



Recent progresses on nickel-rich layered oxide positive electrode materials used in lithium-ion batteries for electric vehicles



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HIGHLIGHTS

- Advances on layered $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ ($x \geq 0.5$) positive electrode materials.
- Detailed discussion on the preparation, microstructure, modification, etc.
- Structure stability, interface compatibility of the positive electrode materials.
- The challenges and prospects of nickel-rich layered oxide materials.

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ABSTRACT

High energy density lithium-ion batteries are eagerly required to electric vehicles more competitive. In a variety of circumstances closely associated with the energy density of the battery, positive electrode material is known as a crucial one to be tackled. Among all kinds of materials for lithium-ion batteries, nickel-rich layered oxides have the merit of high specific capacity compared to LiCoO_2 , LiMn_2O_4 and LiFePO_4 . They have already become one of the most attractive candidates for the mainstream batteries in industries. In this work, the recent advances on three commonly concerned nickel-rich layered oxides are presented. The preparation, microstructure, electrochemical performances are focused, the modification including coating design as well as dopant selection is specially discussed in details, which is essential to enhance the durability and energy density of lithium-ion batteries. Additionally, the prospects and challenges are also systematically discussed, as well as the potential applications in the field of energy storage technologies.

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1. Introduction

Nowadays, energy and environment are playing crucial roles in the sustainable development of human society. In the context of low-carbon economy, new energy vehicles becomes one of the important ways to save energy and reduce emission. Battery, as the main or auxiliary power source of new energy vehicles, has become the choke point in the development of new energy vehicles [1–4]. Compared to other batteries, lithium-ion batteries (LIBs) have the advantages of high operating voltage, high energy and

power densities, good cycle ability, low self-discharging, being environmentally friendly and so on. It has been widely applied in plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs) [5]. EVs application, in particular, has strict demands for safety, long-range, service life and other relevant performance. In order to promote the growth of EVs, researchers are committed to searching for preeminent electrode materials, especially positive electrode materials (PEMs) for LIBs. Ideal PEMs need to have such characteristics as follows [6]: (1) high positive potential, which can ensure battery a higher output voltage of the battery; (2) good reversible lithium-ion intercalation/de-intercalation ability, which can ensure the material a high reversible capacity; (3) stable structure without irreversible phase transformation (4) high electronic and ionic conductivities, which is to guarantee the high current charging and discharging performance; (5) an inertness to the electrolyte and a good compatibility; (6) low cost of raw materials,

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environmental friendliness, facile preparation for commercialization. Although at present no PEMs can completely meet conditions above, with the research achievement over the past years, some transition metal (such as Ni, Co, Mn) oxides and polyanion-type materials (such as LiFePO_4) have been proved to be appropriate for the PEMs of LIBs.

In 1980, Goodenough's team first reported that LiCoO_2 could be used as PEMs of rechargeable lithium battery [7]. Nevertheless, it took nearly ten years to understand the concept of LIBs due to the absence of suitable negative electrode materials and electrolyte for matching use. In the 1990s, negative electrode materials were made a breakthrough. Carbonaceous materials were discovered as excellent candidates because of their highly reversible capacity and low potential platform of lithium-ion intercalation/de-intercalation. LIB (C/ LiCoO_2) which is commercialized by SONY is still the mainstream of the electronic market today [8]. Hexagonal α - NaFeO_2 -type LiCoO_2 belongs to R3m space group. With this typical layered structure, LiCoO_2 has good lithium-ion intercalation/de-intercalation capability, and it had been widely studied by many institutions [9–14]. However, the structural stability of LiCoO_2 rapidly deteriorates when over half of lithium ions are removed from the host structure during charging. And researchers improved its cycle performance by limiting the cutoff voltage. As a result, it only delivers about 140 mAh g^{-1} capacity which is half of theoretical capacity. Besides, cobalt is relatively scarce and expensive, more importantly, it is a strategic resource. Since then, a great interest and enthusiasm has been committed to LiNiO_2 positive material because it is considerably cheaper and more environmentally friendly than LiCoO_2 [15]. LiNiO_2 has high theoretical specific capacity (274 mAh g^{-1}) and the same structure as LiCoO_2 . However, stoichiometric LiNiO_2 compound is very difficult to obtain, and the reasons are: [16–26] (1) The ionic radius of Ni^{2+} is similar to Li^+ , some Ni^{2+} of Ni layer move to Li layer because of the loss of lithium from the host structure during high temperature calcination; (2) Ni^{2+} are hard to oxidize to Ni^{3+} , the remnant of Ni^{2+} will move to Li^+ position; (3) LiNiO_2 is prone to phase transition and decomposition reaction during high temperature calcination. Non-stoichiometric layer LiNiO_2 material exhibits poor electrochemical performance. High cation mixing ratio leads to the high initial capacity loss and low cycle life. Because Ni^{2+} at the lithium positions are oxidized to Ni^{3+} or Ni^{4+} during charging, which gives rise to the partial collapse of the crystal layer (LiO_6) and hinders Li^+ diffusion during discharging. Obviously, the more Ni^{2+} in the lithium layer, the worse the cycling performance, which means the cation mixing ratio is a very important parameter to evaluate the electrochemical performance of this material. Additionally, LiNiO_2 undergo a phase change from an active hexagonal phase to an inactive cubic phase during charging, and this phase transition is irreversible. These problems have seriously hindered its commercialization and application in energy storage system.

LiMn_2O_4 , as another PEM for LIBs has the advantages of low raw material cost, environmental friendliness and natural abundant. The spinel LiMn_2O_4 was proposed as the PEM of LIBs by Thackeray et al. in 1983 [27–29]. This material has a three-dimensional channel for lithium-ions diffusion, and shows good charge-discharge rate performance [30–33]. However, the cycle performance of this material is very poor under elevated temperatures, such as 50°C . Two reasons are presented: the electronic configuration of Mn^{3+} encounters the Jahn-Teller distortion easily; hydrofluoric acid generates by a small amount of water and fluorine ions, which will dissolve Mn ions. More importantly, the energy density of LiMn_2O_4 has no competitive advantage compared with other PEMs due to the low theoretical specific capacity (148 mAh g^{-1}), and its actual specific capacity is merely $120\text{--}130 \text{ mAh g}^{-1}$ [34–39]. The olivine phosphates LiFePO_4 is another very attractive PEM due to its excellent electrochemical properties, low cost, non-toxicity, and great

thermal stability. Since the Goodenough' teams conducted pioneering work on LiFePO_4 as the PEM, a large number of researchers have begun to put painstaking efforts into the study of electrochemical mechanism and optimized the material for better electrochemical performance. LiFePO_4 has low intrinsic conductivity and lithium-ion diffusion coefficient, all of these will limit the batteries' operation at low temperature, such as ten below zero. In addition, the charge-discharge rate performance of LiFePO_4 is also poor. Much work has been done to resolve these problems and significant results have been achieved [40–53]. However, the discharge platform of LiFePO_4 is around 3.4 V , and its theoretical capacity is 170 mAh g^{-1} (actual specific capacity is about 160 mAh g^{-1}). It is hard to meet the requirements of high energy density for EVs. Recently, layered $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ (NCM) has received a growing attention as a promising PEM because it combines the rate performance of LiCoO_2 , the high capacity of LiNiO_2 , and the structural stabilization with the presence of Mn^{4+} . After Ohzuku and Makimura reported $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM111) in 2001 [54], this material has attracted world-wide attentions due to its high specific capacity, stable structure, thermal stability and low cost [55–62].

All materials that we mention above can be used as the candidate PEMs for LIBs. However, with the demand for long-range electric vehicle applications, high energy density battery is necessary. PEMs with a high specific capacity are essential to high specific energy batteries. It is found that the energy density of $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ can be greatly enhanced by increasing the value of x to exceed 0.5 and the cutoff voltage to more than 4.5 V . But these materials show high initial reversible capacity loss, low cycle life, poor thermal stability and so on. Researchers have been committing to solving these problems so as to promote the development of EVs. In this work the recent advances on three commonly concerned nickel-rich layered oxides $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523), $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622), $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811) are presented. The preparation, microstructure, electrochemical performances are focused, the modification including coating design as well as dopant selection is specially discussed in details, which is essential to enhance the durability and energy density of lithium-ion batteries. Additionally, the prospects and challenges are also systematically discussed, as well as the potential applications in the field of energy storage technologies.

2. Estimation on the energy density of lithium-ion battery

As is known, high energy density of LIB is still one of the first priorities that are endeavored to pursue in the field in despite of some significant progresses appear impressive. Then, what kind of positive and negative electrode materials can achieve the goal of high energy density, e.g. over 300 Wh kg^{-1} ? Based on the Faraday's law, the amount of the substance participating in the reaction on the electrode is proportional to the amount of electricity passing through, which is one mole of active material participates in the reaction, the release of electricity is F . F is Faraday constant,

$$F = e \times N_A \quad (1)$$

where e is the elementary charge, 1.6×10^{-19} , N_A is Avogadro's number, 6.02×10^{23} , so the value of F is $96,500 \text{ C}$ or 26.8 Ah . Accordingly, we can get the formula for theoretical capacity of active material:

$$C = \frac{m}{M} \times n_e \times 26.8 \text{ (Ah)} \quad (2)$$

where m is the amount of active material (g), M is the molar mass of the active material (g mol^{-1}), n_e is the number of electron in electrode reaction, so the theoretical specific capacity of active material is as follows:

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