $\mu_B$ and Co$^{3+}$ ions to Co$^{4+}$ ones (where one electron is lost in the $t_2g$ band for each Co$^{3+}$, see Table 2). In this case, Ni and Mn ions are not involved in the redox reactions. For 1 $\geq x \geq 2/3$ and for GGA$+$U$_3$ calculations, Table 4 suggests that 24 Ni$^{2+}$ ions are now oxidized, changing from Ni$^{2+}$ to Ni$^{3+}$ and their magnetic moments from 2 $\mu_B$ to 1 $\mu_B$. Actually, 12 of the 24 Ni$^{2+}$ ions lose one spin-up electron in the $e_g$ band (see Table 2); the other 12 Ni$^{2+}$ ions lose one spin-down electron in the $e_g$ band. Clearly, the charge compensation mechanisms during delithiation for 1 $\geq x \geq 2/3$ are completely different for GGA$+$U$_1$ and GGA$+$U$_3$ results. For 2/3 $\geq x \geq 1/3$, when 24 Li$^+$ ions are further extracted from the supercell, the results for GGA$+$U$_1$ shown in Table 4 suggest that there are 24 Ni$^{2+}$ ions oxidized, changing their magnetic moments from 2 $\mu_B$ to 1 $\mu_B$ and Ni$^{2+}$ to Ni$^{3+}$. However, for 2/3 $\geq x \geq 1/3$ and for GGA$+$U$_3$ calculations, Table 4 indicates that 24 Ni$^{2+}$ ions are oxidized, changing from Ni$^{2+}$ to Ni$^{3+}$ and their magnetic moments from 1 $\mu_B$ to 0 $\mu_B$. In this case, again, the charge compensation mechanisms during delithiation for 2/3 $\geq x \geq 1/3$ are different for GGA$+$U$_1$ (where Ni$^{2+}$ oxidized to Ni$^{3+}$) and GGA$+$U$_3$ (where Ni$^{2+}$ oxidized to Ni$^{3+}$) calculations.

When NCM111 are fully delithiated (i.e., 1 $\geq x \geq 0$), that is, the remaining 24 Li$^+$ ions in the supercell are fully deintercalated, for the GGA$+$U$_1$ calculations, there are 24 Ni$^{3+}$ ions oxidized, changing from Ni$^{2+}$ to Ni$^{3+}$ and their magnetic moments from 1 $\mu_B$ to 0 $\mu_B$. However, for GGA$+$U$_3$ calculations, the results in Table 4 suggest that 24 Co$^{3+}$ ions are oxidized, transforming from Co$^{3+}$ to Co$^{4+}$ and their magnetic moments from 0 $\mu_B$ to 1 $\mu_B$ (see Table 2, where one electron is lost in the $t_2g$ band for each Co$^{3+}$). Again, the charge compensation mechanisms are different for GGA$+$U$_1$ and GGA$+$U$_3$ calculations. During the whole delithiation process, all 24 Mn$^+$-ions in the supercell are now participating in the redox reactions. The charge compensation mechanism from GGA$+$U$_1$ and GGA$+$U$_3$ calculations is in agreement with the experimental results; however, the GGA$+$U$_3$ calculations are not.

As we discussed previously, different sets of $U$ values (reminding that they all come from careful studies in the literatures) can lead to different charge compensation mechanisms in the delithiation process. In the following discussions, the spin-polarized partial density of states (PDOS) of TM ions are analyzed to further understand the charge compensation mechanisms during the delithiation, under different values of $U$ employed.

We first discuss the results of PDOS calculated by using the GGA method (with $U = 0$). When 24 Li$^+$ ions are extracted from the supercell (i.e., $1 \geq x \geq 2/3$), it is clear that only the green peaks of Ni-3$d$ electrons on the PDOS plot cross the Fermi level, indicating the valence electron loss of Ni-3$d$ orbitals (see Figure 3a,b). That is, the Ni$^{2+}$ ions are oxidized into Ni$^{3+}$ ones, and the redox reaction is Ni$^{2+}$/Ni$^{3+}$. For 2/3 $\geq x \geq 1/3$, where another 24 Li$^+$ ions are now participating in the redox process, with Co$^{3+}$ ions oxidized to Co$^{4+}$ ones. During the whole delithiation process, the purple peaks of Mn-3$d$ electrons do not cross the Fermi level, keeping Mn$^{4+}$ valence unchanged. That is, Mn$^{4+}$ ions are not involved in the redox reactions. All the charge compensation mechanisms of TM ions discussed based on the PDOS here are consistent with the analysis of the changes of the magnetic moments of TM ions during delithiation.

We now compare the charge compensation mechanisms of TM ions from the calculated PDOS’s by using GGA$+$U$_1$ and GGA$+$U$_3$ methods. Figures 4 and 5 present the calculated PDOS’s of the Ni-3$d$, Co-3$d$, Mn-3$d$, and O-2$p$ from both the GGA$+$U$_1$ ($U_1 = 6.0$ $3.4$ $3.9$) and GGA$+$U$_3$ ($U_3 = 6.0$ $5.5$ $4.2$) calculations, respectively, for Li$_x$NCM111 ($x = 1, 2/3, 1/3, 0$) during the delithiation process. For 1 $\geq x \geq 2/3$ and for GGA$+$U$_1$ calculations, 24 Li$^+$ ions are extracted from the supercell; we can clearly see from Figure 4a,b that only the blue peaks of Co-3$d$ electrons cross the Fermi level, which indicates that redox reaction of Co$^{3+}$/Co$^{4+}$ takes place. For the same range of 1 $\geq x \geq 2/3$ but for GGA$+$U$_3$ calculations, however, Figure 5a,b shows that only the green peaks of Ni-3$d$ electrons cross the Fermi level, suggesting that Ni ions participate in the
redox reaction and Ni$^{3+}$ ions are oxidized to Ni$^{4+}$. For $2/3 \geq x \geq 1/3$ and for GGA+$U_1$ calculations, where 24 Li$^+$ ions are further extracted from the supercell, only the green peaks of Ni-3$d$ electrons are found to cross the Fermi level (see Figure 4b,c), indicating that redox reaction of Ni$^{2+}$/Ni$^{3+}$ takes place in this range of $2/3 \geq x \geq 1/3$. For GGA+$U_2$ calculations and for the same range of $2/3 \geq x \geq 1/3$, from Figure 5b,c, the green peaks of Ni-3$d$ electrons cross the Fermi level, suggesting that Ni ions take part in the redox reaction and Ni$^{3+}$ ions are oxidized to Ni$^{4+}$. Finally, for $1/3 \geq x \geq 0$, when the remaining 24 Li$^+$ ions are fully deintercalated, it is shown that green peaks of Ni-3$d$ electrons cross the Fermi level for the GGA+$U_1$ calculations (see Figure 4c,d), here, Ni$^{3+}$ ions are oxidized to Ni$^{4+}$ ones from the GGA+$U_1$ method, while it is the Co$^{3+}$ ions that are oxidized to Co$^{4+}$ ones from the GGA+$U_2$ method. The Mn$^{3+}$ ions are not involved in the redox reaction during the whole delithiation process because no peaks of Mn-3$d$ electrons cross the Fermi level. Again, analysis based on PDOS is consistent with the analysis based on the changes of the magnetic moments.

In summary, the charge compensation mechanisms are completely different for GGA+$U_1$ and GGA+$U_2$ calculations during the whole delithiation process. The Co$^{3+}$/Co$^{4+}$ couples were shown to dominate the redox reaction for $1 \geq x \geq 2/3$ from the GGA+$U_1$ ($U_1 = 6.0~3.4~3.9$) method; however, it is the Ni$^{2+}$/Ni$^{3+}$ couples who dominate the redox reaction for the same range of $1 \geq x \geq 2/3$ from the GGA+$U_2$ ($U_2 = 6.0~5.5~4.2$) method. Furthermore, Ni$^{2+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{4+}$ couples dominated the redox reactions for $2/3 \geq x \geq 1/3$ and $1/3 \geq x \geq 0$, respectively, for the GGA+$U_1$ calculations; however, it is the Ni$^{3+}$/Ni$^{4+}$ and Co$^{3+}$/Co$^{4+}$ couples who dominated the redox reactions in the same regions of concentrations for the GGA+$U_2$ calculations. Considering that all the $U$ values of TM metals come from careful studies in the literature (the theoretical calculations are declared as ab initio), it seems that the experimental charge compensation processes during delithiation are still of great importance to evaluate the theoretical calculations.

Although cationic redox reactions are shown to dominate the electrochemical processes in NCM111 electrode material, it has also been shown that both cationic and anionic redox reactions exist in the NCM111. Reversible intrinsic lattice oxygen redox reactions at high potentials were clearly revealed. Therefore, the understanding of O activities are important for utilizing the full potential of these cathode materials.

The calculated PDOS’s of O-2$p$ states by the GGA, GGA+$U_1$, and GGA+$U_2$ methods in Li$_x$NCM111 for $x = 0.2$ and $x = 0.125$ are compared in Figure 6. It can be seen that PDOS plots for $x = 0.2$ and $x = 0.125$ are rather close. It is also clear
that the PDOS plots of O-2p electrons for both the GGA+U1 and GGA+U2 schemes are quite alike. However, the calculated PDOS’s of O-2p electrons by the GGA (U = 0) method are quite different from those by the GGA+U1 and GGA+U2 methods. For lower levels of delithiation (i.e., relatively low potentials) in Li_xNCM111, our calculations indicate that O anions do not participate in the redox process, which is in agreement with the previous theoretical and experimental studies. For deep delithiation levels (i.e., high potentials), Figure 6 demonstrates that O anions are visibly involved in the redox reactions (for x = 0.2 and x = 0.125), which is also consistent with the previous experimental and theoretical results.

The involvement of oxygen in the redox process in NCM111 can be understood through the analysis of the interactions of oxygen with their neighboring ions. Oxygen atoms in NCM111 are coordinated with both the Li+ and TM ions. Therefore, the interactions of O with the coordinated atoms come from two aspects: one is the attractive electrostatic interactions between Li and O ions, and the other is the hybridization of the TM-O orbitals which is mainly covalent in nature. The delithiation process weakens the attractive electrostatic interaction between Li-O ions and strengthens the TM-O hybridizations. When the number of the removed lithium ions is small (lower potential), although some of the O-2p energy levels are pushed toward the Fermi level, the O-2p orbitals do not cross to the Fermi surface. This indicates that O ions are not involved in the redox reaction at low potentials. However, at high potentials (see Figure 6), the attractive electrostatic interaction between the Li-O ions is much weakened and the TM-O hybridizations are further strengthened. Such combined ionic and covalent interactions of O with the neighboring ions result in some of the energy levels of oxygen being pushed to cross the Fermi surface, suggesting that oxygen ions are capable of participating in the anionic redox processes in NCM111 at high potentials.

3.3. Formation Energy of an Oxygen Vacancy in NCM111 Material. The release of oxygen in the NCM111 cathode is directly related to the formation energy of oxygen vacancy in this material. Here, we study the variation of the oxygen vacancy formation energy in NCM111 versus the temperature and oxygen partial pressure in order to understand the stability of the lattice oxygen. The oxygen vacancy is calculated by extracting one oxygen atom from the supercell of NCM111. The formation energy of oxygen vacancy in charge state $q$, $E_f(O^{q})$, can be defined according to the following equation:

$$E_f(O^{q}) = E(O^{q}) - E(0) + \Delta n \mu_O + q(E_{VBM} + \epsilon_f) \quad (3)$$

where $E(O^{q})$ is the cohesive energy of the supercell with an oxygen vacancy in charge state $q$, $E(0)$ is the cohesive energy.
of the perfect supercell in the bulk phase of NCM111 (without vacancy), and \( \Delta n \) represents the number of oxygen atoms which have been removed from the perfect supercell in forming the oxygen vacancies. \( e_F \) is the Fermi level. In this paper, only the neutral oxygen vacancy is calculated; therefore, \( q = 0 \) and the formation energy of an oxygen vacancy is independent of the charge state of the O vacancy and the Fermi level of the system.

In eq 3, \( \mu_O \) is the chemical potential of O atom, representing the energy of the reservoir with which the extracted O atoms

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**Figure 5.** Partial density of states calculated by the GGA+U method with \( U_1 = (6.0 \ 5.5 \ 4.2) \), for (a) \( x = 1 \), (b) \( x = 2/3 \), (c) \( x = 1/3 \), and (d) \( x = 0 \). Fermi levels are represented by dashed vertical lines.

**Figure 6.** PDOS of O-2p states calculated by GGA, GGA+U1, and GGA+U2 methods with \( U_1 = 6.0 \ 3.4 \ 3.9 \) and \( U_2 = 6.0 \ 5.5 \ 4.2 \) for (a) \( x = 0.2 \) and (b) \( x = 0.125 \) in \( Li_xNCM111 \). Fermi levels are represented by dashed lines.
are exchanged. We calculate the oxygen chemical potential $\mu_O$ by the following formula: \[\mu_O(P, T) = \mu_O(P_0, T_0) + \mu_O(R, T) + \frac{1}{2} k_B T \ln \left( \frac{P}{P_0} \right) \]

where $\mu_O(P_0, T_0)$ represents the oxygen chemical potential at zero pressure ($P_0 = 0$) and zero temperature ($T_0 = 0$), which is approximated to half of the total cohesive energy of an isolated O$_2$ molecule obtained by the DFT calculations ($\frac{1}{2} E(O_2)$). The second term in eq 4, $\mu_O(R, T)$, originated from experimental data, expressing the contribution of the temperature to the oxygen chemical potential at a particular pressure $P_1$ (here, $P_1 = 1$ atm). The third term in eq 4 represents the contribution of pressure to the chemical potential of oxygen $\mu_O(P, T)$, when the gas-phase oxygen is treated as an ideal gas. $k_B$ is the Boltzmann’s constant.

There are three kinds of nonequivalent oxygen vacancies (represented by $O_1$, $O_2$, and $O_3$) in NCM111. The formation energy of an oxygen vacancy in NCM111 is calculated by using GGA+U methods with three sets of $U_i$ (i.e., $U_1 = 6.0$ 3.4 3.9, $U_2 = 6.0$ 5.5 4.2, and $U_3 = 5.0$ 5.0 5.0) as well as for three nonequivalent oxygen vacancies. The O-vacancy formation energies under zero temperature and zero pressure are given in Table 5. Table 5 suggests that the oxygen vacancy formation energies for different $U$ values and for nonequivalent oxygen vacancies ($O_1$, $O_2$, and $O_3$) in NCM111 are all relatively close. Therefore, in the following discussions, the results only from GGA+U$_1$ with $U_1 = (6.0$ 3.4 3.9) will be presented and analyzed.

![Figure 7](https://doi.org/10.1021/acsomega.2c00375)

According to eqs 3 and 4, the formation energy of an oxygen vacancy is a function of the oxygen chemical potential which is dependent on the experimental conditions, such as the temperature and pressure. We now discuss the relationship of the O vacancy formation energy versus the temperature and the oxygen partial pressure. Figure 7 presents the formation energies of an oxygen vacancy as a function of temperature for three different types of oxygen vacancies, at the given oxygen partial pressure $P = 0.2$ atm and $P = 100$ atm, respectively. Results in Figure 7 indicate that the O vacancy formation energy decreases with increasing temperature for both oxygen partial pressures $P = 0.2$ atm and $P = 100$ atm, as expected. Upon comparing panels a and b of Figure 7, the results also suggest that the formation energy of an oxygen vacancy decreases with temperature faster at lower oxygen partial pressure $p$. Figure 8 shows the formation energies of an oxygen vacancy as a function of oxygen partial pressures, at the given $T = 300$ K and $T = 1500$ K, again for the three different types of oxygen vacancies. The results indicate that the formation energy of the O vacancy increases with the increase of oxygen partial pressure, implying that higher pressure should inhibit the formation of O vacancies. Upon comparing panels a and b of Figure 8, it is found that the O vacancy formation energy increases with the oxygen partial pressure more substantially at higher temperatures.

Then, the effects of both the temperature and oxygen partial pressure on the formation energy of an O vacancy are investigated, and the results are shown in Figure 9. Generally speaking, the formation energy of O vacancy decreases with the increase of temperature and the decrease of oxygen partial pressure, which is consistent with the previous discussions. For example, at the highest temperature of 1500 K and the lowest pressure of $10^{-10}$ atm shown in Figure 8b, the formation energy of oxygen vacancy consequently reaches the lowest value. From the gradient of color shown in Figure 9, we can also see that the formation energy of an O vacancy changes more severely with the temperature, while less obviously with the oxygen partial pressure. In summary, the calculations show that the decreased temperature and the increased oxygen

| NCM111 | O-vacancy formation energies (eV) |
|--------|----------------------------------|
|        | $U_1 = 6.0$ 3.4 3.9 | $U_2 = 6.0$ 5.5 4.2 | $U_3 = 5.0$ 5.0 5.0 |
| $O_1$  | 3.43 | 3.13 | 3.06 |
| $O_2$  | 3.50 | 3.22 | 3.16 |
| $O_3$  | 3.38 | 3.08 | 3.02 |
partial pressure can suppress the formation of the oxygen vacancy. Therefore, to govern the appearance of oxygen vacancies, one can decrease or increase the temperature and/or the pressure. These results are helpful for us to understand the factors that control the formation of oxygen vacancies and provide guidance for reducing the oxygen release and improving the stability of the lattice oxygen in the cathode materials of lithium-ion batteries.

4. CONCLUSIONS

In conclusion, we have employed first-principles calculations to study the electronic structures and electrochemical properties of LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 during the delithiation process. In particular, charge compensation mechanisms during the delithiation were compared carefully with the GGA and GGA+U methods under different U values reported in the literature. Comparisons between ferromagnetic and antiferromagnetic configurations were also conducted. The results suggested that the electrochemical properties (e.g., the redox reactions) were clearly dependent on the values of parameter U, i.e., different sets of U values could lead to different charge compensation mechanisms in the delithiation process. For example, Co^{3+}/Co^{4+} couples were shown to dominate the redox reaction for \(1 \geq x \geq 2/3\) by using the GGA+U_1 method (\(U_1 = 6.0, 3.4, 3.9\) for Ni, Co, and Mn, respectively). However, the Ni^{3+}/Ni^{4+} couple should be responsible for the redox reaction for \(1 \geq x \geq 2/3\) by using the GGA+U_2 (\(U_2 = 6.0, 5.5, 4.2\)) method. According to our studies, experimental charge compensation processes during delithiation are then of great importance to evaluate the theoretical calculations (although theoretical calculations are declared as ab initio). The results also suggest that all the GGA+U_i methods predict better voltage platforms than the GGA method. The oxygen anionic redox reactions are also compared under different sets of U values. The electronic density of states and the magnetic moments of transition metals during the lithium extractions are employed to illustrate the redox reactions, under the GGA and GGA+U calculations with different values of U.

We have also investigated the formation energies of an oxygen vacancy in the bulk phase of NCM111 employing different U values, which is important for understanding the possible occurrence of the oxygen release. The increased temperature and/or decreased oxygen partial pressure decrease the formation energy of the O vacancy; that is, the lower temperature and higher oxygen partial pressure can suppress the formation of the oxygen vacancy. These calculations can help understand the formation of oxygen vacancies and provide guidelines for reducing the oxygen release and improving the stability of the lattice oxygen in this cathode material.

### AUTHOR INFORMATION

**Corresponding Author**

Zizhong Zhu – Department of Physics and Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, Xiamen University, Xiamen 361005, China; orcid.org/0000-0003-3479-8148; Email: zzzhu@xmu.edu.cn

**Authors**

Xiao-Hong Shi – Department of Physics, Xiamen University, Xiamen 361005, China
Ya-Ping Wang — Department of Physics, Xiamen University, Xiamen 361005, China
Xinrui Cao — Department of Physics and Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, Xiamen University, Xiamen 361005, China; orcid.org/0000-0002-2545-0054
Shuqing Wu — Department of Physics, Xiamen University, Xiamen 361005, China; orcid.org/0000-0002-2545-0054
Zhufeng Hou — State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 35002, China; orcid.org/0000-0002-0069-5573

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c00375

Notes
The authors declare no competing financial interest.

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