Study on Electrochemical Performance of LiMg$_{0.06}$Mn$_{1.94}$O$_{4}$ Synthesized by Solid-State Combustion Method

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Spinel LiMg$_{0.06}$Mn$_{1.94}$O$_{4}$ cathode materials for lithium-ion batteries were prepared by a solid-state combustion method at 500°C in different time (1, 3, 6 and 9h). The structure and morphologies of LiMg$_{0.06}$Mn$_{1.94}$O$_{4}$ samples were characterized by scanning X-ray diffraction (XRD) and electron microscopy (SEM), respectively. It turned out that all samples show a single phase LiMn$_2$O$_4$ spinel structure with a good crystallinity. The electrochemical performances of the samples were investigated by charge-discharge cycling test and cyclic voltammetry. By means of charge-discharge cycling test, LiMg$_{0.06}$Mn$_{1.94}$O$_{4}$ synthesized at burning reaction time 6h had a better electrochemical performance, which presents a capacity retention rate of 81.25% after 500th cycles at 1C (1C=148 mAh/g) with initial discharge capacity of 101.9 mAh/g. Simultaneously, LiMg$_{0.06}$Mn$_{1.94}$O$_{4}$ prepared at 6h exhibits the lowest apparent activation energy than other samples, which indicated that Li$^+$ with a higher diffusion rate in the lattice, and show a better electrochemical performance.

Keywords: Solid-state combustion synthesis, Mg-doped, Spinel LiMn$_2$O$_4$, Lithium-ion batteries (LIBs), Cathode materials

1. INTRODUCTION

Rechargeable Lithium-ion batteries has been occupied the energy supply market because they are widely used for portable energy storage, portable devices, electric vehicles (EVs). The cathode materials play a crucial role in the improvement of energy storage capacity of LIBs.[1] There are three mainstream types of cathode materials for LIBs, such as layer structure (LiCoO$_2$ and LiNiO$_2$), olivine
structure (LiFePO₄) and spinel structure (LiMn₂O₄)[2]. Among these cathode materials, spinel LiMn₂O₄ is still well recognized as one of the most promising cathode materials for Lithium-ion batteries[3,4] due to its low cost, good safety and environmental friendliness, and has been attracted extensively attention[5,6]. However, the large-scale application of LiMn₂O₄ is confined by seriously capacity decay during the prolonged electrochemical cycles[7]. Capacity attenuation of spinel LiMn₂O₄ results from: (1) Jahn-Teller effect in the spinel structure; (2) disproportionation reaction of manganese into the electrolyte solution[8].

The cation ions doping has been researched extensively as one of the most comprehensive and effective ways to limit the Jahn-Teller effect, and improve the structural stability of LiMn₂O₄ cathode material[9]. At present, metal cation doping have been widely studied, such as Al³⁺[10], Mg²⁺[11], Cr³⁺[12], Ni²⁺[13], La³⁺[14], Nb⁵⁺[15] and so on. Among these cations, Mg²⁺ has been regarded as one of the most appropriate dopants since it is eco-friendly, low-cost, resource-rich and so on. Currently, Mg-doped LiMn₂O₄ has been reported less. Huang et al[16]. Reported the LiMg₀.₀₅Mn₁.₉₅O₄ sample was prepared by molten-salt combustion method, which presented a remarkable cycling stability with an initial discharge specific capacity of 122.0 mAh/g and capacity retention of 86.4% after 100 cycles at 1C. Xiang et al.[17] studied the influences of reaction temperature on LiMg₀.₀₈Mn₁.₉₂O₄ cathode materials. The as-prepared sample at 600℃ exhibited excellent capacity retention rate of 98.1% after 40 cycles with an initial discharge capacity of 101.3 mAh/g at 0.2C. Besides, Zhang et al.[18] prepared LiMg₀.₀₅Mn₁.₉₅O₄ cathode materials by microwave sintering method, the sample was present a good initial discharge capacity of 122 mAh/g at 1C. Liu et al. [19] synthesized spinel LiMg₀.₀₄Mn₁.₉₆O₄ via solid-state combustion method at various combustion reaction time, results shows that the LiMg₀.₀₄Mn₁.₉₆O₄ sample calcined in 600℃ for 6h delivered better electrochemical properties, Its initial discharge capacity is 112.4 mAh/g, and the capacity retention rate was 93.0% after 40 cycles. However, the effect of the combustion time on the apparent activation energy of Mg-doped spinel LiMn₂O₄ has not been reported. This paper explored in detail the relationship between apparent activation energy and calcination time.

In this work, LiMg₀.₀₆Mn₁.₉₄O₄ samples were synthesized by a solid-state combustion reaction using manganese carbonate and lithium carbonate as raw materials, magnesium acetate as Mg²⁺ dopant, citric acid as fuel. The effect of reaction time on the crystal structure, morphology, electrochemical performance, its evaluated temperature performance, and the apparent activation energy of LiMg₀.₀₆Mn₁.₉₄O₄ cathode material were investigated.

2. EXPERIMENTAL

2.1 Preparation of LiMg₀.₀₆Mn₁.₉₄O₄ materials

LiMg₀.₀₆Mn₁.₉₄O₄ samples were synthesized by a citric acid-assisted solid-state combustion reaction .take advantage of absolute ethyl alcohol as medium lithium carbonate(AR, Sinopharm Chemical reagent Co, Ltd.), manganese carbonate (AR, alading) and magnesium acetate (AR, Sinopharm Chemical reagent Co., Ltd.) were weighted according to a stoichiometric ratio of 1: 1.94: 0.06(Li: Mn: Mg) with a total mixture mass of 30.0g and put it into a agate jar. Then mass fraction of
5% citric acid (AR, Sinopharm Chemical reagent Co., Ltd) as fuel, which was also dispersed into the jar. Then, the mixture was ball-milled. The resultant mixture was powder after drying at 80°C in an oven. Subsequently, the powder of 5.5g was put in an alumina crucible and calcined in a muffle furnace at 500°C for different time (1, 3, 6 and 9h) in air atmosphere. After cooling naturally to ambient temperature, the black LiMn$_{1.94}$Mg$_{0.06}$O$_4$ powders were obtained.

2.2 Characterization of LiMg$_{0.06}$Mn$_{1.94}$O$_4$ materials

Characterization of the LiMg$_{0.06}$Mn$_{1.94}$O$_4$ powders was explored by X-ray diffraction (XRD, D/max-TTRIII, Japan) with CuKα radiation (λ=0.154 nm) to confirm the crystal structure and the scanning range was from 10° to 70° with 0.02° step size and scan speed was 2° min$^{-1}$ at an operation current of 30 mA and voltage of 40 kV. Lattice parameters were obtained by means of the Jade 5.0 soft-ware. The morphology of the LiMg$_{0.06}$Mn$_{1.94}$O$_4$ samples was observed by scanning electron microscopy (SEM, QUANTA-200 America FEI Company).

2.3 Electrochemical studies of LiMn$_{1.94}$Mg$_{0.06}$O$_4$ samples

The electrode were study by roll-pressing a mixed paste of LiMg$_{0.06}$Mn$_{1.94}$O$_4$, acetylene black, and PVDF with a weight ratio of 8:1:1 in a 100mL agate jar mill filled with appropriate N-methyl-2-pyrrolidone (NMP) solvent using as binder for 1 hours and 30 minutes and then spread uniformly on an aluminum foil by using doctor-blade technique, drying in an oven at 80°C for 4h, and lastly punched into circular disks with 16mm diameter after pressure rolling. All as-prepared cathode disks were dried at 120°C in vacuum oven for 12 h before cell assembling. The electrolyte was 1.0 M LiPF$_6$ solved in EC/DMC (1:1 in volume). The electrochemical evaluation was performed by using CR2025 coin-type cells assembled in a dry argon-filled glove box with lithium metal as the negative electrode. A Celgard 2320-type microporous membrane was used as the separator. The cyclic performance was studied by Land electric test system CT2001A(Wuhan Jinnuo Electronics CO., LTD. ) at a current density of 1 C between 3.00 and 4.50V (vs Li/Li$^+$). Cyclic voltammogram (CV) tests were performed on ZAHNER Zennium IM6 Electrochemical Workstation (ZAHNER-elektrik GmbH&Co.KG, kronach, Germany) at a scanning speed of 0.05 mV S$^{-1}$.

3. RESULT AND DISCUSSION

3.1 Structure and Morphology

Fig.1 shows the XRD patterns of LiMg$_{0.06}$Mn$_{1.94}$O$_4$ synthesized at 500°C for different time. All samples present the characteristic diffraction peaks of the cubic spinel LiMn$_2$O$_4$ with the Fd3m space group, corresponding to eight crystal planes of (111), (311), (222), (400), (331), (511), (440) and (531).
Figure 1. XRD patterns of LiMg$_{0.06}$Mn$_{1.94}$O$_4$ samples synthesized at 500℃ for different time (1h, 3h, 6h and 9h).

Table 1. The lattice parameter of LiMg$_{0.06}$Mn$_{1.94}$O$_4$ samples synthesized at 500℃ for different combustion reaction time (1h, 3h, 6h and 9h).

<table>
<thead>
<tr>
<th>Combustion reaction time (h)</th>
<th>Lattice constant (Å)</th>
<th>Cell volume (Å$^3$)</th>
<th>$2\theta$ (400) peak (°)</th>
<th>FWHM (400) peak (°)</th>
<th>Crystal grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1h</td>
<td>8.2463</td>
<td>560.76</td>
<td>44.05</td>
<td>0.421</td>
<td>187</td>
</tr>
<tr>
<td>3h</td>
<td>8.2459</td>
<td>560.68</td>
<td>44.01</td>
<td>0.337</td>
<td>218</td>
</tr>
<tr>
<td>6h</td>
<td>8.2452</td>
<td>560.54</td>
<td>43.97</td>
<td>0.325</td>
<td>234</td>
</tr>
<tr>
<td>9h</td>
<td>8.2387</td>
<td>559.21</td>
<td>43.94</td>
<td>0.298</td>
<td>267</td>
</tr>
</tbody>
</table>

The characteristic peaks of the spinel LiMn$_2$O$_4$(JCPDS, PDF 35-0782), all as-prepared samples are single phase, which demonstrates the crystal structure of LiMn$_2$O$_4$ wasn’t transformed after Mg-doping and combustion for different time. As can be seen from the Table 1, with the increase of the combustion reaction time, the FWHM of (400) gradually reduced. Besides, the cell parameters of the samples was decrease, which was indicated that extend the combustion time can be enhance crystallinity, and all the cell parameter was less than standard value of spinel LiMn$_2$O$_4$(8.427 nm), this phenomenon can be explained as follow: the Mn$^{3+}$ is substituted by Mg$^{2+}$ because of radius of Mg$^{2+}$ ion (r=0.065 nm) is smaller than leads the radius of Mn$^{3+}$ (r=0.066 nm), which lead the shrinkage of the spinel lattice[16, 20]. Furthermore, according to the Scherrer formula $D_c = \frac{0.89\lambda}{B \cos \theta}$ ($\lambda=0.154$ nm, B was the FWHM, $\theta$ was the Diffraction angle of (400) Planes)[21]. It can be find that with the addition of combustion reaction time, the crystal grain size grows slightly, it shows that increasing the calcination time has an effect on the grain size, but it is not significant.
Figure 2. SEM images of LiMg$_{0.06}$Mn$_{1.94}$O$_4$ samples synthesized at 500℃ for different time. (a) 1h, (b) 3h, (c) 6h and (d) 9h.

Fig.2 shows the SEM images of LiMg$_{0.06}$Mn$_{1.94}$O$_4$ calcined at 500℃ for various reaction time. It can be observed that all the samples were agglomerated, which are composed of much small crystallites. With the increase of the combustion time, the phenomenon of agglomeration gradually weakened, and the outline and boundary of truncated octahedral morphology of LiMg$_{0.06}$Mn$_{1.94}$O$_4$ become more clear, which indicated that with the addition of reaction time the crystallinity of LiMg$_{0.06}$Mn$_{1.94}$O$_4$ gradually increased. Besides, with the addition of reaction time, crystal particles gradually grow completely, the size distribution of the crystal particles gradually uniform, as can be clearly seen from Fig.2(d), the particle size of the crystal is about 200nm, this is consistent with the result obtained in Table 1.

3.5 XPS(X-ray photoelectron spectra)

Figure 3. (a) XPS spectra of LiMg$_{0.06}$Mn$_{1.94}$O$_4$ (500℃-6h) sample, (b) fitted profiles of specific Mn 2P$_{3/2}$ peak of LiMg$_{0.06}$Mn$_{1.94}$O$_4$
In order to further study the valence of manganese in LiMg_{0.06}Mn_{1.94}O_4, XPS analysis was characteristic to identify the surface valence of Mn of the LiMg_{0.06}Mn_{1.94}O_4 samples, we chose the best performance sample (500°C-6 h) for XPS analysis. There is a broad peak width located at range of 636.0 eV to 648.0 eV, which indicated that the Mn exist in more than one oxidation state. To exactly calculate the contents of Mn^{3+} and Mn^{4+}, specific Mn 2P_{3/2} peak of LiMg_{0.06}Mn_{1.94}O_4 was fitted and the result is exhibited in Fig.3(b). Wherein the content of Mn^{3+} is 48.12%, the content of Mn^{4+} is 51.88%. Theoretically, for pristine LiMn_2O_4, the contents of Mn^{3+} and Mn^{4+} are equal, however, for LiMg_{0.06}Mn_{1.94}O_4 samples, the ratio of the contents of Mn^{4+} and Mn^{3+} is 1.078, which was higher than 1, it can be demonstrated that Mg-doping can reduce the content of Mn^{3+}, and increase the average valence of Mn. Besides, because of radius of Mg^{2+} ion (r=0.065 nm) approaches the radius of Mn^{3+} (r=0.066 nm), the Mn^{3+} is substituted by Mg^{2+} in the octahedral 16d site. To balance the system valence electrons, residual Mn^{3+} in 16d sites partially convert into Mn^{4+} ions, resulting in an increase in the average valence of Mn and suppresses the Jahn-Teller effect[22, 23]. It means Mg-doped can enhance the stability of the lattice. However, the characteristic peaks of Mg can not be seen in Fig.3(a), this is due to doping amount of Mg is too little, can not be detected by the instrument.

3.2 Galvanostatic Cycling

![Figure 4](image-url)

**Figure 4.** Cycling performance of LiMg_{0.06}Mn_{1.94}O_4 sample synthesized at 500°C for different combustion reaction time (1h, 3h, 6h and 9h) between 3.0 and 4.5 V at 1 C rate

**Table 2.** Discharge specific capacity and capacity retention of LiMg_{0.06}Mn_{1.94}O_4

<table>
<thead>
<tr>
<th>Combustion reaction time (h)</th>
<th>Discharge specific capacity (mAh/g)</th>
<th>Capacity retentions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First cycle</td>
<td>500th cycle</td>
</tr>
<tr>
<td>1</td>
<td>96.1</td>
<td>71.3</td>
</tr>
<tr>
<td>3</td>
<td>100.4</td>
<td>81</td>
</tr>
<tr>
<td>6</td>
<td>101.9</td>
<td>82.8</td>
</tr>
<tr>
<td>9</td>
<td>97.3</td>
<td>72.9</td>
</tr>
</tbody>
</table>
Fig. 4(a) and Table 2. displays cycling performance of LiMg$_{0.06}$Mn$_{1.94}$O$_4$ samples (1, 3, 6 and 9h) at 1C rate in the voltage range of 3.00-4.50 V(vs.Li/Li$^+$). The LiMg$_{0.06}$Mn$_{1.94}$O$_4$ calcined for 6h shows the highest initial discharge specific capacity of 101.9 mAh/g. Meanwhile, The LiMg$_{0.06}$Mn$_{1.94}$O$_4$ combustion for 6h shows the best capacity retention, the capacity retention rate is 81.25% after 500$^{th}$ cycles, which is better than other samples. It is suggesting that lengthing heat-treating time improved capacity retention of LiMg$_{0.06}$Mn$_{1.94}$O$_4$ significantly, because of long reaction time can be improved the stability of the lattice, but when the reaction time to 9h, the capacity retention of LiMg$_{0.06}$Mn$_{1.94}$O$_4$ is attenuating. When the crystallinity is good, the diffusion path of lithium ions becomes longer, thus a better crystallity does not mean a good cycle stability.

3.3 Cyclic Voltammetry

**Figure 5.** Cyclic voltammogram curves of the LiMg$_{0.06}$Mn$_{1.94}$O$_4$ sample synthesized at 500$^\circ$C for different time(1h, 3h, 6h and 9h) (a) first time, (b) after 500$^{th}$ cycles

Fig.5(a) present the first cyclic voltammetry of LiMg$_{0.06}$Mn$_{1.94}$O$_4$ samples at the scanning rate of 0.05 mV S$^{-1}$, ranging from 3.6~4.5 V at room temperature. For all of the LiMg$_{0.06}$Mn$_{1.94}$O$_4$ samples, there were two pairs of redox potential peaks around 4.09 V/3.95 V and 4.23 V/4.10 V, which corresponded to the two step reversible (de)intercalation of Li$^+$ in the spinel phase. It reveals that Mg-doping is not alters the electrochemical mechanism of LiMn$_2$O$_4$ during cycling[24]. With the increase of combustion reaction time, the cathodic peak potential of LiMg$_{0.06}$Mn$_{1.94}$O$_4$ samples have been shift to positive direction, the anodic peak potential have been move to negative direction, the results makes two pairs of redox peak potential difference is becoming smaller and smaller, which was imply that increasing combustion reaction time, can be promote the electrochemical reversibility of the LiMg$_{0.06}$Mn$_{1.94}$O$_4$ samples. The Fig.4(b) present the cyclic voltammetry after 500$^{th}$ cycles, it can be clearly find that, The peak area of all samples has been become smaller, which indicated that after 500$^{th}$ cycles, The specific capacity of the material has been reduce. But it can be seen that the peak symmetry of 500$^\circ$C-6h is still good, indicating that the sample still have good electrochemical reversibility after 500$^{th}$ cycles.
3.4 Calculation of the apparent activation energies

To understand further the electrode kinetics, a series of electrochemical impedance spectroscopies (EIS) were performed at different temperature to calculate the apparent activation energies ($E_a$) of all samples electrodes, Fig.6(a), (b), (c) and (d) display the Nyquist plots of the electrodes at different temperatures, respectively.

![Nyquist plots](image)

**Figure 6.** The Nyquist plots of the LiMg$_{0.06}$Mn$_{1.94}$O$_4$ samples following different combustion reaction time(a) 1h, (b) 3h, (c) 6h and (d) 9h at different temperatures and (f) Arrhenius plots of log $i_0$ vs. 1000/T for the electrodes of the LiMg$_{0.06}$Mn$_{1.94}$O$_4$ samples at different temperatures

The $R_{ct}$ values can be obtained using the equivalent circuit model shown in Fig.6(e). It can be observed that the $R_{ct}$ values of four electrodes decrease with the increase of temperature. The apparent activation energies ($E_a$) of all the samples can be determined on the basis of the following equations:
\[ i_0 = \frac{RT}{nF} \]  
\[ i_0 = A \exp(-E_a/RT) \]

Where \( i_0 \) stand for the exchange current, \( R \) is the gas constant (8.314 J·mol\(^{-1}\)·K\(^{-1}\)), \( T \) (K) is the absolute temperature, \( F \) is the Faraday constant (96484.5 C·mol\(^{-1}\)) \[25\]. \( A \) is a temperature-independent coefficient, and \( n \) is the number of transferred electrons. Arrhenius plots of \( \log i_0 \) vs. 1000/T for the electrodes of 1, 3, 6 and 9h is exhibited in Fig. 6(f). The apparent activation energies (\( E_a \)) of all the samples can be calculated to be 23.71 kJ/mol, 28.22 kJ/mol, 15.24 kJ/mol and 24.94 kJ/mol, respectively. Among them, samples obtained at 500°C for 6h have the smallest apparent activation energy, which is 15.24 kJ/mol, it was indicated that it is more conducive to the dissociation and embedding of Li\(^+\) ions in this condition.

4. CONCLUSIONS

Spinel \( \text{LiMg}_{0.06}\text{Mn}_{1.94}\text{O}_4 \) were successfully synthesized by a solid-state combustion method. It is using lithium carbonate and manganese carbonate as raw material, magnesium acetate as dopant, and citric acid as fuel, and combustion reaction at 500°C in different reaction time (1, 3, 6 and 9h). The compounds were characterized by XRD, SEM and XPS. Electrochemical performances were evaluated by cyclic voltammetry, EIS, and galvanostatic cycling. As can be seen from the XRD diagram, all as-prepared samples are single phase. With the increasing of reaction time, the crystallinity of \( \text{LiMg}_{0.06}\text{Mn}_{1.94}\text{O}_4 \) was increased, particle size became bigger, crystal morphology gradually developed to regular octahedrons morphology, and the distribution size of particles became more homogeneous. Among the synthesized materials, the \( \text{LiMg}_{0.06}\text{Mn}_{1.94}\text{O}_4 \) combustion for 6h exhibited the optimal electrochemical properties, which discharge specific capacities of 101.9 mAh/g, after 500th cycles with capacity retention rate of 81.25%. By Cyclic voltammogram curves can be find that after 500th cycles the sample synthesized by 6h still with a good symmetry. The apparent activation energies (\( E_a \)) of all the samples is calculated to be 23.71 kJ/mol, 28.22 kJ/mol, 15.24 kJ/mol and 24.94 kJ/mol, respectively. Among them, samples obtained at 500°C for 6h have the smallest apparent activation energy.

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