Study on Mo-doped of Li$_{1.18}$Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ Lithium-rich Ternary Cathode Materials

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Abstract: The layered Li$_{1.18}$(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)$_{4-x}$Mo$_x$O$_{4}$ cathode material was prepared by mixing lithium carbonate with precursor-nickel cobalt manganese hydroxide complex which was prepared by co-precipitation method with Mo-doped. The physical and chemical parameters, crystal structure, morphology and electrochemical properties were investigated by ICP analysis, X-ray diffraction, SEM and electrochemical tests, respectively. XRD results showed that doping Mo had no effect on the structure of pristine materials. However, the second phase of Li$_2$MoO$_4$ was dissected until the Mo loading reached 4 at%. The SEM images exhibited that the primary particles size decreased with the increase of Mo loading. Electrochemical measurements showed that the high rate discharge capability and cycle stability of the material can be improved significantly by a small amount of Mo (2 at%). The sample with 2 at% Mo-doped amount exhibited a high initial discharge capacity of 146.3 mAh g$^{-1}$ at 0.3C rate under the voltage range of 2.5~4.2V, as well as better cycle stability after 50 cycles. Therefore, Mo-doped is a useful method to improve large current discharge capability of the lithium insertion nickel cobalt manganese oxides.

1. Introduction

With the development of large-scale battery systems such as electric vehicles (EVs) and energy storage systems (ESSs), the higher demand for various performance indicators of lithium-ion batteries has been put forward. Therefore, the development of new cathode materials with good stability and high specific capacity is the key to further increasing the energy density of lithium-ion batteries [1-2]. As an active cathode material, LiCoO$_2$ has been widely used in commercialized lithium-ion batteries due to its good cycling performance, low irreversible capacity loss, and easy of synthesis. However, the high cost and toxicity of cobalt limit its application in large capacity lithium-ion batteries such as electric vehicles. Therefore, researches about other materials to replace LiCoO$_2$ as lithium-ion battery cathode materials have become a hot spot [3]. LiNi$_{1-x}$Co$_x$Mn$_{1/3}$O$_2$ series which integrate the features of LiCoO$_2$, LiNiO$_2$ and LiMnO$_2$ are regarded as promising candidates and have attracted much attention due to high capacity, low cost, excellent cycling performance and safety [4-6]. LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ is more likely to replace LiCoO$_2$ because of its good safety and stability [7,8].

Recently, lithium-rich LiNi$_{1-x}$Co$_x$Mn$_{1/3}$O$_2$ has been considered as one of the most promising materials owing to its high voltage and capacity [9]. However, lithium-rich cathode materials still exist...
some problems in practical applications, such as high initially irreversible capacity, poor rate performance and decomposition of the electrolyte in the high voltages which deteriorate the cycle performance and safety problems. Therefore, the material is limited to laboratory research and development without reports on industrial application.

In this study, the layered Li$_{1.18}$(Ni$_{0.2}$Co$_{0.13}$Mn$_{0.67}$)O$_2$ cathode material was prepared by mixing lithium carbonate with Mo-doped precursor-nickel cobalt manganese hydroxide complex. And the influence of Mo-doped on physical and chemical parameters, morphology, structure, and electrochemical properties of the material were investigated by ICP analysis, X-ray diffraction, scanning electron microscopy (SEM) and electrochemical tests, respectively.

2. Experimental

2.1. Synthesis of materials

The Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$(OH)$_2$ as precursor was synthesized by hydroxide co-precipitation method. The solution of NiSO$_4$•6H$_2$O, CoSO$_4$•6H$_2$O, MnSO$_4$•H$_2$O (n(Ni):n(Co):n(Mn)=1:1:1) with a total concentration of 90 g L$^{-1}$ combined with NaOH and NH$_4$OH solution by peristaltic pump were transferred to a 30 L continuous stirred reactor with quantitative pure water, ammonia, and hydrazine hydrate. The reactor was protected by N$_2$ atmosphere. At the same time, the reaction is controlled by the stirring strength, temperature, the pH value, etc. Then, the precipitate was centrifuged and dried at 80°C overnight. Finally, the precursor Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$(OH)$_2$ was obtained.

Synthesis of Mo-doped Li$_{1.18}$(Ni$_{0.2}$Co$_{0.13}$Mn$_{0.67}$)O$_2$ sample: Based on the ratio of n(Mo):n(Mo+Ni+Co+Mn)=x(x=0, 0.05, 0.01, 0.02, 0.04), the precursor, lithium carbonate (n(Li):n(Ni+Co+Mn+Mo)=1.18:1) and molybdenum oxide was mixed and ground uniformly. The obtained mixture was preheated at 750°C for 8h (5°C min$^{-1}$), and then sintered at 900°C for 8h (1°C min$^{-1}$) in the Box type atmosphere resistance furnace. After cooling to room temperature, the sample was obtained by crushing and sieving.

2.2. Sample characterization

The elements analysis of samples was investigated by ICP spectrometer (IRIS Intrepid II XSP, Thermo Electron Corporation). The morphology of the samples was observed by scanning electron microscopy (SEM, JSM-6700F, Japan). The crystal structure of the samples were analyzed by XRD(D8 ADVANCE, Brooke, Germany). The particle size distribution of the samples was measured by Mastersizer 2000 laser particle sizer manufactured by the British company Malvern. The specific surface area of the sample was tested with the ASAP2010 fast specific surface area and pore size distribution analyzer manufactured by American Mack Company. The tap density of the samples was measured by the FZS4-4 tap density tester manufactured by Beijing Iron and Steel Research Institute.

2.3. Electrochemical tests

The positive electrode of the cell was made from a slurry containing 85 wt% active material, 8 wt% conductive acetylene black as a conductive agent and 7 wt% polyvinylidene fluoride (PVDF) as a binder dissolving in n-methyl pyrrolidinones. The slurry was evenly coated onto an aluminum foil and then dried in a vacuum oven at 120°C overnight. The foil was then punched into a circular electrode. Experimental cells were assembled in an argon atmosphere glove box using a lithium sheet as the anode material, the as-prepared electrode as the cathode material and a Celgard (2300) porous polypropylene as the separator material. The electrolyte is LBE-201 produced by Beijing Chemical Reagent Research Institute. Electrochemical measurements of LNCM/Li cells were carried out on a LAND CT2001A tester (Wuhan, China) in the voltage range of 2.5-4.2 V at room temperature.

3. Results and Discussion

3.1. The physical and chemical parameters of different Mo-doped amounts of samples
The content of each element in the final synthetic material was determined by ICP analysis. The physical and chemical parameters of different Mo amount of Li$_{1.18}$(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)$_{1-x}$Mo$_x$O$_2$ samples were shown in Table 1.

Table 1. The physical and chemical parameters of different Mo amount of samples.

| Sample number | Principal element content (wt%) | Residual lithium content (wt%) | physical parameters |
|---------------|---------------------------------|-------------------------------|---------------------|
|               | Li     | Ni     | Co     | Mn     | Mo     | LiOH   | Li$_2$CO$_3$ | D50 (μm) | TD (g cm$^{-3}$) | BET (m$^2$ g$^{-1}$) |
| Mo-0          | 8.09   | 19.26  | 18.76  | 17.79  | 0      | 0.087  | 0.15       | 7.54     | 1.8            | 0.47               |
| Mo-0.005      | 8.04   | 19.32  | 19.29  | 18.15  | 0.41   | 0.087  | 0.16       | 10.19    | 1.7            | 0.473              |
| Mo-0.01       | 7.84   | 19.21  | 19.22  | 18.13  | 0.86   | 0.14   | 0.19       | 10.01    | 1.7            | 0.476              |
| Mo-0.02       | 7.38   | 19.15  | 19.15  | 18.09  | 1.75   | 0.39   | 0.24       | 8.57     | 2.1            | 0.450              |
| Mo-0.04       | 7.06   | 18.55  | 18.58  | 17.55  | 2.53   | 0.40   | 0.25       | 9.56     | 2.1            | 0.375              |

As shown in Table 1, it can be seen that the specific surface area (0.47 m$^2$ g$^{-1}$) and the tap density of samples remained static fairly when the Mo loading is less than 1 at%. But the sharp increase of D50 is presumed to be a measurement error. When the Mo loading is greater than 1 at%, the specific surface area of sample gradually decreased to 0.375 m$^2$ g$^{-1}$. At the same time, the tap density of sample increased from 1.8 g cm$^{-3}$ to 2.1 g cm$^{-3}$ while the D50 increased slightly. It is showed that Mo-doped can improve the above three physical indicators. Moreover, the mass percentage of Li reduced drastically from 8.09 wt% to 7.06 wt% with the increase of Mo loading. It is mainly due to the atomic weight of Mo is almost twice than that of Ni, Co, and Mn. The replacement of Ni, Co, and Mn by the same mole number will inevitably lead to an increase in the total mass of the main metal element and the decrease of mass percentage of Li. However, the residual lithium content of LiOH and Li$_2$CO$_3$ increased from 0.087 wt% to 0.40 wt% and 0.15 wt% to 0.25 wt% with the increase of Mo loading, respectively. The possible explanation may be that the raw MoO is too alkaline before calcination incorporation and the introduced OH$^-$ reacted with Li in the lattice to form excessive LiOH residues.

3.2. Analysis of crystal structure of samples

![XRD patterns of Li$_{1.18}$(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)$_{1-x}$Mo$_x$O$_2$.](image)

Figure 1 shows the X-ray diffraction spectrum of different Mo amount in Li$_{1.18}$(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)$_{1-x}$Mo$_x$O$_2$ samples. It can be seen that the Mo-doped did not change the crystal structure of the samples and remained the layered lattice of α-NaFeO$_2$. With the increased amount of Mo, the intensity of the characteristic diffraction peak decreased gradually and the half width of the
(104) characteristic crystal plane peak increased gradually. Based on lattice strains and fault-tolerance theory, diffraction peak broadening may be due to crystal refinement or crystal distortion. Additionally, it can be seen that the second phase of Li$_2$MoO$_4$ appeared when the Mo amount reached 4 at%. It may be the main reason for the blurring of the grain boundaries.

3.3. Analysis of morphology of samples

![Figure 2. SEM images samples with of different x values.](image)

Figure 2 shows the typical SEM images of the Li$_{1.18}$Ni$_{0.333}$Co$_{0.333}$Mn$_{0.333}$$_x$Mo$_x$O$_2$ samples with different Mo amount. The changes of particle size and morphology are observed clearly in the figure 2. Apparently, the primary particles size is decreased and the boundary becomes more and more blurring with the increase of Mo amount, indicating that the calcination is not completely or the second phase is dissected. The XRD pattern of the samples showed that the second phase of Li$_2$MoO$_4$ begin to dissect until the Mo amount reached 4 at%. It may be the main reason for the blurring of the primary particles boundary at one time.

3.4. Study on electrochemical properties of samples

![Figure 3. Discharge capacities at different rates.](image) ![Figure 4. Discharge ability at different rates.](image)

Figure 3 shows the discharge capacities of the samples with different Mo amount at different rates. It can be observed that the initial discharge capacities of the all the samples with Mo content X=0, X=0.005, X=0.01, X=0.02, X=0.04 are 136.9 mAh g$^{-1}$, 138.4 mAh g$^{-1}$, 140.3 mAh g$^{-1}$, 146.3 mAh g$^{-1}$ and 138.5 mAh g$^{-1}$ at the rate of 0.3 C, respectively. As the amount of Mo increased, the discharge capacity shows the trend of increasing first and then decreasing and almost larger than undoped samples. The discharge capacity at 0.3 C increased from 136.9 mAh g$^{-1}$ (undoped) to 146.3 mAh g$^{-1}$ (2 at% Mo) and then decreased to 138.5 mAh g$^{-1}$ (4 at% Mo). Figure 4 shows the discharge ability of samples with different Mo amount. As can be seen, only the sample with 1 at% Mo content exhibits greater discharge ability at 5 C than undoped samples.
Figure 5 shows the cycle performance of the samples of $\text{Li}_{1.18}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{Mo}_x\text{O}_2$ with different Mo amount at 0.3C. Obviously, both undoped samples and samples with Mo amount less than 2 at\% show better cycle stability after 50 cycles, and the cycle discharge capacity declines rapidly from 35 cycles only when the Mo amount reached 4 at\%.

4. Conclusions
$\text{Li}_{1.18}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{Mo}_x\text{O}_2$ (x=0, 0.005, 0.01, 0.02, 0.04) cathode materials have been prepared by co-precipitation and high-temperature solid state method. The second phase of $\text{Li}_2\text{MoO}_4$ is dissected when Mo amount is above 4 at\%. The discharge capacity of the sample increased from 136.9 mAh g$^{-1}$ (0 at\% Mo) to 146.3 mAh g$^{-1}$ (2 at\% Mo) and then decreased to 138.5 mAh g$^{-1}$ (4 at\% Mo) in the range of 2.5-4.2 V. In conclusion, it is founded that the samples with Mo-doped amount less than 2 at\% shows a better cycle stability after 50 cycles of charge and discharge.

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