Preparation and Electrochemical Performance of Spinel LiAl\textsubscript{0.08}Co\textsubscript{0.05}Mn\textsubscript{1.87}O\textsubscript{4} Cathode Materials for Long Cycle Life Lithium-ion Batteries

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Spinel LiAl\textsubscript{0.08}Co\textsubscript{0.05}Mn\textsubscript{1.87}O\textsubscript{4} cathode materials were prepared by a facile solid state combustion method. The effects of different calcination temperatures from 600 to 750 °C on the structure and properties of the material were studied. The XRD results show that the Al, Co-co doping does not change the crystal structure of spinel LiMn\textsubscript{2}O\textsubscript{4}. The SEM displays that the LiAl\textsubscript{0.08}Co\textsubscript{0.05}Mn\textsubscript{1.87}O\textsubscript{4} sample calcined at 650 °C has a typical octahedron structure. Moreover, the LiAl\textsubscript{0.08}Co\textsubscript{0.05}Mn\textsubscript{1.87}O\textsubscript{4} sample calcined at 650 °C exhibits a better electrochemical reversibility and rate performance than that of other samples calcined at 600, 700 and 750 °C, which is due to the faster Li\textsuperscript{+} de-intercalation/intercalation and inhibited Jahn-Teller distortion. Hence, the spinel LiMn\textsubscript{2}O\textsubscript{4} cathode material delivers a high initial discharge capacity of 113.4 mAh·g\textsuperscript{-1} with a good capacity retention of 83.5% after 400 cycles and an excellent rate performance. This work will lay a certain foundation for the development of high-performance lithium-ion batteries in the future.

Keywords: LiAl\textsubscript{0.08}Co\textsubscript{0.05}Mn\textsubscript{1.87}O\textsubscript{4}; Spinel LiMn\textsubscript{2}O\textsubscript{4}; Combustion method; calcination temperatures; Lithium-ion battery

1. INTRODUCTION

Because of their unusual properties such as an excellent working voltage, high energy density, recyclable performance and environment-friendly, lithium-ion batteries have been widely applied in these fields of portable electronic products, electric vehicles as well as hybrid electric vehicles [1-3]. Specially, the spinel LiMn\textsubscript{2}O\textsubscript{4} has been demonstrated to be a promising cathode material due to its three-
dimensional lithium-ion diffusion channels, great rate capability and relatively high operating voltage [4, 5]. Despite some advantages, LiMn$_2$O$_4$ cathode material suffers from fading capacity and poor electrochemical performance, which mainly because of Jahn-Teller distortion, the dissolution of Mn ions and oxygen defects [6, 7]. So far, these problems have severely limited the large-scale application of lithium-ion batteries.

Thus far, several strategies, such as element doping, surface coating and morphology control have been proposed to suppress the structural and performance degradation problems of the LiMn$_2$O$_4$ cathode materials. Li et al. successfully prepared the Al-F doped LiMn$_2$O$_4$ single crystal material, and the capacity retention rate was 80% after 367 cycles at 0.1C. The performance enhancement is due to inhibition of the Jahn Teller effect and decrease of Mn dissolution [8]. Zhao et al. found that the LiMn$_{1.90}$Mg$_{0.05}$Si$_{0.05}$O$_4$ delivered the initial discharge capacity of 126.9 mAh g$^{-1}$ and remained 123.5 mAh g$^{-1}$ after 100 cycles at 0.5 C in the voltage range of 3.20 ~ 4.35 V [9]. In addition, many synthesis methods, including solid-state method, sol-gel process, microwave sintering method, hydrothermal synthesis, co-precipitation have been used to obtain the spinel LiMn$_2$O$_4$ with improved electrochemical performance [10-12]. Xu et al. synthesized a series of LiTi$_x$Mn$_{2-x}$O$_4$ (0≤x≤0.5) samples by hydrothermal treatment, and they clarified that Ti-doping is beneficial to form the spinel LiMn$_2$O$_4$ with excellent crystal structure [11]. Yao et al. prepared LiMn$_2$O$_4$ materials by the sol-gel method. Comparing the effects of different calcination temperatures on the material structure and battery performance, they found that The LiMn$_2$O$_4$ sample calcined in 650 °C and 750 °C has high crystallinity, good dispersion and excellent electrochemical properties [12]. However, these methods not only have complicated synthesis process, but also have harsh reaction conditions and long reaction time, which affect the large-scale production of materials.

In this work, LiAl$_{0.08}$Co$_{0.05}$Mn$_{1.87}$O$_4$ cathode materials were synthesized at different temperatures of 600 °C, 650 °C, 700 °C and 750 °C by a solid combustion synthesis method. The phase structure, dynamic characteristics and electrochemical performance of LiAl$_{0.08}$Co$_{0.05}$Mn$_{1.87}$O$_4$ material were studied by X-ray diffraction, scanning electron microscope and other tests. The related reasons for crystallization and electrochemical performance of LiMn$_2$O$_4$ are revealed. This strategy in this study provides an important technical process for the spinel LiMn$_2$O$_4$ cathode material with the excellent crystallinity and electrode with high cycling performance.

2. EXPERIMENTAL SECTION

2.1. Materials preparation

Spinel LiAl$_{0.08}$Co$_{0.05}$Mn$_{1.87}$O$_4$ cathode materials were prepared by a solid state combustion method, in which Li$_2$CO$_3$, MnCO$_3$, Al(NO$_3$)$_3$·H$_2$O and CoCO$_3$ as raw materials were weighed in a stoichiometric ratio of 1: 0.08: 0.05: 1.87 (Li: Al: Co: Mn). 1.5 g citric acid was added into the mixture as fuel, and ethanol was used as medium to mix for 10 h by a planetary ball mill. Secondly, the resulted mixture slurry was dried in an oven to vaporize the ethanol solvent. Finally, the dried powder was combusted in a muffle furnace at 500 °C for 1 h, and then was further calcined at 600 °C, 650 °C, 700 °C and 750 °C for 6 h to obtain the products. These samples were marked LACMO-600, LACMO-650,
LACMO-700 and LACMO-750, respectively. The mass loading of the electroactive materials on the working electrode was about 1.0 mg/cm². The above process diagram is shown in Figure 1.

![Process Diagram](image)

**Figure 1.** The preparation process of the LACMO electrodes by a solid-state combustion method.

2.2. Lithium-ion batteries synthesis

The spine LiMn₂O₄ cathode material, conductive carbon black and polyvinylidene fluoride (PVDF) were mixed in a N-methyl-pyrrolidone (NMP) solvent in a weight percentage of 80:10:10 to prepare a slurry. Then the mixed slurry was uniformly coated on the aluminum foil collector by a doctor-blade technology to get the cathode film. The cathode films were cut into discs, and then dried in an oven. The CR2032 batteries were assembled in a high purity argon glove box, in which lithium metal, 1 M LiPF₆ in EC/DMC (1:1 in volume) and Celgard 2320-type membrane were used as anode, electrolyte and separator, respectively.

2.3. Characterization techniques

X-ray diffraction (XRD) test were carried out by an X-ray power diffractometer (D8 ADVANCE, BRUCKER) in 2 range of 10-70°. The morphological properties and lattice structure of the samples were characterized by the scanning electron microscope (SEM, NOVA NANOSEM 450, America FEI) and transmission electron microscope (HRTEM, JEM-2100). X-ray photoelectron spectroscopy (XPS, PHI5000) was performed to identify the surface chemical composition and valence state. The lithium-ion batteries were cycled by a galvanostatical charge-discharge tests were measured by the Land electric test system CT2001A (Wuhan Jinnuo Electronic Co., Ltd) in the voltage from 3.0 to 4.5 V (versus Li / Li⁺). The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out by an electrochemical workstation (CHI660D, Shanghai Chenhua, China). The scan rate and potential region are 0.1 mV/s and 3.6-4.5V, respectively. The frequency range is from 100 kHz to 1.0 Hz.

3. RESULT AND DISCUSSION

The X-Ray diffractograms (XRD) were investigated to study the crystal structure of spinel LiAl₀.₀₈Co₀.₀₅Mn₁.₈₇O₄ cathode materials calcined at different temperature from 600 to 750 °C, and the
results shown in Fig. 2(a). All the diffraction peaks of the samples can correspond to the diffraction peaks of spinel LiMn$_2$O$_4$ (JCPDS No. 35–0782) with a space group of $Fd3m$ space group, indicating that spinel structure of the LiMn$_2$O$_4$ is not changed by an appropriate amount of Al, Co co-doping, and there are no other impurity peaks [4,13]. With the increase of calcination temperature, the intensity of diffraction peak first increases and then decreases. LACMO-650 electrode has strongest diffraction peak intensity than that of LACMO-600, LACMO-700 and LACMO-750 samples, suggesting a higher crystalline quality. That possibly because the calcination temperature of 650 °C makes the combustion reaction more complete, which is conducive to the growth of spinel LiMn$_2$O$_4$ crystal.

In order to reversibility and kinetics of LACMO electrodes calcined at different temperature from 600 to 750 °C, Fig. 2(b) gives the CV curve before the first cycle. All the curves show two pairs of redox peaks, corresponding to the Li ion deintercalation/intercalation process [14], indicating that the electrochemical reaction mechanism of spinel LiMn$_2$O$_4$ cathode material has not been changed at the calcination temperature of 600-750 °C. As shown, the peak current and integral area of the electrode first increase and then decrease, which corresponds to the cycle performance of each product LACMO calcinated at different temperature.

![Figure 2(a). XRD patterns of LACMO electrodes calcinated at different temperature (600-750 °C).](image)

The CV curve of LAMCO samples before the first cycle

Fig. 3. presents the SEM images of LACMO samples calcinated at different temperature (600-750 °C). The LACMO-600 shows small particles with irregular morphology. With the increase of the calcination temperature, the sample particles gradually increase. Compared to the samples calcinated at 600, 700 and 750 °C, the LACMO-650 cathode material displays a relatively regular octahedral structure morphology with uniform particle distribution. When the temperature rises to 750 °C, the material shows an irregular morphology, and the sample particles are agglomerated together, which may be related to the poor crystallinity in the XRD results.
Figure 3. SEM images of (a) LACMO-600, (b) LACMO-650, (c) LACMO-700 and (d) LACMO-750

Here, we conduct XPS test on LACMO-650 and the result is shown in Fig. 4. Typical peak signals of Mn 3p, Li 1s, Al 2p, O 1s, Mn 2p3/2, Mn 2p1/2 and Co 2p3/2 shown in Fig. 4(a), confirming that the surface chemical compositions of the LACMO-650 sample consist with the theoretical LiAl0.08Co0.05Mn1.87O4 compound. Fig 4(b) shows the Mn 2p fit of this sample in which the content of Mn3+ and Mn4+ is 44.2% and 55.8%, respectively. The R(R=[Mn4+]/[Mn3+]) value of 1.26 is larger than 1.18, indicating the Jahn-Teller distortion can be availably inhibited [15,16].

Figure 4. XPS patterns of LACMO-650: (a) survey scan spectrum, (b) fitting curves of Mn2p3/2.
In order to evaluate the electrochemical performance of the LiMn$_2$O$_4$ electrodes, the constant current charge and discharge test is carried out. Fig. 5(a) shows the cycling curves of LACMO samples in lithium-ion batteries at 1.0 C. Table 1 displays the discharge specific capacity and capacity retention of LACMO samples at 1 C, 5 C and 10 C. Owing to the calcination treatment, the LACMO-650 electrode delivers higher initial capacity of 113.4 mAh/g with 83.5% after 400 cycles. In contrast, the capacity retention rate of LACMO-600, LACMO-700 and LACMO-750 are 78.7%, 73.3% and 64.6%, respectively. At 5.0 C, the LACMO-650 sample delivers high initial capacity of 109.3 mAh·g$^{-1}$, retaining 83.1 mAh·g$^{-1}$ after 1000 cycles. While the other electrodes are all less than 90 mAh/g, as shown in Fig. 5(b) and Table 1., as shown in Fig. 4(b). Fig. 5(c) displays that the specific capacity of the electrode LACMO-650 for the first discharge at 10.0 C is 100.6 mAh/g with the capacity retention rate of 79.3%, which is higher than that of other LACMO electrodes. Fig. 5 (d) shows the cyclic performance curves of LACMO electrode materials at different rate (0.5 C-10.0 C). With the increase of current density from 0.5 C to 10 C, the discharge specific capacity of the products has a downward trend, which mainly due to the limitation of lithium-ion migration rate in the spinel structure. At the current densities of 0.2, 1.0, 2.0, 5.0, 8.0 and 10.0 C, the specific capacities of the LACMO-650 are 113.6, 110.9, 107.5, 101.4, 94.7 and 87.1 mAh/g, respectively.

Figure 5. The cycling performance curves of LACMO samples at (a)1.0 C, (b) 5.0 C and (c) 10.0 C, (d) Rate capability at 0.5 C-10.0 C (1 C = 148 mAh·g$^{-1}$.)

Returning to 0.5 C again, it shows a reversible capacity of 109.3 mAh/g, which reaches 96.2% compared with the initial reversible capacity. To further compare the electrochemical performance of
the LiMn$_2$O$_4$ between our work and those previous work reported in literature, the comparison results are listed in Table 2. It is clearly seen that the LACMO-650 displays more excellent or comparable electrochemical performance than that of the other LMO samples. This study constructed a facile and meaningful method to prepare spinel LiMn$_2$O$_4$ cathode material, which may facilitate the development of lithium-ion batteries.

Table 1. Discharge specific capacity and capacity retention of LACMO samples at 1 C, 5 C and 10 C.

<table>
<thead>
<tr>
<th>Samples</th>
<th>1C</th>
<th>5C</th>
<th>10C</th>
</tr>
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<tr>
<td></td>
<td>The initial discharge capacity (mAh/g)</td>
<td>Capacity retention rate</td>
<td>The initial discharge capacity (mAh/g)</td>
</tr>
<tr>
<td>LACMO-600</td>
<td>102.9</td>
<td>78.7%</td>
<td>83.7</td>
</tr>
<tr>
<td>LACMO-650</td>
<td>113.4</td>
<td>83.5%</td>
<td>109.3</td>
</tr>
<tr>
<td>LACMO-700</td>
<td>101.0</td>
<td>73.3%</td>
<td>85.4</td>
</tr>
<tr>
<td>LACMO-750</td>
<td>88.2</td>
<td>64.6%</td>
<td>60.9</td>
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</table>

Table 2. Comparison of the cycling performances of LMO between our work and literature.

<table>
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<th>Sources</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial capacity (mAh g$^{-1}$) and capacity retention after n cycles</td>
</tr>
<tr>
<td>Our work</td>
<td>113.4, 83.5% after 400 cycles</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$ + $\text{B}_2\text{O}_3$ coated LMO (Ref. 5)</td>
<td>109.3, 76.0% after 1000 cycles</td>
</tr>
<tr>
<td>$\text{Al}$, $\text{F}$-co doped LMO (Ref. 8)</td>
<td>101.7, 96.3% after 300 cycles</td>
</tr>
<tr>
<td>$\text{Mg}$, $\text{Si}$-co doped LMO (Ref. 9)</td>
<td>111.3, 80.0% after 382 cycles</td>
</tr>
<tr>
<td>LMO (Ref. 12)</td>
<td>123.5, 97.3% after 100 cycles</td>
</tr>
<tr>
<td>LMO (Ref. 13)</td>
<td>120.0, 78.7% after 100 cycles</td>
</tr>
<tr>
<td>Cu-doped LMO (Ref. 14)</td>
<td>121.1, 73.9% after 500 cycles</td>
</tr>
<tr>
<td>$\text{Al}$, Ni-co doped LMO (Ref. 15)</td>
<td>111.2, 66.1% after 1000 cycles</td>
</tr>
<tr>
<td>$\text{Al}$, Ni-co doped LMO (Ref. 16)</td>
<td>133.0, 82.0% after 400 cycles</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$ coated LMO (Ref. 17)</td>
<td>105.6, 63.7% after 1000 cycles</td>
</tr>
</tbody>
</table>

To further understand the kinetics of LACMO-650 electrode, the electrochemical impedance spectroscopy (EIS) analysis was carried out, and the result is shown in Fig. 6(a) and (b). Fig. 6(a) shows the impedance diagram at temperatures of 298.15 K-328.15 K, and the insets of Fig. 6(a) is the corresponding equivalent circuit diagram, including the ohmic resistance of electrolyte ($R_s$), charge transfer resistance ($R_{ct}$), double layer capacitance (CPE), and Warburg impedance ($W_o$) [16, 17]. It can be seen that the impedance of the electrode becomes lower and lower with the increase of temperature,
indicating a more active electrode reaction. Fig. 6(b) shows the fitting diagram of 1000/T and Log\(i_0\). The activation energy (\(E_a\)) can be calculated from the following equations [18, 19]:

\[ i_0 = \frac{RT}{nF} \]
\[ i_0 = A \exp\left(-\frac{Ea}{RT}\right) \]

Where \(R\) and \(F\) are the gas constant and Faraday constant, respectively, \(A\) is the temperature-independent coefficient, and \(T\) is the absolute temperature. The corresponding parameters are listed in the Table 3. The \(E_a\) of LACMO-650 electrode was calculated as 35.57 kJ/mol. During the charge discharge cycle, the smaller activation energy provides a more favorable active site for \(Li^+\) deintercalation/intercalation process, which enhances the ion mobility and reaction kinetics.

![Figure 6](image)

**Figure 6.** (a) Nyquist plots and the equivalent circuit diagram of LACMO-650; (b) the fitting diagram of 1000/T and Log\(i_0\).

**Table 3.** The corresponding parameters in the EIS analysis.

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>Rct((\Omega))</th>
<th>Log(i_0)</th>
</tr>
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<tbody>
<tr>
<td>298.15</td>
<td>256.1</td>
<td>-3.99862</td>
</tr>
<tr>
<td>303.15</td>
<td>246.5</td>
<td>-3.97481</td>
</tr>
<tr>
<td>308.15</td>
<td>162.1</td>
<td>-3.78567</td>
</tr>
<tr>
<td>318.15</td>
<td>117.7</td>
<td>-3.63279</td>
</tr>
<tr>
<td>328.15</td>
<td>80.33</td>
<td>-3.45345</td>
</tr>
</tbody>
</table>

4. CONCLUSION

In summary, the spinel LiAl\(_{0.08}\)Co\(_{0.05}\)Mn\(_{1.87}\)O\(_4\) cathode material was successfully prepared by a solid-state combustion method. In this work, we studied that the influence of calcination temperature from 600 to 750 °C on crystal structure, morphology, electrochemical performance and kinetics property of LiAl\(_{0.08}\)Co\(_{0.05}\)Mn\(_{1.87}\)O\(_4\) samples. The results exhibit that the optimized LACMO-650 sample shows a
single crystal truncated-octahedral LiMn$_2$O$_4$ structure. This high crystallinity performance mainly is due to the selective growth of the (110) and (100) crystal planes promoted by high temperature recalcination treatment. Compared to the other electrodes, the LACMO-650 sample possesses better electrochemical reversibility and kinetics in the CV and EIS tests, which provides a more favorable active site for Li$^+$ deintercalation/intercalation process. As a result, the LACMO-650 sample give the higher cycling and rate performance. This study constructed a facile and meaningful method to prepare spinel LiMn$_2$O$_4$ cathode material, which may facilitate the development of lithium-ion batteries.

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