Advances in Machinery, Materials Science and Engineering Application
M. Chen et al. (Eds.)

doi:10.3233/ATDE220436

Modified Ni-Rich $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ Cathode Material via Li_3BO_3 Coating for Lithium Batteries

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Abstract. High nickel ternary cathode materials are less expensive, more productive, and less environmentally harmful than conventional cathode materials. Thus, it becomes one of the best cathode materials for lithium-ion batteries. However, there are also clear drawbacks to high nickel ternary materials, for instance its inadequate cycle life, poor structural and heat stability, which limit its future development. In this work, $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) material was studied and modified using Li_3BO_3, a lithium-ion conductor-type compound, as its coating layer. Studies reveal that after 1 wt percent -Li_3BO_3 coating, the first discharge capacity at a 2 C rate rose from 162.7 mAh g^{-1} to 185.9 mAh g^{-1}. After 250 cycles, the capacity retention of the Li_3BO_3-coated sample was 87%, compared to just 82.5% for the uncoated sample. The introducing of Li_3BO_3 coating material of NCM811 can significantly improve the electrochemical performance of materials for lithium-ion battery cathodes that are high in nickel ternary.

Keywords. Lithium-ion battery, coating, $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$, Li_3BO_3

1. Introduction

As lithium-ion batteries are used in everyday items, they have gained a certain share in the market by virtue of their high operating voltage, small self-discharge rate, no memory effect and high energy density [1, 2]. The cathode material, among them, has a significant effect on the overall performance of lithium-ion batteries, accounting for about forty percent of the whole lithium-ion battery. As a result, it is crucial to conduct work into cathode materials for lithium-ion batteries in order to advance the current battery industry.

The ternary cathode materials have excellent electrochemical properties, and compared with $LiCoO_2$, in addition to having a more stable structure, they also perform well in terms of safety. However, ternary materials also have some disadvantages of their own, especially the high nickel ternary materials [3, 4], the increase of nickel increases the specific capacity, but the cycle performance decreases; It is simple for ternary materials to react with moisture and atmospheric carbon dioxide to produce LiOH and Li_2CO_3,thus making the cycle performance poor at high voltage, the low electronic conductivity leads to high internal resistance and poor multiplier performance, etc. As a result, in order to meet the demand for further enhancing its power density for Li-ion

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batteries, it is vital for us to improve its cycle performance and rate performance of NCM811.

Numerous researchers have modified NCM811 materials using a variety of techniques, such as ion doping, protective coating modification, and cathode material structure design, to enhance their overall electrochemical performance [5, 6].

A very efficient way to enhance the electrochemical characteristics of cathode materials is surface coating modification. Surface coating has the following effects [7, 8]: (1) It can enhance the interface effect and minimize direct interaction of cathode material and electrolyte; (2) it can improve the charging and discharging performance under high current; (3) It can enhance the material's cycling performance. Monomer coating, oxide coating, fluoride coating, phosphate coating, and other popular coating compounds are examples. As a result, it's critical to increase the cathode materials' electrochemical performance by preventing the side-effects with the electrolyte through surface coating.

In order to improve the stability of the crystalline structure and the NCM811's electrochemical performance, lithium borate was used as a surface coating in this research.

2. Experiment

2.1. Material Preparation

2.1.1. Preparation of Original NCM811 Materials

$Ni(NO_3)_2$-$6H_2O$(AR), $Co(NO_3)_2$-$6H_2O$ (AR), $Mn(NO_3)_2$-$4H_2O$(AR) and NaOH (AR) were used as synthetic raw materials to prepare a mixed solution with a concentration of 2 mol/L (n(Ni):n(Co):n(Mn) = 8:1:1) in proportion to 2 mol/L of NaOH solution. In a water bath at 50 °C, the prepared solution was added to the reaction vessel with an appropriate amount of ammonia at the same time, and the pH was controlled in a certain range, and the reaction was conducted for five minutes with stirring at an 800 rpm speed to produce the precipitate. To obtain $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ precursor, the precipitate was collected, cleaned, and dried in a vacuum drying oven. The precursor was mixed with an appropriate amount of LiOH-H_2O and sent into a programmed temperature-controlled tube furnace, fed with O_2 and roasted at 800 °C for 15 h. To generate NCM811 material, the precursor was removed until cooling to ambient temperature.

2.1.2. Preparation of 1 wt% Li_3BO_3 Coating Material

500 mg of NCM811 powder was homogeneously mixed with 60 ml of 0.05 mol L^{-1} LiOH solution and agitated at 25°C for 5 h. Subsequently, 10 ml of H_3BO_3 solution with the same concentration was added dropwise and stirred at 80°C for 24 h until all the water was evaporated. The dried material was then put into a muffle furnace immediately then sintered for three hours at 450°C in an air environment. The modified sample of Li_3BO_3 coating of lithium ion conductor was obtained by natural cooling.

2.2. Materials Characterization

In this work, a DX-1000 X-ray diffractometer from Thermo, USA, was used for structural analysis of the material with a tube voltage setting of 40 KV, a tube current setting of 25 mA, a step size of 0.1°, a step interval of 0.2 s, and a scan range of 10°-90°. The scanning electron microscope NSPECT F from Thermo, USA, was employed to examine the samples' morphology in this paper. Escalab-250Xi X-ray photoelectron spectrometer from Thermo Fisher, USA was used to analyze the samples.

2.3. Electrochemical Measurements

First, electrode sheets were prepared in the ratio of active substance: conductive agent (acetylene black): binder (PVDF)=85 wt.%: 10 wt.%: 5 wt.%, and the composition of electrolyte was l mol/L LiPF6/EC+DMC+EMC (volume ratio 1:1:1), and lithium sheets were selected for electrodes, Celgard 2316 polypropylene microporous membrane. The electrochemical test was performed on the Land CT2001A charge/discharge test system, and the voltage range selected for the charge/discharge test was 2.5-4.3 V. The material was first charged at a constant current to 4.3 V, and then discharged to 2.5 V. The charge/discharge test is performed at 2C rate.

3. Results and Discussion

The XRD patterns of pure phase NCM811 and samples with a 1 wt percent-Li_3BO_3 coating are displayed in figure 1. The figure demonstrates that both samples' diffraction peaks are rather crisp and no other heterogeneous phases are seen, which indicates that the crystallinity of the material is relatively high and NCM811 has a typical layered α-$NaFeO_2$ structure. By comparison, It is evident that the XRD patterns of the Li_3BO_3 coated battery and the uncoated NCM811 battery are basically the same, and no new diffraction peaks appear, thereby showing that the crystallite architecture of the NCM811 powder is not appreciably altered by the Li_3BO_3 coating.

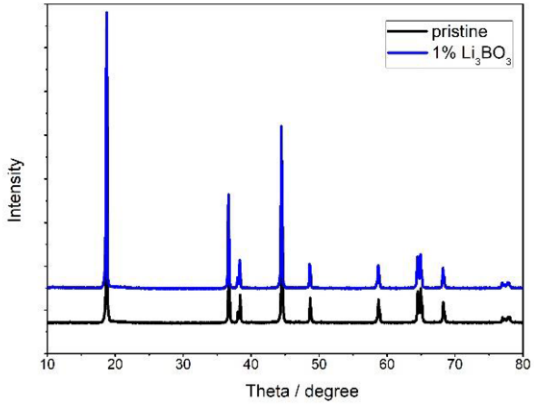

Figure 1. XRD patterns of NCM811 samples with pure phase and 1 wt%-Li_3BO_3 coating.

Figure 2 shows SEM patterns of NCM811 samples with pure phase and 1wt%-Li_3BO_3 coating content, the a, c show the original samples and figures 2(b), (d) display the samples with 1wt%-Li_3BO_3 coating. The figure shows that there is no appreciable difference in the samples' shapes before and after coating, both samples are packed secondary particles that composed of nanometre original particles with an averagecrystallite of 200-500 nm, 200-500 nm. Indicating that this coating method has almost no effect on the morphology of the NCM811 material. Comparing figures 4(c) and (d), it is obvious that Li_3BO_3 wrapping sample has larger particle size than the pure phase sample, and the faint traces of crystalline coating of Li_3BO_3 phase can be observed from the red square frame. As a protective layer, the Li_3BO_3 coating layer can lessen the electrolyte's ability to corrode the NCM811 powder, increase its structural integrity of the NCM811 electrode, and enhance the cycling performance of the cell.

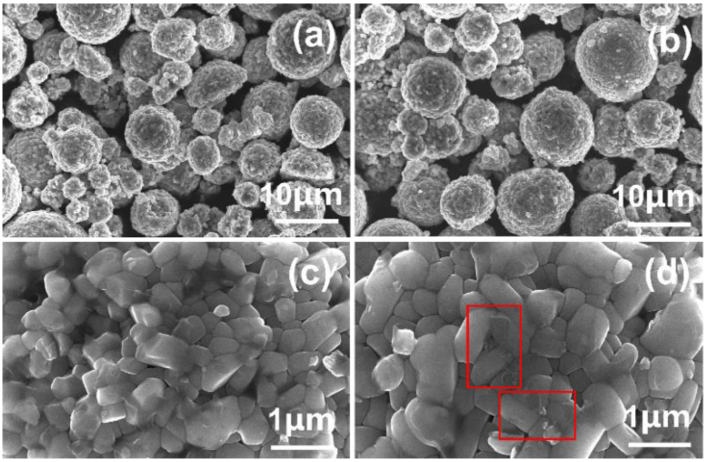

Figure 2. SEM patterns of NCM811 samples with pure phase and 1 wt%- Li_3BO_3 coating.

To look into how the Li_3BO_3 coating affected the electrochemical performance of NCM811 cathode material, a cycling performance test was performed. The cycling performance of the pure material at 2C magnification is depicted in figure 3 and compared with that of the 1 wt%-Li_3BO_3 coated NCM811 sample. It can be seen that the Li_3BO_3 coated modified sample has significantly higher discharge capacity, better cycle stability and longer service life than the original sample at 2C rate. The 1 wt%-Li_3BO_3 modified sample had an initial discharge capacity of 187 mAh g^{-1} compared to the original material's 165 mAh g^{-1}. For the beginning of the discharge, original sample showed a process of performance activation, while the Li_3BO_3 modified sample had a smoother discharge capacity, the trend of the two curves was basically the same when the number of cycles exceeded 15 times, and as the number of cycles increased, the sample capacity became more stable. The Li_3BO_3 coated modified samples are more stable and have better electrochemical performance than the pure phase original samples. As can be observed, a protective layer of Li_3BO_3 has been applied to the edge of the original grains to decrease direct interaction across electrode and electrolyte, suppress side reactions and guard against HF and other electrolyte components corroding the active material.

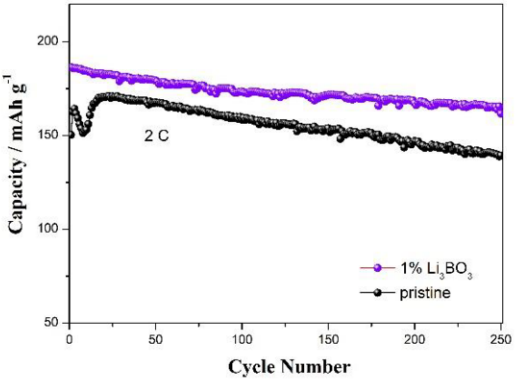

Figure 3. Cycling performance of pure phase NCM811 and 1 wt%-Li_3BO_3 coating samples at 2C rate.

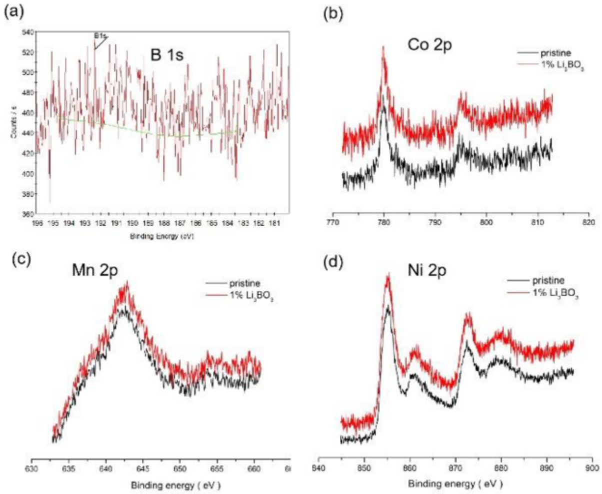

Figure 4. (a) XPS spectra of B, (b-d) XPS spectra of Co-Mn-Ni.

Next, we used XPS to further analyze their chemical elemental components and valence states on the surface of the materials. The element B's XPS spectrum is shown in figure 4(a), and it shows that Li_3BO_3 has been successfully coated on the sample's surface. According to figures 4(b)-(d), the binding energies of Ni 2p1/2 , Co 2p1/2 and Mn 2p1/2 are located at 874.8, 803.2 and 657.1 eV, comparable to Ni^{2+} , Co^{3+} and Mn^{4+} ions in the samples, respectively. In contrast, the XPS peak positions of the above transition metal elements in the Li_3BO_3 coated sample did not shift significantly, indicating that the coating of Li_3BO_3 did not alter the electron status of the native material's transition metal ions [9, 10].

4. Conclusion

In this work, NCM811 was investigated for Li_3BO_3 surface coating modification. The results of SEM, XRD and XPS tests confirmed that introducing Li_3BO_3 wasn't really change the morphology, structure of the crystal or elemental valence of the original material. The cycling performance of the prepared materials was tested, and the initial capacity of the original powder was 165 mAh g^{-1} at 2C rate, and the sample modified by 1 wt%-Li_3BO_3 coating was 187 mAh g^{-1}, the cycle performance of the sample modified by Li_3BO_3 coating was much stable. This is because the protective Li_3BO_3 coating layer serves as a layer, which reduces the corrosion of the active material by HF and other substances in the electrolyte, prevents adverse effects, increases the cycling stability of the material, and improves the electrochemical performance of NCM811 material.

Acknowledgements

The funding support for this project came from the Research of Dongguan Science and Technology of Social Development Program (No.20211800905482); Scientific Research Project of Guangdong University of Science and Technology (No. GKY-2021KYZDK-4); Project of Characteristic Innovation of Guangdong Province(No.2021KTSCX148); 2021 Teaching Quality and Teaching Reform Project of Undergraduate Colleges and Universities in Guangdong Province (Yue Jiao Gao Han [2021] No. 29); Dongguan Sci-tech Commissoner Program (No.20201800500592; No.20201800500622);

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