Influence of the Li/TM Ratio on Electrochemical Properties of LiNi_{0.5}Co_{0.1}O_{2} Cathodes

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Abstract. The layered Nickel-rich LiNi_{x}M_{y}O_{2} (Ni ≥60%) cathodes have attracted much attention owing to their high energy density, promising cycle property and low cost. Nevertheless, their electrochemical performances greatly depend on the synthesis conditions, especially for the ratio of lithium to transition metal (Li / TM). Herein, we have systematically investigated the influence of Li/TM on structure and electrochemical performance of LiNi_{0.5}Co_{0.1}O_{2} cathodes. The optimized LiNi_{0.5}Co_{0.1}O_{2} (Li/TM is 1.02) exhibits highest initial capacity of 189.8mAh g^{-1} at 1 C and much better capacity retention of 82.19% after 100 cycles between 2.8 and 4.35 V at 1 C.

Keywords. LiNi_{0.5}Co_{0.1}O_{2}, Lithium-ion batteries, Li/TM, electrochemical performance.

1. Introduction
The massive combustion of fossil fuels has led to the release of greenhouse gases such as carbon dioxide into the atmosphere, causing serious damage to the environment and a shortage of resources [1-3]. The rechargeable lithium-ion batteries (LIBs) have received widespread attention due to their environmentally friendly and superior energy storage properties [4-5]. However, the performance of LIBs largely rely on the property of the cathode [6-7]. Among various advanced cathode materials, layered nickel-rich LiNi_{x}M_{y}O_{2} (x ≥0.6, LNMO) is considered as the most prospective cathode materials for LIBs on account of their high discharge specific capacity, excellent rate capability and low cost [8-10]. LNMO was usually produced by mixing the hydroxide precursors Ni_{x}M_{y}(OH)_{2} with Li salts and then followed by a step of high temperature solid state reaction [11]. The ratio of lithium to transition metal (Li/TM) is a prominent factor in the practical production of lithium ion batteries[12-13]. The residual lithium on the surface of the LNMO materials, such as Li_{2}O/LiOH, easily reacts with H_{2}O and CO_{2} in air, leading to production of LiOH/Li_{2}CO_{3} layer. Consequently, the cycling stability of LNMO cathodes could be deteriorated resulted from side reactions between LiPF_{6} with LiOH and Li_{2}CO_{3} decomposition [14].

Herein, we have systematically studied the impact of the Li/TM on the surface composition, microstructure and electrochemical property of LiNi_{0.5}Co_{0.1}O_{2}(LNCO) layered materials.
2. Experimental Section

2.1. Preparation and Characterization
The spherical Ni_{10.9}Co_{0.1}OH precursor was synthesized by means of a conventional co-precipitation method. To get the LiNi_{10.9}Co_{0.1}O_2 cathode materials, the dried precursor was mixed with an excess of LiOH•H_2O, and then pre-calcined 6 h at 500 °C, sintered at 720 °C for 12 h under an oxygen atmosphere. The molar ratios of Li/TM materials are 1, 1.02, 1.05, and 1.07, which are represented by 0-LNCO, 1-LNCO, 2-LNCO, and 3-LNCO.

The chemical compositions, morphology, microstructure, crystal structure and the surface state of the samples were observed by Fourier transform infrared spectrometry (FT-IR, Hitachi FTIR-8900), X-ray diffraction (XRD, Rigaku UltimaIV-185), scanning electron microscopy (SEM, FEI Quanta 250 instrument).

2.2. Electrochemical Measurements
The electrode electrochemical properties of all materials were measured by fabricating CR2025 coin-type cells. The electrode was prepared via mixing active materials, polyvinylidene fluoride, (PVDF) and acetylene black (AB) at a weight ratio of 8:1:1. And then the gained slurry was coated onto aluminum foil and dried at 80 °C for 24 h.

The obtained cathodes were assembled in a glovebox under argon atmosphere. The cyclic voltammograms (CV) at a scan rate of 0.1 mV s\(^{-1}\) from 2.8-4.35 V and electrochemical impedance spectroscopy (EIS) from 100 kHz to 0.01 Hz were tested by a CHI604D electrochemical workstation.

3. Results and Discussion
The FT-IR spectra of LNCOs with different Li/TM ratios was shown in Figure 1a. The characteristic peaks at 3453 cm\(^{-1}\) and 1431 cm\(^{-1}\) are related to the carbonate vibration [15]. It indicates that the LNCO reacts with CO\(_2\) and H\(_2\)O due to its surface chemical instability, leading to the generation of Li\(_2\)CO\(_3\) and LiOH on the surface of samples. There are no LiOH characteristic signals in the spectra may be ascribed to its low content in LNCOs.

![Figure 1. FT-IR spectra (a), XRD patterns (b) of LiNi\(_{10.9}\)Co\(_{0.1}\)O\(_2\) prepared with different lithium content.](image)

X-ray powder diffraction (XRD) was conducted to characterize the crystal structure of the materials with different lithium content. As presented in figure 1b, all materials show typical diffraction peaks, which can be well defined as hexagonal \(\alpha\)-NaFeO\(_2\) with the R\(3\)m space group. Besides, the clear split of the (006)/(102) and (108)/(110) peaks means that all LNCOs have a relatively good crystal structure. The degree of cation mixing can be expressed by the value of \(I_{(003)}/I_{(104)}\). When the ratio exceeds 1.2, it can be considered that the material has a low degree of cation mixing [16]. The \(I_{(003)}/I_{(104)}\) intensity ratio for LNCOs are 0.99, 1.14, 1.07 and 1.01, respectively, showing that the 1-LNCO has the smallest Li\(^+/\)Ni\(^{2+}\) cation disorder.
Figure 2. SEM images of LiNi_{0.9}Co_{0.1}O_{2} with different Li/TM ratios: (a, e) 1, (b, f) 1.02, (c, g) 1.05, and (d, h) 1.07.

The scanning electron microscope (SEM) images of LiNi_{0.9}Co_{0.1}O_{2} samples are shown in Figure 2. It is clear that the particle shapes and particle sizes have no changes when mixing the precursor with different stoichiometric equivalent of LiOH•H_{2}O. All samples are constructed by spherical secondary particles (with a mean diameter of about 6-12 μm) that consist of primary nanoscale particles. Notably, the surface roughness of 2-LNCO and 3-LNCO slightly differ from those of 0-LNCO and 1-LNCO attributed to formation of Li_{2}CO_{3} and LiOH on the samples surface, hindering the cell electrochemical performance.

Figure 3 shows the influence of different Li/TM ratios on the electrochemical performance of LiNi_{0.9}Co_{0.1}O_{2}. Figure 3a displays the initial discharge and charge curves for the different electrodes at 1 C (1 C = 190 mA g⁻¹) from 2.8 to 4.35 V. The 1-LNCO cathode has the highest initial discharge capacity of 189.8 mAh g⁻¹, while the 0-LNCO, 2-LNCO and 3-LNCO exhibit the discharge capacities of 177.1 mAh g⁻¹, 183.5 mAh g⁻¹ and 178.4 mAh g⁻¹, respectively. Meanwhile, the 1-LNCO cathode possesses a better capacity retention (82.19%) after 100 cycles than that of 0-LNCO (80.29%), 2-LNCO (80.32%) and 3-LNCO samples (81.00%). Here, we ascribe the excellent electrochemical performances of 1-LNCO materials to the lower cation mixing, better hexagonal ordering, and minimal residual lithium content due to the optimal Li/TM ratio. Figure 4 shows the cyclic voltammograms (CV) curves of all materials for the first three cycles at a scan rate of 0.1 mV s⁻¹ from 2.8 to 4.35 V. The ΔE (E_{oxidation}}
- $E_{\text{reduction}}$ values of the samples are 0.212 V, 0.179 V, 0.188 V and 0.194 V during the initial cycle, indicating the minimal polarization when the (Li/TM) ratio is 1.02. Besides, the 1-LNCO also exhibits better overlap between the second and the third curves compared with other three samples, demonstrating the excellent electrochemical reversibility [11].

**Figure 4.** CV profiles for the first 3 cycles of the all materials: (a) 0-LNCO, (b) 1-LNCO, (c) 2-LNCO, (d) 3-LNCO.

In order to further understand the influence of Li/TM on the electrode interface resistance, the electrochemical impedance spectroscopy (EIS) was measured under a charged state (4.35V) from 100 kHz to 0.01Hz after 100 cycles. The gained Nyquist plots consist of a slope line and two semicircles, as shown in figure 5. The larger semicircle in the medium frequency region reflects the charge-transfer resistance, and the smaller semicircle in the high-frequency region is associated with the surface film resistance. The straight line in the low-frequency corresponds to Li$^+$ diffusion coefficient [17]. The fitting results for all materials are shown in Table 1. It reveals that $R_{ct}$ values are very small compared to the $R_{ct}$ of all samples, thus the electrochemical reaction is mainly determined by the $R_{ct}$. The 1-LNCO has the lowest $R_{ct}$ value of 65.42 $\Omega$ among all the materials, indicating a better interfacial stability and electrochemical performance.

**Figure 5.** Nyquist plots of all materials at 2 °C after 100 cycle and equivalent circuit model.
Table 1. The impedance data of all samples was simulated by using equivalent circuit.

| Sample | $R_{eq}$ [$\Omega$] | $R_{ct}$ [$\Omega$] |
|--------|---------------------|-------------------|
| 1      | 3.082               | 91.43             |
| 1.02   | 2.863               | 65.42             |
| 1.05   | 2.497               | 77.5              |
| 1.07   | 3.112               | 85.39             |

4. Conclusions
In this study, we have clearly demonstrated that Li / TM ratio has an important effect on the surface composition, microstructure and electrochemical property of LiNi$_{10.0}$Co$_{0.1}$O$_2$. Our particular research shows that 1-LNCO possess the best structural stability and electrochemical property. The 1-LNCO exhibits the highest initial discharge specific capacity of 189.8 mAh g$^{-1}$ at 1 C between 2.8 to 4.35V and a capacity retention of 82.19% after 100 cycles. The better hexagonal ordering, lower cation mixing and the minimal residual lithium on the particle surface contribute to excellent electrochemical property of 1-LNCO (Li/TM = 1.02).

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