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**Abstract**

Electrical Vehicles (EVs) are very important in reducing fossil oil consumption and carbon emission in cities. Spinel $LiNi_{0.5}Mn_{1.5}O_4$ is one promising cathode material for lithium ion batteries used in EVs owing to its high power density. Here $AlF_3$ coated $LiNi_{0.5}Mn_{1.5}O_4$ is prepared through an newly developed method. The spinel oxide sintered at 900°C presents the best electrochemical performance with a specific discharge capacity of 132.4 mAh/g at 0.5 C. 81.0% of the initial specific capacity can be retained after 50 cycles. $AlF_3$ coating can further improve the electrochemical performance. The initial specific capacity at 10 C is enhanced from 104.6 to 109.1 mAh $g^{-1}$ with the capacities retention increasing from 80.6 to 92.1% after 100 cycles.


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# Spinel oxide cathode material for high power lithium ion batteries for electrical vehicles

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**Abstract**

Electrical Vehicles (EVs) are very important in reducing fossil oil consumption and carbon emission in cities. Spinel $LiNi_{0.5}Mn_{1.5}O_4$ is one promising cathode material for lithium ion batteries used in EVs owing to its high power density. Here $AlF_3$ coated $LiNi_{0.5}Mn_{1.5}O_4$ is prepared through an newly developed method. The spinel oxide sintered at 900 ℃ presents the best electrochemical performance with a specific discharge capacity of 132.4 mAh/g at 0.5 C. 81.0% of the initial specific capacity can be retained after 50 cycles. $AlF_3$ coating can further improve the electrochemical performance. The initial specific capacity at 10 C is enhanced from 104.6 to 109.1 mAh $g^{-1}$ with the capacities retention increasing from 80.6 to 92.1% after 100 cycles.


Peer-review under responsibility of the organizing committee of CUE 2015

**Keywords:** Lithium ion batteries; Electrical Vehicals; Spinel oxide; High power density

## 1. Introduction

With the energy crisis and environmental pollution concerns, using Electrical Vehicles (EVs) and Hybrid Electrical Vehicles (HEVs) instead of traditional vehicles are very important in reducing fossil oil consumption and carbon emission in cities. Lithium ion batteries (LIBs) are the most promising power sources for EVs and HEVs because of their several advantages over other kinds of batteries[1]. In 1997, Gao and co-workers firstly reported the $LiNi_{0.5}Mn_{1.5}O_4$ with lithium ions intercalating at 4.7 V [2]. Its

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theoretical specific capacity is 146.7 mAh/g, and energy density is 20% higher than that of the commercial $LiCoO_2$[3]. For these reasons, spinel $LiNi_{0.5}Mn_{1.5}O_4$ is considered to be a promising cathode material for LIBs with high-power and high energy density. However, this material suffers from the poor stability due to the side reactions with the electrolyte at high voltage and the dissolution of Mn and Ni ions at elevated temperatures. Different approaches have been proposed to improve the electrochemical performance of $LiNi_{0.5}Mn_{1.5}O_4$ including lattice doping and surface modification. Recently, various dopants, e.g. Mg[4] and Ru[5], and various surface coatings, e.g. BiOF[6], ZnO[7], $Bi_2O_3$[8] and $AlPO_4$[9] have been applied to improve the electrochemical performance of $LiNi_{0.5}Mn_{1.5}O_{4.}$

In the present study, high crystallinity and homogenous $LiNi_{0.5}Mn_{1.5}O_4$ was synthesized using an improved solid-state method. The obtained $LiNi_{0.5}Mn_{1.5}O_4$ exhibits high rate performance, good cyclic stability and a nearly single plateau at 4.7 V. Furthermore, $AlF_3$ was successfully coated by a newly developed method on the surface of $LiNi_{0.5}Mn1_{.5}O_4$ particles to improve the electrochemical performance be reducing the interfacial reactions with the electrolyte.

**Nomenclature**

| | | | |
|---|---|---|---|
| LIBs | Lithium ion batteries | EVs | Electrical vehicles |
| HEVs | Hybrid electrical vehicles | XRD | X-ray diffraction |
| SEM | Scanning electron microscopy | | |

## 2. Material and methods

### *2.1. Synthesis methods*

$LiNi0_{.5}Mn_{1.5}O_4$ was synthesized using an improved solid-state method. $Mn(Ac)_2{\cdot}4H_2O$ and $Ni(Ac)_2{\cdot}4H_2O$ were dissolved in distilled water and stirred at 90 ℃ for 5 h. The mixture was then dried at 120 ℃in air for 10 h to form a solid-state phase mixture followed by a calcination process at 400℃ for 6 h to form the precursor. The precursor was mixed with $Li_2CO_3$ and sintered at 900 ℃ for 16 h in the muffle furnace, and then maintainied at 650 ℃ for 10 h before the cooling process to get the final products. The samples were denoted as A-900. $AlF_3$-coated $LiNi0_{.5}Mn_{1.5}O_4$ were prepared by using A-900 as the starting material. $Al(NO_3)_3{\cdot}9H_2O$ and A-900 were mixed in distilled water under stirring, and then $NH_4F$ solution was dropped into the turbid liquid. The suspended mixture was stirred at 80℃ until the solvent was completely evaporated and dried in air at 110℃ for 3 h. The resulting powders were calcined at 550℃ for 5 h to get $AlF_3$-coated $LiNi_{0.5}Mn_{1.5}O_4$.

### *2.2. Physical characterization*

The structure of the samples were characterized by X-ray diffraction (XRD)(Bruker, D8) with Cu Kα radiation at 40 KV and 40 mA in steps of 0.02° from 10° to 80°. The surface morphology was examined using a JEOL 6300F scanning electron microscopy (SEM) at 20 KV.

### *2.3. Electrochemical characterization*

The electrochemical performance of the samples was estimated using coin cells using Polypropylene microporous membrane (Celgard 2400) as the separator, Li metal as the anode and $LiNi_{0.5}Mn_{1.5}O_4$ as the cathode. The cathode was composed of 80% $LiNi_{0.5}Mn_{1.5}O_4$, 12% acetylene black and 8% PVdF binder. The electrolyte was 1 M $LiPF_6$ in a mixture of ethylene carbonate, diethyl carbonate, dimethyl carbonate and Fluoroethylene carbonate (1:1:1:1, v/v/v/v). The cells were assembled in a glove-box (MBraun, Lab Master130) filled with argon. The charge/discharge tests were performed on a Neware instrument.

## 3. Results and discussions

### *3.1. Structure and morphology*

All the characteristic XRD peaks were in compliance with that of $LiNi_{0.5}Mn_{1.5}O_4$(ICDD/JCPDS, PDF#46-0810), indicating that the sample exhibits well-defined cubic spinel structures with a space group of Fd3m. $LiNi_{0.5}Mn_{1.5}O_4$ greatly suffers from reacting with electrolyte at high voltage and Mn dissolving at high operating temperature. To address this issue, surface coating with $AlF_3$ has been applied on $LiNi_{0.5}Mn_{1.5}O_4$. Fig.1 shows the SEM images of pristine sample A-900, 1 and 3 wt.% $AlF_3$-coated $LiNi_{0.5}Mn_{1.5}O_4$. $AlF_3$ can be found on the surface of spinel $LiNi_{0.5}Mn_{1.5}O_4$ crystals. The surface roughness of the samples increases while increasing the coating amount of $AlF_3$ from 0 wt% to 3 wt%.

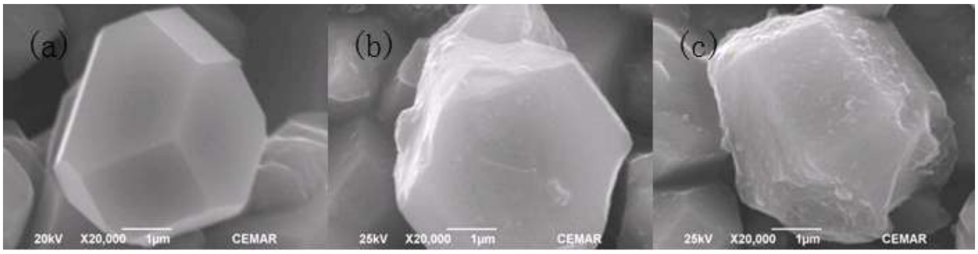


**Fig.1 S**EM images of the pristine sample A-900(a), 1(b) and 3(c) wt.% $AlF_3$-coated $LiNi_{0.5}Mn_{1.5}O_4$.

### *3.2. Electrochemical performance*

The specific discharge capacities at the 2$^{nd}$ cycle of A-900 at 0.5 and 10 C are 125.6 and 104.1 mAh/g, respectively. Comparing to the bare sample, the 1 wt.% $AlF_3$-coated $LiNi_{0.5}Mn_{1.5}O_4$ has better discharge capacities, which are 127.1 and 108.3 mAh/g, respectively. In contrast, the 3 wt.% $AlF_3$-coated $LiNi_{0.5}Mn_{1.5}O_4$ exhibits a worse discharge capacities,120.9 and 93.9 mAh/g at 0.5 and 10 C, respectively. The 1$^{st}$ charge/discharge curves cycled at 0.5 C of pristine sample A-900 and 1wt.% $AlF_3$-coated $LiNi_{0.5}Mn_{1.5}O_4$ indicate that surface modification did not improve the efficiency of the 1$^{st}$ cycle, we consider that the decomposition of the electrolyte is the main reason for the irreversible charge capacity.The above results indicated that proper amount of $AlF_3$ coating can increase the discharge capacity, and therefore need to be optimized in the future research.

The cyclic performance of pristine sample A-900, 1 and 3 wt.% $AlF_3$-coated $LiNi_{0.5}Mn_{1.5}O_4$ at the low and high current densities over the voltage range of 3.5-4.9 V, respectively. The charge and discharge voltages platforms did not show significant changes after 50$^{th}$ cycles at 0.5 C and 100$^{th}$ cycles at 10 C, indicating that the polarization phenomenon is not serious(Fig. 2a). The capacity retention of the pristine sample A-900 is 84.3%, while 91.8% and 90.3% of the initial discharge capacities can be retained for 1 and 3 wt.% $AlF_3$-coated $LiNi_{0.5}Mn_{1.5}O_4$, respectively. In high charge/discharge rate, the specific discharge capacities of pristine sample A-900, 1 and 3 wt.% $AlF_3$-coated $LiNi_{0.5}Mn_{1.5}O_4$ after 100 cycles are 84.3, 99.7 and 98.5 mAh/g, respectively( Fig.2b). On the contrast, the 1.0 wt.% $AlF_3$-coated $LiNi_{0.5}Mn_{1.5}O_4$ shows the best capacity retention (91.8% at 0.5 C and 92.1% at 10 C). The best cyclability of 1 wt.%

$AlF_3$-coated $LiNi_{0.5}Mn_{1.5}O_4$ might be attributed to the suppression of side reaction of the electrolyte and the electrode surface. $AlF_3$-coated $LiNi_{0.5}Mn_{1.5}O_4$ shows superior electrochemical performance especially at high rate to the commercial cathode material $LiFePO_4$ used in lithium ion batteries [10].

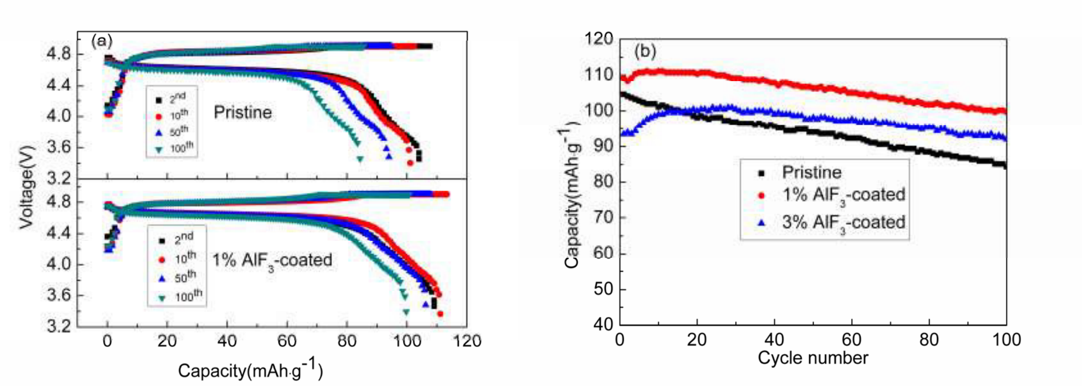


**Fig.2** The charge-discharge curves (a) and cycling performance (b) of the pristine sample A-900, 1 and 3 wt.% $AlF_3$-coated $LiNi_{0.5}Mn_{1.5}O_4$ at 10 C.

## 4. Conclusions

$LiNi_{0.5}Mn_{1.5}O_4$ was successfully prepared by a modified solid-state method for high power LIBs for EVs and HEVs. The $LiNi_{0.}5Mn_{1.5}O_4$ sintered at 900 ℃ shows the largest initial specific discharge capacity. A newly developed $AlF_3$ coating on $LiNi_{0.5}Mn_{1.5}O_4$ particles can remarkably improve the initial specific discharge capacity and the capacity retaining especially at high current densities. These results show that high power LIBs using $AlF_3$-coated $LiNi_{0.5}Mn_{1.5}O_4$ as cathode materials are promising power sources for EVs and HEVs to reduce energy consumption and carbon emission.

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