



Pre-oxidizing the precursors of Nickel-rich cathode materials to regulate their $\text{Li}^+/\text{Ni}^{2+}$ cation ordering towards cyclability improvements

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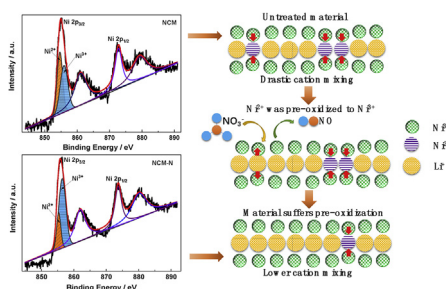
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HIGHLIGHTS

- A novel approach is proposed to pre-oxidize the precursors of Ni-rich cathodes.
- $\text{Ni}^{2+}/\text{Ni}^{3+}$ ratio of the cathodes decreases due to the pre-oxidation treatment.
- Pre-oxidized materials shows enhanced cyclability with decreased $\text{Li}^+/\text{Ni}^{2+}$ mixing.
- This method realizes synthesis of quality Ni-rich cathodes under air atmosphere.

GRAPHICAL ABSTRACT



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ABSTRACT

Layered Nickel-rich cathode materials ($\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$) with high Ni content attract much attention of public owing to their higher specific capacity compared with LiCoO_2 . However, the rapid capacity fading hinders the commercialization of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$. The severe $\text{Li}^+/\text{Ni}^{2+}$ mixing, which should become more serious with higher Ni content, is one of the main reasons for poor cycling stability. In this paper, we synthesize $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ under air atmosphere with an additional pre-oxidation process using nitrates. X-ray powder diffraction and Rietveld refinement reveal that the pre-oxidation treated Nickel-rich cathode material shows lower $\text{Li}^+/\text{Ni}^{2+}$ mixing degree, which is also supported by the incremental ratio of $\text{Ni}^{3+}/\text{Ni}^{2+}$ obtained from the X-ray photoelectron spectroscopy results. The electrochemical tests show that the pre-oxidation treated Nickel-rich cathode material exhibits superior cycle performance; after 100 cycles, the capacity retention is improved from 79.04% to 90.73% with the pre-oxidation treatment, and the corresponding Nyquist plots exhibits sharply declined impedance. The promoted electrochemical properties are owed to decreased charge transfer and more ordered cation arrangement, which is benefit from the pre-oxidization treatment that induces the increased content of Ni^{3+} . Hence, it is concluded that the pre-oxidization process can regulate the $\text{Li}^+/\text{Ni}^{2+}$ cation ordering to improve the cycling stability of layered Ni-rich materials.

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1. Introduction

In recent years, lithium ion batteries (LIBs) have attracted much public attention as kinds of outstanding portable energy storage devices [1–3]. LIBs have been widely used in many fields such as portable equipments, electric vehicles and hybrid electric vehicles because of the long life, high specific capacity and cycle stability [4–7]. LiCoO_2 , as the first commercial cathode material used in LIBs, has taken over much market share of LIBs in the past years [2,5,8]. But the prospect of LiCoO_2 has been limited by their high price and toxicity, which is contrary to the requirement of green chemistry [9–11]. Nickel-rich layered materials $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ (NCM) have been investigated to replace commercial LiCoO_2 in the recent years, due to their higher specific capacity, lower cost and toxicity [2,4,12–16].

However, the commoditization of nickel-rich layered materials is still a challenge until now [17–19]. The slow development of nickel-rich layered materials in large-scale application should be attributed to their drawbacks of structural instability, capacity fade and safety problems related with oxygen release [10,20,21]. The $\text{Li}^+/\text{Ni}^{2+}$ mixing, caused by similar ion radius between Li^+ and Ni^{2+} (0.76 Å and 0.69 Å), is the chief reason for above mentioned issues as for Nickel-rich cathodes [7,22–24]. In essence, the structure of Nickel-rich layered materials, i.e. $\alpha\text{-NaFeO}_2$ structure with R-3m space group, is closely related to the rock-salt structure; the similar unit cell dimensions of these two structures lead to the easy exchange of $\text{Li}^+/\text{Ni}^{2+}$ without a dimensional mismatch [25–28]. Thereby, increasing the ratio of Ni^{3+} content in final Nickel-rich cathodes can relieve $\text{Li}^+/\text{Ni}^{2+}$ mixing benefit from the inappropriate size of Li^+ and Ni^{3+} (0.76 Å and 0.56 Å) [29]. Nevertheless, as reported in the previous literature, the Ni^{3+} ions are unstable under high-temperature solid-state reaction [30]. And because of that, it is difficult to synthesize stoichiometric Nickel-rich layered materials in air atmosphere.

Much research has been taken to relieve $\text{Li}^+/\text{Ni}^{2+}$ mixing of Nickel-rich layered materials. For example, element doping and surface coating have been considered to regulate the degree of $\text{Li}^+/\text{Ni}^{2+}$ mixing. Zuguang Yang et al. had testified that K-doped $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ could promote electrochemical properties and decrease the degree of cation mixing by enlarged interlayer space of Li slabs [31]. Xunhui Xiong et al. reported that the transformation from Ni^{3+} to Ni^{2+} in $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ after 30 days stored was suppressed by V_2O_5 coating [32]. Another way is adjusting the ratio of $\text{Ni}^{3+}/\text{Ni}^{2+}$, which aims to facilitate Ni^{2+} to transform to Ni^{3+} and control $\text{Li}^+/\text{Ni}^{2+}$ mixing in a low level. Chaochao Fu et al. achieved different $\text{Li}^+/\text{Ni}^{2+}$ disordered extents by tuning the amount of lithium source [24]. Duc-Luong Vu et al. adopted KMnO_4 to pre-oxidize the $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ precursor to increase the ratio of $\text{Ni}^{3+}/\text{Ni}^{2+}$, which reached the standard of calcination process in pure oxygen atmosphere [33].

Here, we proposed a novel pre-oxidization method towards reducing the $\text{Li}^+/\text{Ni}^{2+}$ exchange of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$. $\text{Mn}(\text{NO}_3)_2$ has been employed as an oxidant in our work. With the help of that, Ni^{2+} can be oxidized to Ni^{3+} at a large degree before calcination process, which shows positive impact on decreasing the degree of $\text{Li}^+/\text{Ni}^{2+}$ cation mixing in the final cathode material, even $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ was synthesized under air atmosphere. The pre-oxidization process for $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ is illustrated in Fig. 1. During the pre-oxidization process, as illustrated in Fig. 1, much Ni^{2+} was oxidized to Ni^{3+} , which helped the reduction of $\text{Li}^+/\text{Ni}^{2+}$ mixing in the followed calcination process. Improved electrochemical properties of $\text{Mn}(\text{NO}_3)_2$ treated NCM have been measured in our paper. The results confirmed that pre-oxidizing the precursors of Nickel-rich cathode materials is effective to increase the ratio of $\text{Ni}^{3+}/\text{Ni}^{2+}$ and suppress $\text{Li}^+/\text{Ni}^{2+}$ cation disordering, thus achieving enhanced cyclability for layered Nickel-rich cathode materials.

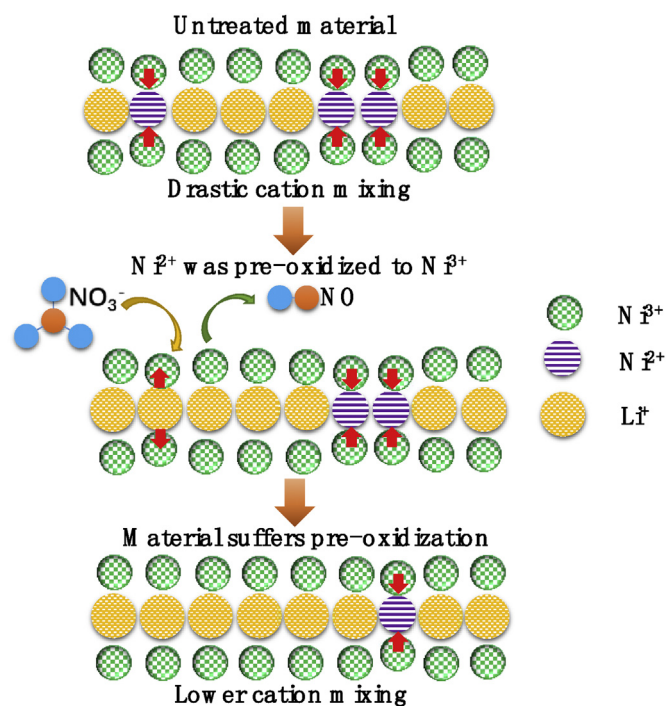


Fig. 1. Schematic illustrations of the pre-oxidization treatment for NCM material with $\text{Mn}(\text{NO}_3)_2$.

2. Experiment

2.1. Synthesis of materials

$\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ was synthesized by solid state reaction from $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ precursors. And co-precipitation method was employed to synthesize $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ precursors. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ with the ratio of 8:1:1 have been prepared as aqueous solution with a concentration of 1 mol L^{-1} and pumped to a continuous stirred tank reactor (CSTR) which suffused by N_2 . A concentration of 1 mol L^{-1} NaOH aqueous solution with optimum proportion of $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added to the CSTR at the same time. The speed of stirring was remained about 600 rpm and the pH value of reaction solution was maintained at 11 by controlling the feed rate of alkali solution. After the aging process of 6 h, the precipitates were washed with deionized water, filtered by vacuum filtration, and then dried in vacuum oven. After that, the $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ powder and $\text{LiOH} \cdot \text{H}_2\text{O}$ with in the molar ratio of 1:1.05 were mixed in agate mortar, using ethyl alcohol as dispersant agent. Then the mixture was pre-calcined at 500°C for 5 h and then calcined at 800°C for 15 h in air atmosphere to obtain the final materials, which was named NCM.

To prepare $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ materials with pre-oxidization step, 0.005 g polyvinylpyrrolidone (PVP) and 2 g $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ were added to 100 mL deionized water with continuous stirring, 3 wt% $\text{Mn}(\text{NO}_3)_2$ were dissolved in these mixing solution and heated at 40°C until the deionized water evaporated completely. Then the obtained powder was mixed with the proper amount of $\text{LiOH} \cdot \text{H}_2\text{O}$ after pre-calcined at 500°C for 5 h and then calcined at 800°C for 15 h in air atmosphere to obtain the final materials, and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ with 3 wt% of $\text{Mn}(\text{NO}_3)_2$ treated was named as NCM-N. In order to explain the oxidation of $\text{Mn}(\text{NO}_3)_2$ to NCM, the non-oxidative $\text{Mn}(\text{CH}_3\text{COO})_2$ with same mass fraction was chosen to substitute $\text{Mn}(\text{NO}_3)_2$ to treat the $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ precursors. And the final cathode material prepared from the precursors that pre-treated by $\text{Mn}(\text{CH}_3\text{COO})_2$ was named as NCM-AC.

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