Atomic-scale understanding of non-stoichiometry effects on the electrochemical performance of Ni-rich cathode materials

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HIGHLIGHTS

- Extra-Ni-defects trigger charge disproportionation reaction.
- Their immobile nature permits "pillar effects" to increase structural stability.
- Intra-layer mobility can be activated via neighboring vacancy sites.
- They generate Li depletion regions, lead to poor rate capacity.
- High valence cation doping combining with ion-exchange synthesis is suggested.

GRAPHICAL ABSTRACT
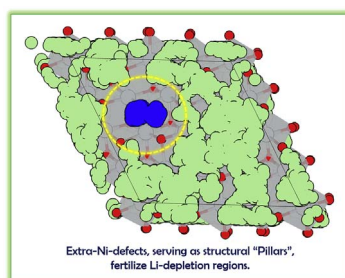
Extra-Ni-defects, serving as structural "Pillars", fertilize Li-depletion regions.

ARTICLE INFO

ABSTRACT

As the next-generation high energy capacity cathode materials for Li-ion batteries, Ni-rich oxides face the problem of obtaining near-stoichiometric phases due to excessive Ni occupying Li sites. These extra-Ni-defects drastically affect the electrochemical performance. Despite of its importance, the fundamental correlation between such defects and the key electrochemical properties is still poorly understood. In this work, using density-functional-theory, we report a comprehensive study on the effects of non-stoichiometric phases on properties of Ni-rich layered oxides. For instance, extra-Ni-defects trigger charge disproportionation reaction within the system, alleviating the Jahn-Teller distortion of Ni^{3+} ions, which constitutes an important reason for their low formation energies. Kinetic studies of these defects reveal their immobile nature, creating a "pillar effect" that increases the structural stability. Ab initio molecular dynamics revealed Li depletion regions surrounding extra-Ni-defects, which are ultimate responsible for the arduous Li diffusion and re-intercalation, resulting in poor rate performance and initial capacity loss. Finally, the method with combination of high valence cation doping and ion-exchange synthesis is regarded as the most promising way to obtain stoichiometric oxides. Overall, this work not only deepens our understanding of non-stoichiometric Ni-rich layered oxides, but also enables further optimizations of high energy density cathode materials.

1. Introduction

Profiting from their higher energy density, Lithium-ion batteries (LIBs) have been often regarded as one of the most important energy storage systems to be used in cellular phones, personal computers, digital cameras, energy storage grids, hybrid or full electric vehicles, *etc.*

As the earliest and most widely commercialized cathode material for LIBs, LiCoO$_2$ has dominated the market for the last two decades. However, due to its low reversible capacity of 140 mAh g^{-1} and the high cost of Cobalt mining, LiCoO$_2$ cannot meet the rapidly growing market of LIBs and the increasing demand for higher energy and power densities in electronic devices and vehicles. For these reasons, Cobalt-

free cathode materials have been actively explored, with Ni-rich layered oxides, noted as $LiNiO_2$-based oxides, being often regarded as the next generation cathode materials [1–4]. These oxides potentially offer a specific capacity as high as 200 mAh g^{-1}, and an energy density over 800 Wh kg^{-1}. Moreover, they are also promising candidates for ultrahigh-rate cathode materials, because of their small band gap of about 0.5 eV (electrical conductivity of 10^{-1} S cm^{-1}) and a low Li ion diffusion barrier below 0.4 eV [5–8].

In spite of the aforementioned advantageous properties of Ni-rich oxides, synthesizing stoichiometric phases has proven to be extremely challenging. Extra Ni ions occupying Li sites are widely observed, giving rise to the formation of non-stoichiometric $Li_{1-x}Ni_{1+x}O_2$ (x = 0.02–0.1) [1–3]. The extra Ni defect concentration normally ranges from 2% to 10%, depending on the synthesis temperature, oxygen pressure, oxygen flow rate, precursor ratios, *etc.* [9–11] Density-functional theory (DFT) calculations showed that extra-Ni-defects in Ni-rich oxides have small formation energies, between 0.5 and 0.8 eV, as reported by different groups [12–14]. From simulated defect concentration *vs.* temperature diagrams, Koyama et al. have suggested that those extra Ni ion defects are unavoidable during synthesis [12]. The low formation energy of such defects was ascribed to the similar ionic radii of Li$^+$ (0.76 Å) and Ni^{2+} (0.69 Å). More recently, Chen et al. have proposed that extra-Ni-defects could be stabilized by 180° Ni-O-Ni superexchange interactions with nearby Ni ions [13].

The non-stoichiometry character of Ni-rich oxides shows detrimental effects on the cathode performance. The appearance of extra-Ni-defects in the Li layer reduces the theoretical capacity limit, since these Ni ions are electrochemically inactive and occupy reversible Li sites [15]. A high concentration of extra-Ni-defects also leads to more capacity loss during the first cycle of charge-discharge [11]. Besides, it also worsens the rate performance, although a unified understanding of this effect has not yet been obtained by the scientific community. Delmas et al. suggested that extra Ni ions in the Li layer can be oxidized to a trivalent state, leading to a local collapse of the inter-slab space and inhibiting Li re-intercalation [16]. Fu et al. attributed the reason to the blocking effect of extra Ni ions on the Li diffusion, observing how the rate performance of Ni-rich LiNiCoMnO$_2$ (NCM) materials was improved after decreasing the amount of extra-Ni-defects [11]. On the other hand, theoretical work by Kang et al. showed that the effect of extra-Ni-defects is not localized. By lowering the overall Li slab distance, Li hopping is impeded due to the increase of the diffusion barrier. They thought that the electrostatic repulsion between Li and Ni ions in the Li layer might not play a determining role [8].

Regardless of the negative effects of non-stoichiometry on the theoretical capacity limit and rate performance of Ni-rich oxides, the beneficial aspect of helping to maintain their layered structure, thus obtaining better capacity retention, has recently attracted considerable attention, and has been used in practice to stabilize the cathode material [1]. Extra-Ni-defect is regarded as a "pillar" to stabilize the layered structure by suppressing undesirable phase reactions or preventing Ni interlayer migration during charge/discharge cycles [17–20]. Cho et al. took advantage of such effect and developed a "pillar"-rich coating layer to stabilize Ni-rich layered oxides [21]. In a recent work by the same group, a Ni "pillar" was used to improve the structural stability of LiCoO$_2$ by screening interlayer oxygen repulsion [22]. The "pillar effect" is based on the immobile nature of the extra-Ni-defects that are pinned to the Li layer during electrochemical cycling. However, this assumption is not consistent with other experimental observations that Ni ions show a high mobility within the Li layer and could then diffuse to surface regions or form NiO-like domain clusters. [15,23] There are no extensive kinetic studies on the mobility of such extra-Ni-defects, and the "pillar effect" remains poorly understood.

In order to improve the electrochemical performance, practically used LiNiO$_2$ compounds are always doped (or forming alloys if the dopant concentration is larger than 10%) with one or multiple elements, resulting in the formation of Li[Ni$_{1-y}$M$_y$]O$_2$ (y = 0.1–0.3,

M = Mn, Al, Fe, *etc.*) compounds. The dopants have revealed a significant influence on the defect chemistry. A recent theoretical work by Hoang and Johannes has compared LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ and LiNi$_{1/3}$Co$_{1/3}$Al$_{1/3}$O$_2$ cathode materials, for which the defect formation energy difference can vary between 0.3 and 0.9 eV [19]. Our recent work on a series of doped Ni-rich NCM materials also shows that the defect formation energy sensitively depends on the doping species [24]. It was experimentally reported that the introduction of Co and Mn or Ti could inhibit and promote Ni occupation at Li sites, respectively [25–29]. Also, a Mg doping concentration below 20% resulted in improved stoichiometry, while a concentration higher than 20% led to a deteriorated stoichiometry [30]. However, due to the lack of systematic studies on doped Ni-rich layered oxides, the fundamental role of doping species and the corresponding rational design strategies to control the stoichiometry of LiNiO$_2$ oxides through doping methods have not yet been well outlined.

In order to address the aforementioned controversies and questions, in this work we performed DFT calculations to conduct a systematic study at the atomic scale on the effects of non-stoichiometry (extra-Ni-defects) on Ni-rich layered oxides. The thermodynamic, kinetic and electronic features of extra-Ni-defects, as well as their correlations with defect formation, "pillar effect", rate performance and capacity loss of Ni-rich oxides are investigated in detail. A wide range of dopants is also systematically investigated, from which the relation between dopant valence state and stoichiometry is discovered and explained. This work not only provides an in-depth understanding of non-stoichiometry in Ni-rich oxides, but also helps to rationally design optimized cathode materials for LIBs. Non-stoichiometry effects have also been observed in other important cathode materials, such as olivine LiMnSiO$_4$, phosphate LiFePO$_4$ or spinel LiMn$_2$O$_4$, and the results of current study will also provide a basis to understand them.

2. Computational methods

In this work, the Vienna *ab initio* simulation package (VASP) and the projector-augmented wave (PAW) method are used to perform all DFT calculations [31–33]. Exchange and correlation interactions are described by the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [34]. The plane wave cutoff energy is 500 eV and the structure optimization is performed with the criteria that the equilibrium force on each atom is less than 0.05 eV Å^{-1} and the total energy is converged up to 10^{-4} eV. Self-consistent calculations are performed with the tetrahedron method using Blöchl corrections [35], and the energy convergence criteria is 10^{-5} eV. Spin polarization calculations are carried out with the initial magnetic moments of Ni ions being set as 4 μ_B. Since GGA cannot describe the localized nature of *d* electrons very accurately, we employed effective on-site Hubbard U_{eff} corrections on the *d* electrons of all transition metal elements included in this work [36]. Using previous theoretical reports as reference, the U_{eff} values are set to be 4.2 eV for Ti, 3.0 eV for V, 3.5 eV for Cr, 5.0 eV for Mn, 4.2 eV for Fe, 4.0 eV for Co, 6.4 eV for Ni, 4.0 eV for Cu, 5.0 eV for Zn, 4.0 eV for Zr, 3.0 eV for Nb, 3.5 eV for Mo, 2.9 eV for Ru [37–43].

Since Ni-rich layered oxides are normally described as LiNiO$_2$-based materials with a small amount of substitutional cations occupying Ni sites, in this work we use LiNiO$_2$ as the reference material. The supercell used in this work contains 32 unit cells (Li$_{32}$Ni$_{32}$O$_{64}$). Then, a supercell with one extra Ni defect represents a defect concentration of 3%, corresponding to a Li$_{0.97}$Ni$_{1.03}$O$_2$ stoichiometry. During *ab initio* simulation, the temperature effect on defect formation energy calculation is a complex procedure that involves the consideration of configurational, electronic, and vibrational excitations. However, for reactions involving oxygen evolution, the reaction entropy would be dominated by the creation of O$_2$ gas [44,45,46]. And O$_2$ chemical potential is lowered if the temperature increases. We determined the Gibbs free energy of gaseous O$_2$ as 8.95 eV/pair at room temperature, based on the JANAF