

A perspective on nickel-rich layered oxide cathodes for lithium-ion batteries



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ABSTRACT

Nickel-rich layered oxides are one of the most promising cathode candidates for next-generation high-energy-density lithium-ion batteries. The advantages of these materials are high reversible capacity, high energy density, good rate capability, and low cost. However, they suffer from poor cyclability, particularly at elevated temperatures, and thermal instability which induces thermal runaway. In this review, we highlight the evolution of nickel-rich layered oxides from LiNiO_2 to $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ ($1-x-y > 0.5$) in view of cationic substitutions, state-of-the-art understanding of the capacity fading mechanisms that is related to a complex surface chemistry of the particles, and various modification strategies to enhance the surface stability. Based on these considerations, the remaining challenges and the future research direction are also discussed.

1. Introduction

As one of the iconic energy-storage technologies in modern-day society, lithium-ion batteries (LIBs) have been powering the daily life of individuals from laptops, cell phones, cameras, to a variety of other electronic devices. In view of the environmental concerns globally, in particular the consequences arising from the excessive emission of Greenhouse Gases like CO_2 , electric vehicles (EVs) are taken into account as one promising solution. However, a universal acceptance of low-cost EVs is highly dependent on the development of rechargeable batteries with higher energy density, longer calendar life, and lower price. On April 1, 2016, Tesla CEO Elon Musk unveiled the Tesla Model 3. It seems to be a landmark event for EV marketing because Tesla Model 3 provides affordable prize and 215 miles of range per charge. The cathode material applied to this EV is $\text{LiNi}_{0.85}\text{Co}_{0.10}\text{Al}_{0.05}\text{O}_2$, which belongs to a family of cathode materials termed as layered Ni-rich oxides (LNOs). Compared to other groups of conventional cathode materials such as layered LiCoO_2 , spinel LiMn_2O_4 , and olivine LiFePO_4 , LNOs offer a combination of high reversible capacity ($200\text{--}250 \text{ mA h g}^{-1}$), high operating voltage ($\sim 3.8 \text{ V vs. Li/Li}^+$), and better chemical stability without oxygen loss due to the lack of a significant overlap of the $\text{Ni}^{3+/4+}$ redox energy with top of the $\text{O}^{2-} : 2p$ band. As well known, $\text{Li}_{1-x}\text{CoO}_2$ suffers from serious chemical instability when $x > 0.5$, while LiMn_2O_4 has limited reversible capacity ($\sim 120 \text{ mA h g}^{-1}$) with the critical issue of Mn^{3+} dissolution. On the other hand, LiFePO_4 delivers only $\sim 160 \text{ mA h g}^{-1}$ at a lower operating voltage of $\sim 3.4 \text{ V}$. Within the group of layered oxides, the Li-rich layered oxides have also drawn much attention due to the high capacity of $\sim 250\text{--}300 \text{ mA h g}^{-1}$,

but it suffers from layered to spinel phase transition due to the facile migration of Mn from the transition-metal plane to the lithium plane during cycling.

Although LNOs offer attractive features, further improvements and optimization in terms of chemical composition, long-term cyclability, and thermal runaway are critically needed to realize their full potential as a next-generation cathode for LIBs. This objective will need a profound understanding of the factors that influence the performance of LNOs. Accordingly, we present here a review of the development history of LNOs starting from the parent LiNiO_2 , current understanding of its capacity fading mechanisms, and strategies to modify the surface chemistry for enhancing the electrochemical performance. Furthermore, a perspective in view of the remaining challenges and approaches to overcome them with future work is presented.

2. LiNiO_2

LiNiO_2 adopts the $\alpha\text{-NaFeO}_2$ structure with the oxide ions forming a cubic close-packed arrangement and the Li^+ and Ni^{3+} ions occupying the octahedral sites on the alternate (111) planes, which is designated as the O3 structure, as shown in Fig. 1a. With a low-spin $\text{Ni}^{3+} : t_{2g}^6 e_g^1$ electronic configuration, although the t_{2g} orbitals remain completely filled during the charge-discharge process unlike in the case of the analogous LiCoO_2 , a strong Ni-O-Ni covalence leads to reasonably high conductivity with a semiconducting behavior [1]. On the other hand, the 2-dimensional lithium-ion diffusion offers good lithium-ion conductivity. Furthermore, a lack of a significant overlap of the redox-active $\text{Ni}^{3+/4+} : e_g$ band with the top of the $\text{O}^{2-} : 2p$ band could facilitate

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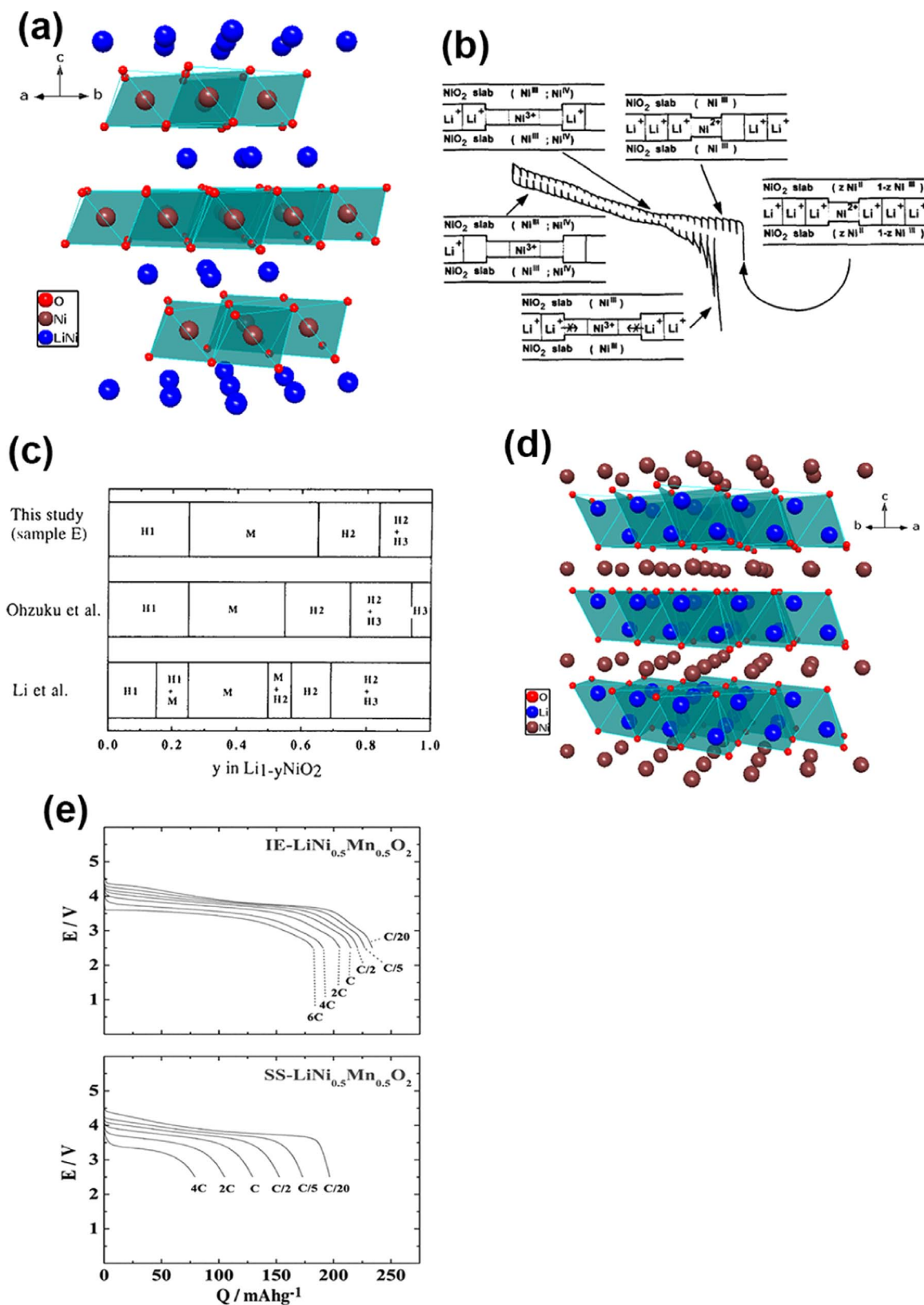


Fig. 1. (a) Crystal structure of LiNiO_2 . (b) Changes in the oxidation state of nickel ions during the first electrochemical cycle, where Ni^{2+} induces a local collapse of the interslab space, which makes the Li re-intercalation difficult. Reproduced with permission [5], Copyright 1997, Elsevier. (c) Phase diagrams of sample E and other $\text{Li}_{1-y}\text{NiO}_2$ samples reported by Ohzuku et al. [4] and Li et al. [194]. H and M denote hexagonal and monoclinic lattices, respectively. Reproduced with permission [6], Copyright 1995, Elsevier. (d) Crystal structure of Li_2NiO_2 . (e) Discharge curves at various C rates for $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ prepared by an ion-exchange (above) and a solid-state reaction (below). Reproduced with permission [20], Copyright 2006, AAAS.

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