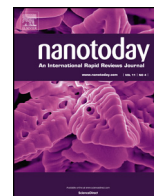




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Review

The roles of oxygen non-stoichiometry on the electrochemical properties of oxide-based cathode materials

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ABSTRACT

Cathode materials with both high energy density and high power capability are in great demand to improve the performance of lithium ion batteries and expand the driving range of electric vehicles. Of particular interest are transition metal oxide-based cathodes. However, electrochemical performance of these cathode materials is very sensitive to the synthetic conditions and, particularly, the oxygen non-stoichiometry that is induced during high temperature synthesis and post treatment. This review highlights the critical roles of oxygen non-stoichiometry in high-energy-density cathode materials including high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, Ni-rich layered $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC, $x > 0.5$), and the Li-rich, Mn-rich layered cathode, with the aim to provide a fundamental understanding on the effects of the oxygen non-stoichiometry governing the crystalline structure, electrochemical performance, and thermal stability of different cathode materials. This review also offers perspectives and directions on how to best utilize oxygen non-stoichiometry in the future development of high-energy-density cathode materials for lithium ion batteries.

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Introduction

Rechargeable lithium ion batteries (LIBs) have been widely used in consumer electronic devices and are quickly entering the electric vehicle (EV) and large-scale stationary energy storage market

Abbreviations: ALMO, annealed Li_2MnO_3 ; EELS, electron energy loss spectroscopy; EV, electric vehicle; LIB, lithium ion battery; LMR, Li-rich Mn-rich; MLMO, quenched Li_2MnO_3 milled with Super P; NMC, $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$; QLMO, quenched Li_2MnO_3 ; TG, thermogravimetric; TM, transition metal.

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[1,2]. The state-of-the-art LIB system typically consists of a graphite anode, a nonaqueous electrolyte, and a lithium-containing cathode [3–5]. The cathode materials, whose available capacities are still smaller than that of graphite anodes, are under intensive exploration in order to further improve the energy density of the whole battery system. Traditional cathodes, such as LiCoO_2 , LiMn_2O_4 , LiFePO_4 , and $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC, $x < 0.5$) have been commercially used as cathode materials for LIBs [1]. However, limitations in energy density, cycle life, cost and/or safety issues of these cathode materials still impede their mass application in long-range EV and large-scale grid applications [6,7]. In addition to these conventional cathode materials, three appealing cathode materials, that have attracted broad research interest and are being inten-

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sively investigated, are high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, Ni-rich layered-structure NMC with nickel content ≥ 0.5 , and the Li-rich Mn-rich (LMR) layered-structure cathode, because of their significant advantages in energy density and/or reduced cost.

Typical discharge voltage profiles of different cathode materials are shown in Fig. 1a, and their achievable energy densities are compared in Fig. 1b. Ranked in the top three are high voltage spinel, Ni-rich NMC, and LMR cathode materials, which have much higher energy density than traditional cathode materials, signifying a significant increase in the driving mileage of EVs [8–11]. The crystal structures of the three kinds of materials, i.e., $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinels with the space group of ordered $\text{P4}_3\text{32}$ and disordered Fd-3m , Ni-rich layered structure with R-3m , and LMR with R-3m and C2/m monoclinic structures, are presented in Fig. 1c–f. High voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is a promising cathode candidate for LIBs because of its high operating voltage (ca. 4.7 V), high energy density (658 Wh kg^{-1}), low cost, and good rate capability [8,12–14]. The three-dimensional tunnels for fast Li^+ ion transport enable the excellent rate capability, while the stable spinel crystalline structure guarantees a good long-term cycle life [15–17]. For layered-structure cathode materials, Ni-rich $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ ($x \geq 0.5$) cathode materials have been regarded as promising cathode alternatives due to their high achievable discharge capacity ($200\text{--}220 \text{ mAh g}^{-1}$) [9,11,18,19], representing a further enhancement in energy density ($\sim 800 \text{ Wh kg}^{-1}$) in comparison with traditional cathodes and the high voltage spinel. Furthermore, LMR layered-structure cathode materials with a composition of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($\text{M} = \text{Ni, Co, Mn}$ or combinations) or $\text{Li}_{1+w}\text{Ni}_x\text{Mn}_y\text{Co}_z\text{O}_2$ deliver the highest energy density of ca. 900 Wh kg^{-1} among all known intercalation compound cathode materials [20–26].

Although the several cathode materials discussed above exhibit very attractive energy densities, their electrochemical performance is very sensitive to the synthesis method and post-calcination treatment conditions [27–29] whose influences cannot be detected immediately from X-ray diffraction patterns. The synthesis methods widely used for preparation of these cathode materials include solid-state reaction, co-precipitation method, sol-gel method, spray-dry method, and a hydrothermal method. All of these methods require a calcination step at high temperatures ranging from $700\text{--}1050^\circ\text{C}$, which inevitably leads to oxygen loss at temperatures higher than ca. 700°C and the consequent formation of variable oxygen non-stoichiometry in the as-synthesized materials [30,31]. In order to satisfy the charge balance, the average oxidation states of the transition metals (TMs) decrease in proportion to the oxygen non-stoichiometry, accompanied by changes in local crystal environments, which adversely or beneficially affect the electrochemical performance of the cathode materials [31–33]. In principle, the degree of oxygen non-stoichiometry changes as a function of calcination temperature and oxygen partial pressure p_{O_2} [31,34]. Oxygen can be recaptured into the material crystal during a cooling process at ca. $600\text{--}700^\circ\text{C}$ [15], and this process is dependent on cooling method [35]. In addition, the degree of oxygen non-stoichiometry is also dependent on the material's crystal structure and composition [30], and should be carefully controlled during the development of different kinds of cathode materials in order to maximize their electrochemical performance. The roles of oxygen non-stoichiometry have been well investigated in the cathode materials for solid oxide fuel cells [34,36,37], but the important role of oxygen non-stoichiometry in the investigation of high-energy-density cathode materials for LIBs is still not well recognized.

In this review, we focus on discussion regarding the roles of oxygen non-stoichiometry on the crystalline structure and electrochemical performance of the three high-energy-density cathode materials: high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, Ni-rich NMC cathode

material, and LMR cathode material. This review aims to provide a full understanding on the positive and negative effects of the oxygen non-stoichiometry governing the electrochemical performance of different cathode materials. The effects of oxygen non-stoichiometry during electrochemical activation and oxygen loss during thermal reactions are systematically analyzed. Finally, perspectives and directions on how to fully utilize the advantages of oxygen non-stoichiometry to further improve the performance of high-energy-density cathode materials for LIBs will be discussed.

Discussion

Oxygen non-stoichiometry in spinel cathodes

The effects of oxygen non-stoichiometry in the traditional LiMn_2O_4 spinel have been well studied before [38–42]. In case of LiMn_2O_4 , oxygen deficiency is considered as a trigger of structural degradation and capacity fading due to the dominating Mn^{3+} and its damaging Jahn-Teller distortion effects. However, oxygen non-stoichiometry shows opposite effect on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. This is because $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ mainly operates with $\text{Ni}^{2+/4+}$ redox couples during charge/discharge processes, whereas the structural damage caused by Mn^{3+} -induced Jahn-Teller distortions is very limited because of the minor content of Mn^{3+} . Here, we focus on discussing the roles of oxygen non-stoichiometry in high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ from the relationship of synthesis-structure-electrochemical properties point of view. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibits two types of phase structures, i.e., ordered $\text{P4}_3\text{32}$ and disordered Fd-3m [43–45]. Ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with space group $\text{P4}_3\text{32}$ has Li at tetrahedral 8a sites, Ni at octahedral 4b sites and Mn at octahedral 12d sites (Fig. 1c). The cubic close-packed O ions are located at 8c and 24e sites. In this ordered Ni/Mn arrangement, all Ni^{2+} ions are coordinated with the six nearest neighboring Mn^{4+} atoms in the crystal lattice. For the disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with space group Fd-3m phase, Ni and Mn distribute randomly in the octahedral 16d sites in a ratio of 1:3, while Li and O are located in 8a and 32e sites, respectively (Fig. 1d).

Formation of ordered or disordered spinel phase is closely related to the oxygen non-stoichiometry that is created during preparation of the material. Recently, Chen et al. employed density functional theory (DFT) first-principles calculation to investigate the origin of the Ni/Mn ordering in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [45]. Their calculation results demonstrate that without oxygen vacancies, the formation of ordered Ni^{2+} and Mn^{4+} ions (1:3 ratio) is energetically favorable in comparison with the disordered Ni^{3+} and Mn^{3+} ions that are formed owing to Ni aggregation in the ordered $\text{P4}_3\text{32}$ phase (Fig. 2a). However, at elevated temperature, increased ionic mobility gives rise to the appearance of Ni aggregated structure as an instantaneous state (Fig. 2b). This Ni aggregated structure is unstable and susceptible to oxygen loss. In the presence of oxygen vacancies, the energy gap between the $\text{P4}_3\text{32}$ super cell and the Ni aggregated structure is greatly decreased (Fig. 2c, d), resulting in the formation of oxygen-deficient $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-d}$ with disordered Ni/Mn distribution. This is how the Ni/Mn disorder is induced and stabilized in the presence of oxygen vacancies.

Calcination temperature has significant effects on the content of oxygen non-stoichiometry in the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, because higher calcination temperature readily leads to more oxygen loss. Kunduraci et al. systematically studied the correlations between material properties (electrical conductivity, lattice constant, morphology) and the electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared at different temperatures [15,46]. Their results show that the onset temperature for oxygen loss is 712°C , where the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ undergoes a thermally driven ordered-to-disordered phase transition, as confirmed with Fourier transform

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