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# The Effect of Calcination Time on the Electrochemical Performance of Spinel LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> Prepared by a Solid-State Combustion Method

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Mg-doped cathode material LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> was synthesized by a solid-state combustion method at 500°C for 1h and then two-stage calcination at 600°C for 3 h, 6 h, 9 h, 12 h, respectively. The effect of two-stage calcination time on the electrochemical properties of spinel LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> was investigated by XRD, SEM, galvanostatic charge-discharge cycling test, cyclic voltammogram (CV) methods, electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS). The XRD results indicate that Mg substituting of Mn does not change the spinel structure of LiMn<sub>2</sub>O<sub>4</sub> as calcination time goes on. SEM observations show particles possess octahedral morphology, with particle size in the range of 125.0-270.8nm. LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> prepared at 500°C for 1h and then two-stage calcination at 600°C for 3 h had excellent electrochemical performance with an initial discharge specific capacity of 107.3 mAh g<sup>-1</sup>, and the capacity retention was 72.97% after 1000 cycles at 1 C, which is correspond to the smallest charge transfer resistance in all samples. The excellent electrochemical performance is due to Mg<sup>2+</sup> dopant can improve structural of LiMn<sub>2</sub>O<sub>4</sub>, as well as reducing the Jahn-Teller effect.

**Keywords:** Solid-State combustion; LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub>; Calcination time; Mg-doping; Lithium ion batteries;

## **1. INTRODUCTION**

As we all known that Lithium-ion batteries (LIBs) are widely considered as a popular rechargeable power source in hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles

(PHEVs), and full electric vehicles (EVs) for its high energy density [1, 2]. Increasing demand for reliable high energy density power source has greatly intensified the research and development of lithium ion batteries [3]. Several kinds of cathode materials are used in practical lithium ion batteries on the market, such as layered LiCoO<sub>2</sub> and LiNiO<sub>2</sub>, spinel LiMn<sub>2</sub>O<sub>4</sub>, and olivine LiFePO<sub>4</sub>. Among all the cathode materials, the spinel LiMn<sub>2</sub>O<sub>4</sub> is considered as one of the most promising cathode materials due to its low cost, abundance resources, fast charge-discharge reaction, high coulombic efficiency, good reliability safety and low toxicity. Spinel LiMn<sub>2</sub>O<sub>4</sub> has been attracted widely attention [4-6]. Nevertheless the spinel LiMn<sub>2</sub>O<sub>4</sub> material has some disadvantages, such as poor cycling stability and capacity retention [7].

In order to enhance the cycling stability and capacity retention of the spinel LiMn<sub>2</sub>O<sub>4</sub>, the partially substitution of Mn by Li, Mg, Al, Ni, Co, Cr, Cu, Zn, Fe, Ti and so on, has become an effective way to improve the performance [8-17]. Among these materials, Mg-doping has generated hug interest, because it is eco-friendly, resource-rich. It was found that Mg<sup>2+</sup> dopant can improve structural of LiMn<sub>2</sub>O<sub>4</sub> [18], as well as reducing the Jahn-Teller effect. Numerous studies have now shown that the synthetic method has great impact on the electrochemical properties of spinel LiMn<sub>2</sub>O<sub>4</sub>. It is well known that spinel LiMn<sub>2</sub>O<sub>4</sub> cathode materials have been synthesized by high-temperature solid-state method [19], coprecipitation method [20], microwave synthesis method [21], sol-gel method [22], solid-state combustion method [23-25], and so on. Compared to other mode of preparation, the solid-state combustion method save the reaction time and energy at the same time [26]. Zhang et al. [27] have prepared LiMg<sub>0.05</sub>Mn<sub>1.95</sub>O<sub>4</sub> via the microwave synthesis method. The sample of  $LiMg_{0.05}Mn_{1.95}O_4$  exhibits the initial discharge capacity of 135.1mAh g<sup>-1</sup> at room temperature at 0.1 C, which is lower than that of pure spinel (ca. 142.2 mAh g<sup>-1</sup>). Zhao et al. [28] synthesized the spinel LiMg<sub>0.06</sub>Mn<sub>1.94</sub>O<sub>4</sub> compounds by acid-assisted sol-gel method, which exhibits a discharge capacity of 120.5 mAh g<sup>-1</sup>, and the capacity retention was 97.5% after 40 cycles at 5.0 C. Xiang et al. [29, 30] not only have investigated the effect of the amount Mg<sup>2+</sup> dopant on the electrochemical performance of spinel LiMn<sub>2</sub>O<sub>4</sub> but also have investigated the temperature of combustion on the electrochemical performance of LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> by a solid-state combustion method. The result reveals that the second roasting sample has high initial discharge specific capacity and capacity retention. The effect of two-stage calcination time on the electrochemical properties of spinel  $LiMg_{0.08}Mn_{1.92}O_4$  is not been investigated.

In this paper, spinel  $\text{LiMg}_{0.08}\text{Mn}_{1.92}\text{O}_4$  were prepared by a solid-state combustion method at 500°C for 1h and then two-stage calcination at 600°C for different heat treatment time with manganese carbonate and lithium carbonate as raw materials, magnesium acetate as  $\text{Mg}^{2+}$  dopant and citric acid as a fuel. The influence of two-stage calcination time on the crystal structure, morphology and electrochemical properties of Mg-doped LiMn<sub>2</sub>O<sub>4</sub> cathode materials were investigated detailedly.

# 2. EXPERIMENTAL

#### 2.1 Preparation of samples

Spinel  $LiMg_{0.08}Mn_{1.92}O_4$  samples were prepared by a solid-state combustion method. The first step is to weight lithium carbonate (AR, Sinopharm Chemical reagent Co., Ltd), manganese carbonate

(AR, alading) and magnesium acetate (AR, Sinopharm Chemical reagent Co., Ltd) as lithium resource, manganese resource and  $Mg^{2+}$  dopant, respectively. After that, put them into a 500 ml polytetrafluoroethylene jar. It is worth noting that the stoichiometric ratio is Li: Mn: Mg = 1:1.98:0.08 with a total mixture mass of 30.0 g. In addition, a mount of 5wt% of gross weight of citric acid (AR, Sinopharm Chemical reagent Co., Ltd) was removed into the jar and then fabricated by planetary ball mill mixing the raw materials for 10 h with ethanol as medium. In the end, drying the above mixture oven for 4 h, we obtained the off-white precursor. The next step is the off-white power of approximate 5.5 gram was put into an alumina crucible and then calcined in a muffle furnace at 500°C for 1 h. The one-stage products were cooled to room temperature and grounded with mortar. Two-stage calcination at 600°C for 3 h, 6 h, 9 h and 12 h, respectively. We obtained the two-stage calcined spinel LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> products in black powers after cooled to room temperature.

### 2.2 Characterization of samples

The crystalline structure of the spinel  $\text{LiMg}_{0.08}\text{Mn}_{1.92}\text{O}_4$  products were identified by X-ray diffraction (XRD, D/max-TTRIII, Japan) with Cu K $\alpha$  radiation (k = 0.15406 nm), a scan speed of 4°/min over the measurement range from 10° to 70° at an operation current of 30 mA and voltage of 40 KV. The microstructure morphologies of the spinel LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> samples were determined by scanning electron microscopy (SEM, FE-SEM, NOVA NANOSEM 450, America FEI). The surface elemental valence states of the samples were characterized by X-ray photoelectron spectrometer (XPS, PHI5000 Versaprobe-II).

#### 2.3 Electrochemical measurements of samples

The LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> electrode were prepared by mixing 80% spinel LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> power, 10% polyvinylidene fluoride (PVDF) and 10% carbon black in a 100ml jar. Then put appropriate Nmethyl-2-pyrolidone (NMP) into it as solvent. The slurry mixture was obtained by adequately ball-mill mixing. After that, the slurry was homogeneously coating onto the polished aluminium foil by doctorblade technique. Put the film in an oven at 80°C for 4 h. Then the film was cut into disk with 16mm diameter. In order to assemble cell successfully, all cathode wafers must be dried at 120°C under a vacuum condition for 12 h. The CR2025 coin-cells were assembled in glove box (MBraun, Germany) filled with high purity argon gas. In the GR2025 coin-cells assemblage process, the as-prepared disks as cathode, lithium mental foil as counter electrode, 1M LiPF6 dissolved in ethylene carbonate (EC)-1,2-dimethyl carbonate (EC and DMC volume radio of 1:1) as electrolyte. Electrochemical performance was test using the as-prepared CR2050 coin-type cells by Land electric test system CT2001A (Wuhan Jinnuo Electronics Co., Ltd.) at a current density of 1 C (1 C = 148mA/g) and cutoff voltage limit of 3.0-4.5V (versus Li/Li<sup>+</sup>). Cyclic voltammogram (CV) measurement was performed under ambient temperature by ZAHNER Zennium IM6 Electrochemical Workstation (ZAHNERelektrik GmbH & Co. KG, Kronach, Germany) in the voltage range between 3.6 and 4.5V at a scanning rate of 0.1 mV/s.

## **3. RESULT AND DISCUSSION**

3.1 Structure and morphology analysis

The XRD result of  $LiMg_{0.08}Mn_{1.92}O_4$  samples at 500°C 1h and then heat treatment at 600°C 3 h, 6 h, 9 h and 12 h are shown in Fig. 1 (a).



**Figure 1.** (a) XRD patterns of original powder of LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> materials prepared two-stage calcination time from 3 h, 6 h, 9 h and 12 h, (b) XRD patterns of positive plates which have completed 1000 cycles.



**Figure 2.** X-ray photoelectron spectra for the LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> prepared at 500°C for 1h and then twostage calcination at 600°C for 3 h.

The well-defined reflection peaks incorporate eight typical crystal planes of  $(1 \ 1 \ 1)$ ,  $(3 \ 1 \ 1)$ ,  $(2 \ 2 \ 2)$ ,  $(4 \ 0 \ 0)$ ,  $(3 \ 3 \ 1)$ ,  $(5 \ 1 \ 1)$ ,  $(4 \ 4 \ 0)$  and  $(5 \ 3 \ 1)$ , which are indexed to the cubic structure of spinel LiMn<sub>2</sub>O<sub>4</sub> (JCPDS File no. 35-0782) with the Fd3m space group. No impurity such as manganese or magnesium oxides were detected in the XRD pattern, which suggesting that Mg substituting of Mn does not change the spinel structure of LiMn<sub>2</sub>O<sub>4</sub>. The samples have better crystallinity as calcination time goes on. In order to verify the effect of charging and discharging on LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub>, the XRD measurements of and positive plate which has completed 1000 cycles were finished. The results are shown in Fig. 1 (b). The results indicate that charging and discharging not change the spinel structure of LiMn<sub>2</sub>O<sub>4</sub> also. In addition, the samples after 1000 cycles reveal that LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> samples have worse crystallinity as calcination time goes on.

Fig. 2 shows the X-ray photoelectron spectra of  $\text{LiMg}_{0.08}\text{Mn}_{1.92}\text{O}_4$  sample at 500°C 1h and then heat treatment at 600°C 3 h. A board peak width for the sample was detected, which indicates that the Mn exist in more than one oxidation state [31]. XPS pattern gives two binding energy values corresponding to the characteristic peaks  $\text{Mn}^{3+}/\text{Mn}^{4+}$  of at 641.8/643.2 eV, which these values are very close in accordance with reported values [32]. XPS pattern shows approximately equal molar ratio of  $\text{Mn}^{3+}/\text{Mn}^{4+}$ . The XPS result reveals that the content of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  are 47.77% and 52.23%, respectively. It indicates a decrease in the  $\text{Mn}^{3+}$  for the Mg-doped cathode materials that confirms substitution of  $\text{Mn}^{3+}$  by Mg ions [33].

Fig. 3 (a)-(d) presents the SEM images of  $LiMg_{0.08}Mn_{1.92}O_4$  samples prepared by one-stage calcination at 500°C for 1 h and two-stage calcination at 600°C for 3 h, 6 h, 9 h, 12 h, respectively. It can be found that the composites not only have better crystallinity and lager particle size, but also weaker agglomerate with calcination time increasing. The materials prepared at 500°C for 1h and then two-stage calcination at 600°C for 6 h, 9 h and 12 h consist of particles possess octahedral structure

obviously. All the particle size in the range of 120-270nm, which is smaller than the particle size of  $LiMg_{0.05}Mn_{1.95}O_4$  cathode materials via the microwave synthesis method [27].





**Figure 3.** SEM images of LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> materials prepared at different two-stage calcination time (a) 3 h, (b) 6 h, (c) 9 h, (d) 12 h and (e) EDXA pattern of LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> materials prepared 500°C for 1h and then two-stage calcination at 600°C for 3 h.

EDXA analysis is performed and the results are presented in Fig. 3 (e). The EDXA patterns of synthesized compounds reveal the presence of manganese, oxygen and magnesium element. Moreover, no impurity peaks were detected in the XRD pattern. The conclusion that magnesium ions were incorporated into the cubic spinel structure can be drawn.

The first galvanostatic charge-discharge profile Fig. 4 (a) and the charge-discharge cycling performance of samples prepared by a solid-state combustion synthesis are displayed in Fig. 4 (b) with 1 C rate and in the voltage range between 3.0 V and 4.5 V. All the products exhibit two charge/discharge plateaus at around 3.90 and 4.20 V, corresponding to Li<sup>+</sup> two-stage intercalation/de-intercalation at two different tetragonal 8a sites in the spinel framework [34], suggesting that Mg substituting of Mn and various two-stage calcination time didn't transform the electrochemical reaction of lithium-ion in the course of charge and discharge process.



**Figure 4.** (a) The first charge and discharge curves at different calcination time 3 h, 6 h, 9 h, 12 h and the current densities of 1.0 C and (b) Cycle performances at current of 1.0 C.

As can be seen from the Fig. 4 and Table 1, the sample calcined at 500 °C for 1 h and 600 °C for 3 h exhibited a initial discharge capacity of 107.3 mAhg<sup>-1</sup> and 78.3 mAhg<sup>-1</sup> after 1000 cycles, which possesses higher discharge capacity than other samples in the process of 1000 cycles. The charge-discharge cycling performance of composites at 600 °C for 6 h, 9 h and 12 h without significant difference after 500 cycles. As this reason, we can draw a conclusion that LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> material calcined at 500 °C for 1 h and 600 °C for 3 h was preferable.

Time(h) -	Discharge specific capacity(mAh g <sup>-1</sup> )		$C_{aposity rotantion}(0/)$
	First cycle	1000th cycle	Capacity retention(%)
3	107.3	78.3	72.97
6	103.2	66.3	64.24
9	93.4	69.9	74.84
12	98.2	71.2	72.51

Table 1. Discharge specific capacity and capacity retention of all samples



**Figure 5.** The rate capacities of  $LiMg_{0.08}Mn_{1.92}O_4$  samples.

Fig. 5 displays the rate capabilities of  $\text{LiMg}_{0.08}\text{Mn}_{1.92}\text{O}_4$  products at rates from 0.5 C to 10 C in the voltage range of 3.0 V between 4.5 V. As can be observed that the all samples of discharge specific capacity minish with the rate increase attribute to electrochemistry polarization. The results reveals that the sample of  $\text{LiMg}_{0.08}\text{Mn}_{1.92}\text{O}_4$  calcined at 500°C for 1h and then 600°C for 3 h had highest discharge capacity at 0.5C to 10C. After 60 cycles at different rates, the composites can recover and deliver the same capacity as the equivalent initial discharge capacities at 0.5 C, indicating that the composites have excellent electrochemical reversibility.

In order to investigate the electrochemical mechanism in lithium ion battery of Mg-doped product synthesised by a solid-state combustion method, the cyclic voltage between 3.6 V and 4.5 V at

an scan rate of 0.1 mV s<sup>-1</sup>. All the samples have two typical pairs of redox peaks around 4.09 V/4.10 V in Fig. 6 suggest intercalation and de-intercalation of Li<sup>+</sup> ions, which are correspond to the voltage plateaus of initial discharge curves demonstrate in Fig. 4. The two pairs of well separated redox peaks in Fig 6. (a) for all positive electrode materials are well-defined and symmetric mean the intercalation and de-intercalation of lithium-ion into or from the spinel phase were reversible [35]. At the same time, the oxidation and reduction peaks currents of LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> composites reduce with the extension of two-stage calcination time from 3 h to 9 h except 12 h at 600°C.



**Figure 6.** (a) The first cyclic voltammogram curves of  $\text{LiMg}_{0.08}\text{Mn}_{1.92}\text{O}_4$  electrode materials prepared by two-stage calcination for different time (b) the cyclic voltammogram curves of  $\text{LiMg}_{0.08}\text{Mn}_{1.92}\text{O}_4$  electrode materials after 1000 cycles.

The reduce of positive electrode and cathodic peak currents suggested the electrochemical activity and specific capacity were not improved. After 1000 cycles, for the sample calcined at 500°C for 1 h and two-stage calcination at 600°C for 3 h still displays the obvious redox peaks and biggest peak current in Fig 6. (b). Fig 6. (b) indicated that the sample calcined at 500°C for 1 h and two-stage calcination at 600°C for 3 h exhibited higher peak current and peak area, implying higher discharge specific capacity and electrochemical activity [36], which was consistent with the results from Fig.4.



Figure 7. Electrochemical impedance spectrum of prepared by two-stage calcination for different time after first cycles.

Electrochemical impedance spectroscopy (EIS) was carried out after first cycles to further investigate the electrochemical performance of  $\text{LiMg}_{0.08}\text{Mn}_{1.92}\text{O}_4$  samples. As shown in the Fig.7, the four Nyquist plots have similar features, a semicircle in the high frequency and sloping line in the low frequency. The R<sub>ct</sub> of the spinel LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> composites at two-stage calcination at 600°C for 3 h, 6 h, 9 h and 12 h after first cycles are 245.4 $\Omega$ , 255.7 $\Omega$ , 282.6 $\Omega$ and 290.1 $\Omega$ , severally. The R<sub>ct</sub> of materials prepared by two-stage calcination for 3h is smallest in all samples, which is correspond to the highest initial discharge specific capacity. The charge transfer resistance is increasing as the time goes on, which is correspond to the cyclic voltammograms.

#### **4. CONCLUSIONS**

In summary, the spinel  $\text{LiMg}_{0.08}\text{Mn}_{1.92}\text{O}_4$  products were synthesized by a solid-state combustion method at various two-stage calcination time. The XRD results indicate that Mg substituting of Mn does not change the spinel structure of  $\text{LiMn}_2\text{O}_4$  as calcination time goes on. SEM observations show particles possess octahedral morphology, with particle size in the range of 125.0-

270.8nm. The products had two-stage calcination at 600°C 3 h, 6 h, 9 h, 12 h showed initial discharge specific capacity of 107.3, 103.2, 93.4, 98.2 mAhg<sup>-1</sup> and capacity retention of 72.97%, 64.24%, 74.84%, 72.51% after 1000 cycles at 1 C, respectively. LiMg<sub>0.08</sub>Mn<sub>1.92</sub>O<sub>4</sub> calcined at 500°C for 1h and then 600°C for 3 h had highest discharge capacity at 0.5C to 10C, which is correspond to the smallest charge transfer resistance in all samples. Consequently, spinel LiMn<sub>2</sub>O<sub>4</sub> by Mg doping prepared via the solid-state combustion method will be a promising cathode materials for lithium-ion batteries.

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