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# Co-effect of $AlF_3$ and $MgF_2$ Coating on the Electrochemical Performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Cathode Material under High Voltage

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**Abstract.** $AlF_3$ and $MgF_2$ were applied to modify the surface of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material. The structural and electrochemical properties of the materials were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), charge–discharge tests and electrochemical impedance spectra (EIS). The results show that the 1 wt.% $AlF_3$ and 1 wt.% $MgF_2$ coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM333) cathode material exhibits an optimized electrochemical performance. It presents an initial capacity of 207.2mAh/g and 169.1mAh/g at 0.2C between 2.8V and 4.7V after charge-discharge 65 cycles. The rate performance is also enhanced because the coating decreases the interface charge transfer impedance.

## Introduction

Recently, lithium ion batteries have been widely used in portable electronic devices, such as portable energy storage, hybrid electric vehicles (HEVs) and electric vehicles (EVs) [1], owing to their high energy density and good cycling performance. It is believed that the cathode material is the key point to the Li-ion batteries. Among them $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ has been successfully commercialized because it exhibits lower cost and better electrochemical performance than $LiCoO_2$, easier synthesis and better thermal stability than $LiNiO_2$. But its cycle performance and rate capacity are unsatisfactory because of the surface reaction between the highly delithiated cathode and the electrolyte at high cut-off voltage (>4.5V) [2-4].There are several ways to overcome these situations, surface-coating of the cathode materials with stable substance (such as oxides, phosphates, and fluorides) is an effective method [5-9]. $AlF_3$ coating has been reported to improve the capacity, rate capability and cycling stability of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ remarkably [10-12]. However, to the best of our knowledge, no work about $AlF_3$-$MgF_2$-coated NCM333 was reported. In this work, $AlF_3$ and $MgF_2$ were introduced as a coating to $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode. As a result, the cycle performance and rate capability of the cathode were improved markedly.

## Experimental

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders (provided by CITIC Guoan MGL Power Technology Co., Ltd.) were used without further purification. Firstly, the active material was slowly poured into the polyvinyl pyrrolidone (PVP) solution with continuous stirring. Then aluminum nitrate nonahydrate and ammonium fluoride were added to the solution in order. The amount of $AlF_3$ in the solution was 1wt.% of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders. The mixture solution was then stirred for 5h until a homogeneous solution was obtained at room temperature. The obtained precipitates were filtered, washed, dried. The dried precipitate was heated at 400°C for 3h in air atmosphere to form $AlF_3$-coated products namely A-NCM333. Afterward, the $MgF_2$-coated A-NCM333 was prepared in the same way.

The electrochemical characterization was performed using CR2025 coin cells. The cell consisted of a cathode with the composition of 84 wt.% active material, 8 wt.% Super P, and 8 wt.% polyvinylidene fluoride (PVDF), and a lithium metal anode separated by a celgard 2400 microporous film. The electrolyte was 1mol•$L^{-1}$ $LiPF_6$/EC+DMC (1:1 in weight). The cells were assembled in glove box filled with pure argon.

Charge-discharge measurement was performed on CT2001A Land tester (Wuhan Jinnuo Electronics Co.,Ltd).Electrochemical impedance spectra(EIS) was measured on CHI6081D..X-ray diffraction (XRD) patterns were measured using an Ultima IV diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) images were taken using a S-4800 electron microscope.

## Result and Discussion

Fig.1 shows XRD patterns of the pristine and $AlF_3$+$MgF_2$-coated NCM333 powders. All the diffraction peaks of the samples can be indexed based on a layered α-$NaFeO_2$-type structure (space group $R\bar{3}m$) and no impurity phases are observed in patterns. The lattice constants are calculated and summarized in Table 1.The values of the coated sample are close to those of the pristine sample, indicating that the $AlF_3$ and $MgF_2$ were not incorporated into the crystal structure.

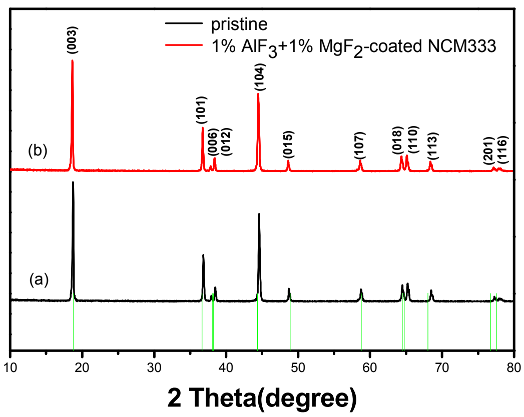
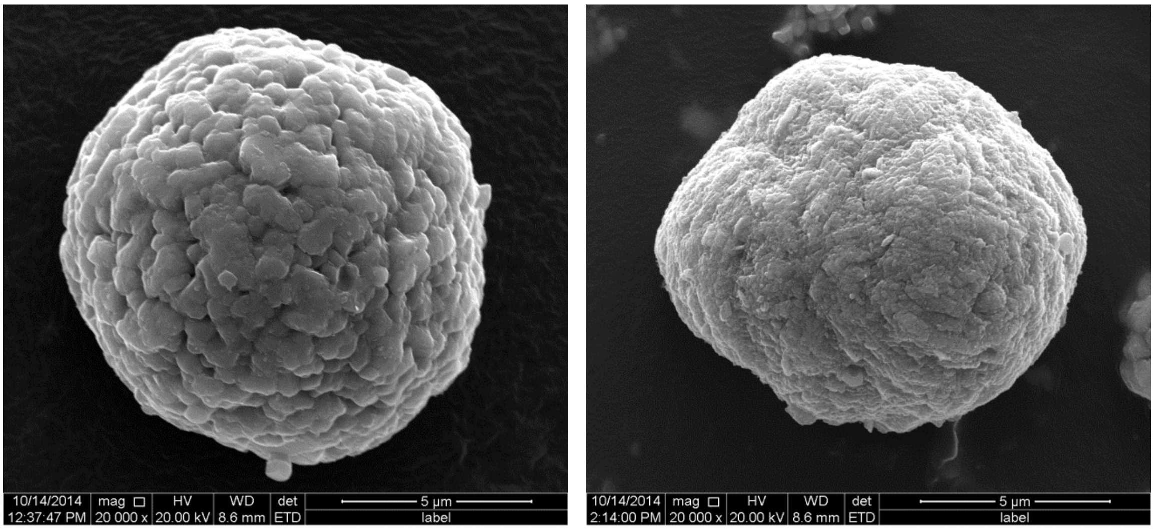



Fig.1. XRD patterns of (a) pristine and (b) $AlF_3$+$MgF_2$-coated NCM333 samples

TABLE 1. THE LATTICE CONSTANTS OF (A) PRISTINE AND (B)$ALF_3$+$MGF_2$-COATED NCM333 SAMPLES

| Sample | a/ Å | c/Å | c/a |
|---|---|---|---|
| a | 2.8593 | 14.2284 | 4.9762 |
| b | 2.8640 | 14.2513 | 4.9760 |

Fig.2 presents SEM images of the pristine and $AlF_3$+$MgF_2$-coated NCM333 powders. The pristine material showed very smooth surface. However, we can observe a rough coating layer on the surface of $AlF_3$+$MgF_2$-coated NCM333.So we believe that $AlF_3$ and $MgF_2$ coated successfully on the surface of the pristine powder. The coating layer could reduce the direct contact between electrolyte and electrode, thus can suppress the occurrence of side reactions especially at high voltage [11].




(a) (b)

Fig.2. SEM images of (a) pristine and (b) $AlF_3$+$MgF_2$-coated NCM333 materials

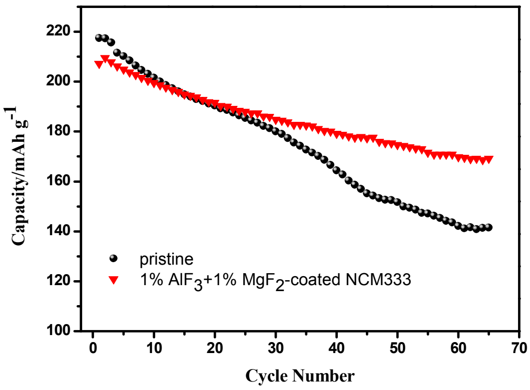



Fig.3. Cycling performance of pristine and $AlF_3$+$MgF_2$-coated NCM333 cathodes at 0.2C

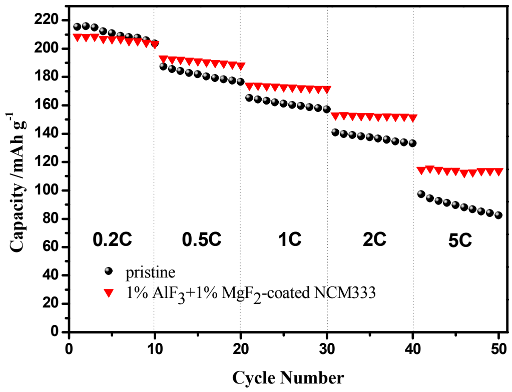
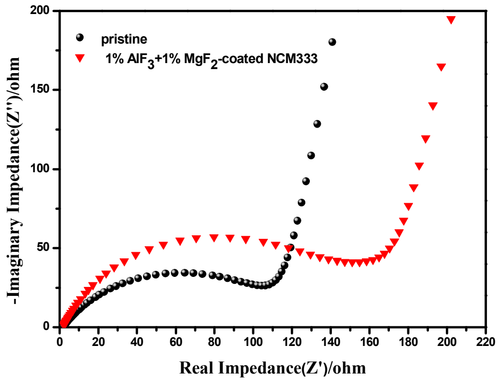


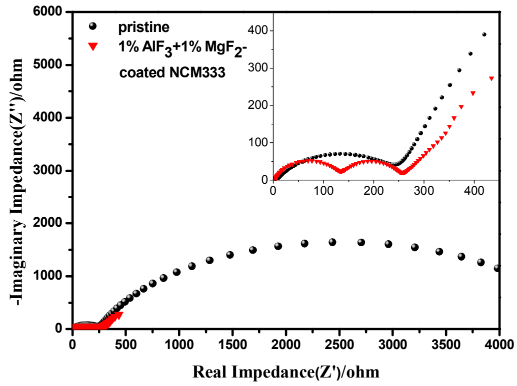

Fig.4. Rate capability of the pristine and $AlF_3$+$MgF_2$-coated NCM333 cathodes, cycled between 2.8V and 4.7 V at rate from 0.2C to 5C for 10 cycles per step.

The cycling performance of the Li/pristine and Li/$AlF_3$+$MgF_2$-coated NCM333 at 0.2C-rate (1C=180mAh/g) between 2.8V and 4.7V are shown in Fig.3.It can be clearly observed that a slight capacity variation occurs for the $AlF_3$+$MgF_2$-coated NCM333.By contrast, there is an abrupt capacity loss with the pristine material. The discharge capacity of the pristine sample charges from 217.5mAh/g to 141.1mAh/g after 65 cycles with capacity retention of 64.87%.While,the coated-sample exerts a higher discharge capacity of 207.2mAh/g and maintains 169.1mAh/g after 65 cycles with capacity retention of 81.61%.Hence, we can conjecture that coating layer($AlF_3$ and $MgF_2$) on the surface of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is very effective in preventing direct contact of the active material with the electrolyte solution, thus suppress the occurrence of side reactions especially at high voltage. It is consistent with the SEM results in Fig.2.

The rate performances of the pristine and $AlF_3$+$MgF_2$-coated NCM333 are shown in Fig. 4. All the cells are charged and discharged at 0.2, 0.5, 1, 2 and 5C-rates, respectively. It is clearly that the coated sample exhibits a superior rate capability than the pristine one. For example, it demonstrates a discharge capacity of 113.7mAh/g with capacity retention of 54.53% after 10 cycles at 5C, while the pristine is only 82.2mAh/g and 38.45%. Thence the coating layer is beneficial to improve the rate capability of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ at high voltage. This could be due to the coating layer suppress the occurrence of side reactions especially at high voltage.




(a)




(b)

Fig.5. Electrochemical impedance spectroscopy (EIS) of Li/pristine and Li/$AlF_3$+$MgF_2$-coated NCM333 cells (a) before cycling (b) after 65 cycles

To further demonstrate the effect of the coating layer on the electrochemical performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, electrochemical impedance spectroscopy tests were performed on all of samples at different cycle number. As shown in Fig.5 the spectroscopy including two resistance factors: the semicircle in the high-to-medium frequency region represents resistance of surface film ($R_{sf}$) that covers cathode particle and the other semicircle in the low frequency region is attributed to the charge transfer resistance ($R_{ct}$) coupled with a double-layer capacitance. Before cycling, the resistance of the $AlF_3$+$MgF_2$-coated NCM333 is larger than that of the pristine, this is consistent with previous results in Fig.3 that the original discharge capacity of the pristine is larger than that of the $AlF_3$+$MgF_2$-coated NCM333. And after cycled 65 times there is a significantly difference between the two materials. The $R_{sf}$ of the pristine is 247.1 Ω, the $R_{ct}$ is as high as 4547Ω, while the $AlF_3$+$MgF_2$-coated NCM333 is 131.7Ω and 115.2Ω respectively. The smaller resistance of the coated sample explains the rate performance improvement.

## Summary

In conclusion, the $AlF_3$+$MgF_2$-coated NCM333 cathode exhibits a high capacity of 169.1mAh/g at 0.2C between 2.8V and 4.7V after charge-discharged 65 cycles, and 81.61% of capacity retention. While the pristine material shows a capacity of only 141.1mAh/g with capacity retention of 64.87%. For the coated sample, a smaller charge transfer resistance than the one in the pristine cathode is due to the formation of a stable interface. These results imply that 1wt.% $AlF_3$ and 1wt.% $MgF_2$ coating on the surface of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ effectively modifies the electrochemical properties of the cathode under high voltage.

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