Synthesis, Modification and Study on the Electrochemical Properties of LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$@ Li$_2$ZrO$_3$

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Abstract. LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (NCM811) is considered as a promising cathode material for lithium-ion batteries (LIBs) due to its advantages of high lithium storage capacity, low cost and excellent safety. However, lithium element of NCM series is easily lost in the preparation process, which leads to the rapid decline of cathode material capacity. Previous researches show that coating is an effective way to reduce the loss of elements, improve the electrochemical properties and thermal stability of the material. In this paper, the author focuses on different synthesis methods and different molar (or weight) ratios of Li$_2$ZrO$_3$, finding out that different synthesis methods can affect the electrochemical performances of target materials and right now research result is that 1wt.% NCM811@ Li$_2$ZrO$_3$ has the best property among other molar (or weight) ratios of NCM811@ Li$_2$ZrO$_3$.

1. Introduction
With the rapid development of industrial production and technology, human’s requirement for energy has been increasing. Of all the kinds of energy, fossil fuel accounts for a large proportion. However, the large-scale development and usage by people leads to energy exhaustion and air pollution. Therefore, developing renewable energy is the biggest project for human. Under this background, as a high-efficient energy conversion and storage system, lithium-ion batteries have caught the attention of scientists. Cathode of LIBs has a great influence on its capacity and electrical performances. The combination of Ni-Mn-Co has a ternary-synergistic effect on the cathode of LIBs, which is worth studying. The author has studied a different synthesis method, which can affect the electrochemical performances of the target material.

2. Analysis
Development of Lithium-ion Batteries. In 1970, Acsoon made the first lithium battery, by using titanium sulfide as cathode material and lithium as anode material. Lithium-ion battery is developed by lithium battery. The first lithium-ion battery is composed by Bell laboratory. In 1983, M. Thackeray, J. Goodenough and others found out that spinel was an excellent cathode material and had good properties of low-cost, stable conductivity and lithium transportation. In 1992, SOONY invented a kind of lithium battery that used carbon material as anode and compounds containing lithium as cathode. During its charging and discharging process, there is no metal lithium existed, only has lithium ions transport inside of it. This kind of battery using LiCoO$_2$ as cathode material, which is the main power supply for portable electronic devices.

Operating Principle of LIBs. The four main parts of LIBs are cathode, anode, separator and electrolyte. The electrodes of LIBs are composed of active and conductive substances.
As shown in figure 1, during the charge process, Li⁺ takes off from cathode, and Li⁺ in electrolyte embeds in anode. After the charging process, cathode is at the state of rich-Li and high potential, while anode is at the state of lack-Li and low potential, which makes electric energy change into chemical potential. During the discharge process, Li⁺ leaves from anode and Li⁺ in electrolyte embeds in cathode, which produces current.

**Figure 1. The structure of all LIBs**[1]

**Current Research of LiNi₀.₃Co₀.₃Mn₀.₄O₂ (NCM).** Much research work has been done to improve cathode materials' electrical performances, like LiNiO₂, LiCoO₂ and LiMnO₂. Ternary-composites NCM material which is emerging now, can be regarded as a combination of these three elements in different molar ratios, thus has the advantages of Ni, Co and Mn. With the existence of Co, to a certain extent, it can reduce the disorder of Li⁺ and Ni²⁺. With the existence of Ni, it can improve the capacity. Although Mn doesn’t participate in chemical reaction, it can strengthen the crystal structure of NCM, which can make the material more stable and reduce the cost of producing the material.

**Figure 2. The crystal structure of LiNi₁/₃Co₁/₃Mn₁/₃O₂[2]**

The structure of NCM (111) has a layered rock salt structure of α-NaFeO₂, which belongs to the R-3m space point group. In this structure, oxygen atoms are located at 6C site, and cubes accumulate to form coplanar octahedrons. Ni²⁺ valence, Co³⁺ valence, Mn⁴⁺ valence, and Li⁺ occupies 3b position and 3a position, respectively. Experiments show that the layered structure is stable during the charge and discharge process. Neither will Jahn-Teller effect occur like LiMn₂O₄, nor will the crystal transformation of LiMnO₂ appear. The reduction of Co concentration also solves the problem of high cost caused by lacking of cobalt mineral resources, and at the same time, it has the advantage of higher specific capacity than LiNiO₂ material.

**Current Research of LiNiₙCoₙMnₙO₂@ Li₂ZrO₃.** One of the biggest problem of NCM is that the ion radius of Ni²⁺ is 0.068 nm, which is very close to the radius of Li⁺ 0.076 nm, so that Ni²⁺ will occupy the position of Li⁺, resulting in the disorder of Ni²⁺ and Li⁺, which greatly reduces the capacity of the battery and electrical performances.

To solve the problem above, the commonly used modification methods are doping modification and coating modification. Doping modification mainly uses other atoms to partly replace the cathode material to improve its structural stability, while coating modification mainly improves its cycling performance by reducing the contact area between cathode material and electrolyte.
Li$_2$ZrO$_3$ is a chemical inert material and has good stability, which is often used as coating material to suppress cathode material. If Li$_2$ZrO$_3$ is completely coated on the surface of NCM, the contact among strongly oxidized Ni$^{3+/4+}$, air and electrolyte can be prevented. Besides, the storage performance, interface stability and interface of ion diffusion ability can be enhanced to a certain extent. J. Ni et al. [5] reported that Li$_2$ZrO$_3$ can decrease the disorder of Ni$^{2+}$ and Li$^+$ and support the Li$^+$ transportation.

3. Experimental Section

3.1. Preparation of Li$_{Ni_{0.8}Co_{0.1}Mn_{0.1}}$O$_2$

**Solid Phase Method.** Most previous researchers have used solid phase method to synthesize Li$_{Ni_{0.8}Co_{0.1}Mn_{0.1}}$O$_2$. By mixing the oxides of Ni, Co and Mn with lithium salt in a certain proportion, grinding mechanically and calcinating at high temperature, the target material can be got. Liubin Song, Jiao Liu et al. [6] use LiOHꞏH$_2$O as the lithium salt to make 1 wt% Li$_2$ZrO$_3$ coated LiNi$_{0.8}Co_{0.1}Mn_{0.1}$O$_2$. The most obvious advantage is that the operation step is quite simple, but long-time reaction and volatilization of lithium during calcination can be its drawbacks.

**Coprecipitation method.** NaOH and Na$_2$CO$_3$ are usually used as precipitants. A certain amount of precipitant is added to certain compounds of nickel-cobalt-manganese salt solution. Then the precipitate is mixed with lithium salt and calcined at high temperature to produce the target material. Xuehui Shangguan, Qinglei Wang et al. [7] used Na$_2$CO$_3$ as precipitants to get Ni$_{0.5}Mn_{0.5}$CO$_3 ꞏ xH$_2$O. The chemical ratio of the product obtained by this method is relatively accurate, the size of particles can be small and particles can distribute uniformly. Besides, the subsequent sintering time is shorter, which reduces the energy consumption. But there are many factors that need to be controlled, such as pH value, the amount of precipitant, speed of stirring, reaction temperature and so on.

**Hydrothermal Method.** Hydrothermal method is the way to increase the temperature and pressure in a closed vessel by heating, in order to get some insoluble substances dissolved. After reaching a certain degree of saturation before recrystallization, it can obtain the target product through separation and proper heat treatment. In this paper, the author successfully prepared NCM811 by using this method.
First is to put Li$_2$CO$_3$, Ni(CH$_3$COO)$_2$ꞏ4H$_2$O, Mn(CH$_3$COO)$_2$ꞏ4H$_2$O, Co(CH$_3$COO)$_2$ꞏ4H$_2$O and CO(NH$_2$)$_2$ into glycol and dissolve them uniformly by using magnetic stirring machine for 30 min under the condition of 40 °C. Second, these precursors are put into Tafel caldron to conduct hydrothermal reaction under the condition of 10h and 180 °C. After cooling down the caldron to room temperature, centrifugal machine and vacuum drying oven are used to get the purer material.

Materials prepared by this method can have very small and even nano particle size, particles are uniform and not easy to agglomerate.

**Others.** Sol-gel method, spray method and Molten salt method are other options for making LiNi$_x$Co$_y$Mn$_z$O$_2$, here the author only focuses on several specific experimental methods.

### 3.2. Preparation of LiNi$_x$Co$_y$Mn$_z$O$_2$@ Li$_2$ZrO$_3$

This kind of core-shell structure can be obtained by using wet coating method. First, CH$_3$COO Liꞏ2H$_2$O will be dissolved in anhydrous alcohol completely. Second step is to add LiNi$_x$Co$_y$Mn$_z$O$_2$ into CH$_3$COO Liꞏ2H$_2$O which has dissolved in anhydrous alcohol before, and use ultrasonic vibrate machine to make them dissolved uniformly. Third, with the condition of constant rate magnetic stirring, organic or inorganic Zr$^{4+}$ salt will be added drop by drop into the solution, next step is to use oil bath or blast dryer to get solid material. Last, in order to get the target material, it needs to be calcined at a certain temperature and specific rate. In this paper, the author adds CH$_3$COO LiꞏH$_2$O and Zirconium butyl alcohol into the previous material, and uses machines to stir and ultrasonic vibrate it. After getting uniformly dissolved material, the author put it into drying box to get material dried. With the calcination condition of 850 °C, the target material LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$@ Li$_2$ZrO$_3$ can be attained.

### 4. Results and Discussion

In the process of making LiNi$_x$Co$_y$Mn$_z$O$_2$@ Li$_2$ZrO$_3$, there are several variables to which this paper pays attention, such as the proportions of Ni, Co and Mn in LiNi$_x$Co$_y$Mn$_z$O$_2$, the molar (or weight) ratios of Li$_2$ZrO$_3$ in NCM, the way to form core-shell structure, and the calcination temperature to get the target material. In the parts down below, the author only focuses on the analysis of LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$@ Li$_2$ZrO$_3$.

#### 4.1. Morphology Analysis

#### 4.1.1. XRD Pattern.

![Figure 5. XRD of 3wt.% LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$@ Li$_2$ZrO$_3$](image-url)
LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} has the structure of layered hexagonal α-NaFeO_{2} with the space group of R3m. From figure 5, by using the calcination temperature of 850 °C, despite the impurity peak of its XRD, the characteristic peaks have clear (003), (101) and (104) peaks, indicating that this material has Ni (Mn)-O-Ni (Mn) basic unit. In figure 6, with the calcination temperature of 650 °C, whether NCM811 is coated or not, because of having clearly characteristic peaks, which should appear in the target material, all of the materials have well-crystallized-layered structure.

4.1.2. SEM and TEM Pattern.

As shown in figure 7 and 8, there is no big difference in bare or coated materials, and the size of these materials remains the same. In bare material, the margin of it remains clear. By contrast, from low weight percentage of coated material to high weight percentage of coated material, the border of them becomes obscured, which implies that the shell Li_{2}ZrO_{3} is coated successfully to NCM811. The
coating shell can reduce the effective contact area between anode materials and electrolyte, which prevents side reaction from happening, and the electrochemical performance of the material is improved.

![Figure 9. TEM of bare and 1 wt.% of LiNi₀.₈Co₀.₁Mn₀.₁O₂@Li₂ZrO₃](image)

In order to prove the existence of Li₂ZrO₃’s shell, in figure 9, the margin of bare NCM811 is clear, by contrast, the border of 1 wt.% coated material is obscured, which implies that the shell of Li₂ZrO₃ is actually on the surface of NCM811 core.

4.1.3. EDS Pattern.

![Figure 10. EDS of 1 wt.%, 2 wt.% and 3 wt.% of LiNi₀.₈Co₀.₁Mn₀.₁O₂@Li₂ZrO₃](image)

In figure 10, EDS shows that Li₂ZrO₃ distributes uniformly on the surface of the material, and as the weight percentage of Li₂ZrO₃ increases, the concentration of it becomes higher. For the height of
Li$_2$ZrO$_3$’s peak, the actual weight percentage of the coated shell is 0.47%, 0.97% and 1.54%, respectively.

4.2. Analysis of Charge & Discharge Curve.

![Figure 11. The first charge & discharge curve of 3 wt.% of LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$@ Li$_2$ZrO$_3$](image1)

Under the condition of 1C and calcination temperature of 850°C, in figure 11, the first discharge capacity is 189 mA·h·g$^{-1}$, and its discharge platform is about 3.8 V. In figure 12, with calcination temperature of 650°C, 1 wt.% coated NCM811 has the best performance among other materials, whose discharge capacity is 180 mA·h·g$^{-1}$. With the increase of the coating amount, the specific discharge capacity of the coated material begins to decrease. Due to the thick-coating shell, it hinders the Li$^+$’s deblocking and embedding process, so the electrochemical performance of the material decreases.

4.3. Cycle Performance Analysis.

![Figure 13. Cycle Performance of 3 wt.% of LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$@ Li$_2$ZrO$_3$](image2)
With the condition of 1C and calcination temperature of 850℃, after 100-times cycles, its cycle efficient remains 94.7%. In figure 14, with the calcination temperature of 800℃, 1 wt.% coated material shows the best performance among these bare and coated materials, which is 93.6%. Although its coated shell hinders the contact between electrode and electrolyte, at the same time, it improves the Li⁺’s deblocking and embedding process, and prevents oxygen from producing, which is mentioned in the previous research paper [3]. The thicker the coated shell is, the worse condition of Li⁺ transfers from Li₂ZrO₃ to NCM811. There is a relationship between the cycle performance of this material and the thickness of its coated shell. All in all, by using hydrothermal method, even the 3 wt.% of Li₂ZrO₃@ NCM811 can have a better electrochemical property.

4.4. Rate Performance Analysis & AC Impedance Analysis.

With the rate becoming higher and cycle number getting larger, the rate performance of coated materials is better than bare one, which implies that the coated shell can protect the structure of its material.
Figure 16. Nyquist plots of bare and 1 wt.% LiNi₀.₈Co₀.₁Mn₀.₁O₂@Li₂ZrO₃ [3]

In figure 16, after 100 cycles, the RCT value of bare material increases from 41.7 Ω to 263.5 Ω, while coated material increases from 29.7 Ω to 106.2 Ω. From above, the coated shell can improve Li⁺'s deblocking and embedding process.

5. Conclusion
Cathode material of NCM811 is becoming commercial in industrial production, but there are so many factors that can affect the electrochemical performances of LIBs. For LiNi₀.₈Co₀.₁Mn₀.₁O₂@Li₂ZrO₃, recent researches focus on the different molar (or weight) ratios of Li₂ZrO₃ in NCM and its calcination temperature to get the target material. As shown in this paper, by using different synthesis methods, even the 3 wt.% of LiNi₀.₈Co₀.₁Mn₀.₁O₂@Li₂ZrO₃ can have a better performance. In the future, finding a better way to form the core-shell structure and a better-performing shell could be the research direction for development.

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