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Short Communication

Preparation and Electrochemical Performance of Spinel LiAl_{0.08}Co_{0.05}Mn_{1.87}O₄ Cathode Materials for Long Cycle Life Lithium-ion Batteries

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Spinel LiAl_{0.08}Co_{0.05}Mn_{1.87}O₄ 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 LiMn₂O₄. The SEM displays that the LiAl_{0.08}Co_{0.05}Mn_{1.87}O₄ sample calcined at 650 °C has a typical octahedron structure. Moreover, the LiAl_{0.08}Co_{0.05}Mn_{1.87}O₄ 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⁺ de-intercalation/intercalation and inhibited Jahn-Teller distortion. Hence, the spinel LiMn₂O₄ cathode material delivers a high initial discharge capacity of 113.4 mAh·g⁻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 lithiumion batteries in the future.

Keywords: LiAl_{0.08}Co_{0.05}Mn_{1.87}O₄; Spinel LiMn₂O₄; 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 LiMn₂O₄ 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, $LiMn_2O_4$ 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 LiMn₂O₄ cathode materials. Li et al. successfully prepared the Al-F doped LiMn₂O₄ 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 $3.20 \sim 4.35$ 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 LiMn₂O₄ with improved electrochemical performance [10-12]. Xu *et al.* synthesized a series of LiTi_xMn_{2-x}O₄ ($0 \le x \le 0.5$) samples by hydrothermal treatment, and they clarified that Ti-doping is beneficial to form the spinel LiMn₂O₄ with excellent crystal structure [11]. Yao et al. prepared LiMn₂O₄ materials by the sol-gel method. Comparing the effects of different calcination temperatures on the material structure and battery performance, they found that The LiMn₂O₄ 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 $LiMn_2O_4$ are revealed. This strategy in this study provides an important technical process for the spinel $LiMn_2O_4$ 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}O₄ cathode materials were prepared by a solid state combustion method, in which Li₂CO₃, MnCO₃, Al(NO₃) $_3$ ·H₂O and CoCO₃ 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.



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

2.2. Lithium-ion batteries synthesis

The spine $LiMn_2O_4$ 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 doctorblade 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 $LiAl_{0.08}Co_{0.05}Mn_{1.87}O_4$ 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 LiMn₂O₄ (JCPDS No. 35–0782) with a space group of F*d3m* space group, indicating that spinel structure of the LiMn₂O₄ 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 LiMn₂O₄ 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 LiMn₂O₄ 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), (b). 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 $2p_{3/2}$, Mn $2p_{1/2}$ and Co $2p_{3/2}$ shown in Fig. 4(a), confirming that the surface chemical compositions of the LACMO-650 sample consist with the theoretical LiAl_{0.08}Co_{0.05}Mn_{1.87}O₄ 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 LiMn₂O₄ 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 $LiMn_2O_4$ 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 $LiMn_2O_4$ cathode material, which may facilitate the development of lithium-ion batteries.

	1C		5C		10C	
Samples	The initial	Capacity	The initial	Capacity	The initial	Capacity
	discharge	retention	discharge	retention	discharge	retention
	capacity(mAh/g)	rate	capacity(mAh/g)	rate	capacity(mAh/g)	rate
LACMO-600	102.9	78.7%	83.7	71.8%	78.0	74.1%
LACMO-650	113.4	83.5%	109.3	76.0%	100.6	79.3%
LACMO-700	101.0	73.3%	85.4	69.4%	70.8	74.8%
LACMO-750	88.2	64.6%	60.9	66.0%	49.9	67.9%

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

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

	Performance	
-	Initial capacity (mAh g ⁻¹) and capacity retention	
Sources	after n cycles	
	113.4, 83.5% after 400 cycles	
Our work	109.3, 76.0% after 1000 cycles	
$Al_2O_3 + B_2O_3$ coated LMO (Ref. 5)	101.7, 96.3% after 300 cycles	
Al, F-co doped LMO (Ref. 8)	111.3, 80.0% after 382 cycles	
Mg, Si-co doped LMO (Ref. 9)	123.5, 97.3% after 100 cycles	
LMO (Ref. 12)	120.0, 78.7% after 100 cycles	
LMO (Ref. 13)	121.1, 73.9% after 500 cycles	
Cu-doped LMO (Ref. 14)	111.2, 66.1% after 1000 cycles	
Al, Ni-co doped LMO (Ref. 15)	133.0, 82.0% after 400 cycles	
Al, Ni-co doped LMO (Ref. 16)	105.6, 63.7% after 1000 cycles	
Al ₂ O ₃ coated LMO (Ref. 17)	111.0, 90.7% after 200 cycles	

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 (Ea) can be calculated from the following equations [18, 19]:

 $i_0 = RT/nFRct$

 $i_0 = A \exp(-Ea/RT)$

Where R and F are the gas constant and Faraday constant, respectively, A is the temperatureindependent coefficient, and T is the absolute temperature. The corresponding parameters are listed in the Table 3. The Ea 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. (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
				2

	Parameters		
Temperature(K)	$\operatorname{Rct}(\Omega)$	Logi	
298.15	256.1	-3.99862	
303.15	246.5	-3.97481	
308.15	162.1	-3.78567	
318.15	117.7	-3.63279	
328.15	80.33	-3.45345	

4. CONCLUSION

In summary, the spinel LiAl_{0.08}Co_{0.05}Mn_{1.87}O₄ 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}O₄ samples. The results exhibit that the optimized LACMO-650 sample shows a

single crystal truncated-octahedral LiMn₂O₄ 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 LiMn₂O₄ cathode material, which may facilitate the development of lithium-ion batteries.

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