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

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Abstract
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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. 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 LiCoO₂. For these reasons, spinel LiNi₀.₅Mn₁.₅O₄ 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 LiNi₀.₅Mn₁.₅O₄ including lattice doping and surface modification. Recently, various dopants, e.g. Mg⁴⁺ and Ru⁵⁺, and various surface coatings, e.g. BiOF⁶⁻, ZnO⁷⁻, Bi₂O₅⁸⁻ and AlPO₄⁹⁻ have been applied to improve the electrochemical performance of LiNi₀.₅Mn₁.₅O₄.

In the present study, high crystallinity and homogenous LiNi₀.₅Mn₁.₅O₄ was synthesized using an improved solid-state method. The obtained LiNi₀.₅Mn₁.₅O₄ exhibits high rate performance, good cyclic stability and a nearly single plateau at 4.7 V. Furthermore, AlF₃ was successfully coated by a newly developed method on the surface of LiNi₀.₅Mn₁.₅O₄ particles to improve the electrochemical performance be reducing the interfacial reactions with the electrolyte.

<table>
<thead>
<tr>
<th>Nomenclature</th>
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<td>LIBs</td>
<td>Lithium ion batteries</td>
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<td>HEVs</td>
<td>Hybrid electrical vehicles</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>EVs</td>
<td>Electrical vehicles</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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2. Material and methods

2.1. Synthesis methods

LiNi₀.₅Mn₁.₅O₄ was synthesized using an improved solid-state method. Mn(Ac)₂·4H₂O and Ni(Ac)₂·4H₂O were dissolved in distilled water and stirred at 90 °C for 5 h. The mixture was then dried at 120 °C in air for 10 h to form a solid-state phase mixture followed by a calcination process at 400 °C for 6 h to form the precursor. The precursor was mixed with Li₂CO₃ and sintered at 900 °C for 16 h in the muffle furnace, and then maintained at 650 °C for 10 h before the cooling process to get the final products. The samples were denoted as A-900. AlF₃-coated LiNi₀.₅Mn₁.₅O₄ were prepared by using A-900 as the starting material. Al(NO₃)₃·9H₂O and A-900 were mixed in distilled water under stirring, and then NH₄F solution was dropped into the turbid liquid. The suspended mixture was stirred at 80°C until the solvent was completely evaporated and dried in air at 110°C for 3 h. The resulting powders were calcined at 550°C for 5 h to get AlF₃-coated LiNi₀.₅Mn₁.₅O₄.

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 LiNi₀.₅Mn₁.₅O₄ as the
The cathode was composed of 80% LiNi0.5Mn1.5O4, 12% acetylene black and 8% PVdF binder. The electrolyte was 1 M LiPF6 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 LiNi0.5Mn1.5O4 (ICDD/JCPDS, PDF#46-0810), indicating that the sample exhibits well-defined cubic spinel structures with a space group of Fd3m. LiNi0.5Mn1.5O4 greatly suffers from reacting with electrolyte at high voltage and Mn dissolving at high operating temperature. To address this issue, surface coating with AlF3 has been applied on LiNi0.5Mn1.5O4. Fig.1 shows the SEM images of pristine sample A-900, 1 and 3 wt.% AlF3-coated LiNi0.5Mn1.5O4. AlF3 can be found on the surface of spinel LiNi0.5Mn1.5O4 crystals. The surface roughness of the samples increases while increasing the coating amount of AlF3 from 0 wt% to 3 wt%.

![Fig.1 SEM images of the pristine sample A-900(a), 1(b) and 3(c) wt.% AlF3-coated LiNi0.5Mn1.5O4.](image)

3.2. Electrochemical performance

The specific discharge capacities at the 2nd 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.% AlF3-coated LiNi0.5Mn1.5O4 has better discharge capacities, which are 127.1 and 108.3 mAh/g, respectively. In contrast, the 3 wt.% AlF3-coated LiNi0.5Mn1.5O4 exhibits a worse discharge capacities, 120.9 and 93.9 mAh/g at 0.5 and 10 C, respectively. The 1st charge/discharge curves cycled at 0.5 C of pristine sample A-900 and 1 wt.% AlF3-coated LiNi0.5Mn1.5O4 indicate that surface modification did not improve the efficiency of the 1st 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 AlF3 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.% AlF3-coated LiNi0.5Mn1.5O4 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 50th cycles at 0.5 C and 100th 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.% AlF3-coated LiNi0.5Mn1.5O4, respectively. In high charge/discharge rate, the specific discharge capacities of pristine sample A-900, 1 and 3 wt.% AlF3-coated LiNi0.5Mn1.5O4 after 100 cycles are 84.3, 99.7 and 98.5 mAh/g, respectively (Fig. 2b). On the contrast, the 1.0 wt.% AlF3-coated LiNi0.5Mn1.5O4 shows the best capacity retention (91.8% at 0.5 C and 92.1% at 10 C). The best cyclability of 1 wt.%
AlF3-coated LiNi0.5Mn1.5O4 might be attributed to the suppression of side reaction of the electrolyte and the electrode surface. AlF3-coated LiNi0.5Mn1.5O4 shows superior electrochemical performance especially at high rate to the commercial cathode material LiFePO4 used in lithium ion batteries.

![Graphs showing charge-discharge curves and cycling performance](image)

**Fig. 2** The charge-discharge curves (a) and cycling performance (b) of the pristine sample A-900, 1 and 3 wt.% AlF3-coated LiNi0.5Mn1.5O4 at 10 C.

4. Conclusions

LiNi0.5Mn1.5O4 was successfully prepared by a modified solid-state method for high power LIBs for EVs and HEVs. The LiNi0.5Mn1.5O4 sintered at 900 °C shows the largest initial specific discharge capacity. A newly developed AlF3 coating on LiNi0.5Mn1.5O4 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 AlF3-coated LiNi0.5Mn1.5O4 as cathode materials are promising power sources for EVs and HEVs to reduce energy consumption and carbon emission.

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