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# Synthesis of Al-doped $LiMn_2O_4$ spinels by mechanical alloying and rotary heating

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$LiMn_2O_4$ has been widely studied as the cathode material for Li-ion batteries because of its low cost, environmental merit and relatively high voltage [1–3]. However, it shows significant capacity fading and poor cycleability. A very effective way for improving the cycling performance of $LiMn_2O_4$ is to synthesize manganese-substituted $LiM_xMn_{2-x}O_4$ spinel phase by doping with divalent or trivalent ions ($M =$ Al, Mg, Co, Ni, Fe, Ti, Zn and Cr, etc.) [4–8].

The conventional synthesis method of $LiMn_2O_4$ is direct solid-solid reaction of oxides and carbonate of manganese and either LiOH, or $Li_2CO_3$ and $LiNO_3$ at high temperatures to enhance the diffusion process and obtain a well-ordered structure. Due to this high temperature, there are some disadvantages such as broader particle size distribution, longer reaction time or other unwanted phases. However, solid-state reaction technology is easy and simple, and is one of the most suitable techniques for industrialization. The obstacles to the solid-state reaction are mainly the higher synthesis temperature and longer high temperature reaction time, together with the difficulties in the effective controls of chemical composition and microstructures.

In recent years great progress has been mode in developing new synthesis methods of $LiMn_2O_4$ [9–13]. One of the main approaches is mechanical alloying. The works of Kosova *et al.* [11–13] on $LiMn_2O_4$ showed that mechanical alloying significantly decreased the synthesis temperature and the resulting products exhibited tolerable electrochemical performances. Mechanical alloying can produce particle and grain sizes down to the nanoscale, together with structure defects. Energetic lattice defects, combined with short diffusion distances, are the driving forces for faster solid-state alloying and chemical reactions at low temperatures.

The high temperature furnaces for solid-state synthesis, at present, are mainly periodical kilns or furnaces. The powders in these equipments are static. Therefore the temperature field within the powders is often non-uniform during heating or cooling, especially for mass production, which will result in non-uniform chemical composition and non-uniform particle size distribution in a batch of synthesized powders. On the other hand, these mechanically alloyed initial powders easily grow during the following high temperature treatment, and sometimes result in abnormal grain growth which causes broader particle size distribution. The particle size, crystalline structure and chemical composition of $LiMn_2O_4$ play critical roles in the electrochemical behavior of the cell [1]. It is very important to control the particle size distribution, the chemical composition and the phase structure.

In this study, mechanical milling and rotary heating are combined to form a new synthesis technique in order to decrease synthesis temperature and shorten reaction time, and also obtain good stoichiometric control of $LiAl_{0.1}Mn_{1.9}O_4$ spinel with homogenous chemical composition and uniform particle size distribution. Here the Al is used as the substitution material because of its lower atomic weight compared with $LiMn_2O_4$ and relative lower cost or environmental merit compared with other doping elements (e.g., Ti, Cr, Ni, Co, Mg, etc.).

Starting materials for preparing $LiAl_{0.1}Mn_{1.9}O_4$ were electrolytic $MnO_2$ (>99%) powders, $LiOH{\cdot}H_2O$ (>99%) and $Al_2O_3$ (>99%). $MnO_2$, $LiOH{\cdot}H_2O$ and $Al_2O_3$ were mechanically alloyed using a planetary ball miller with a weight ratio of stainless steel ball to powder of 10:1 and a rotation rate of 200 rpm. The milling time was 5 h. Subsequent heat treatment was carried out in a self-made rotary furnace (see Fig. 1) at 600 °C for 3 h. The rotation speed of the elevated temperature furnace tube was 40 rpm. The $LiAl_{0.1}Mn_{1.9}O_4$ synthesized in this way was referred to as MAR600 for brevity. In order to investigate the effects of milling and rotary heating on the microstructural characters and electrochemical performance of the final powders, some $LiAl_{0.1}Mn_{1.9}O_4$ samples were synthesized using the conventional solid-state reaction without mechanical alloying and rotary heating at 600 °C (C600) and 800 °C (C800) for 3 h. Some samples were synthesized with mechanical alloying followed by conventional heating at 600 °C (MA600) instead of rotary heating.

The powder X-ray powder diffraction patterns of the milled mixtures and final doped spinels were obtained using the X-ray diffraction method (XRD) with Cu $K_\alpha$ radiation. A scanning electron microscope was used to characterize microstructures of the spinels. The particle size of the prepared powders was measured with a laser particle size analyzer.

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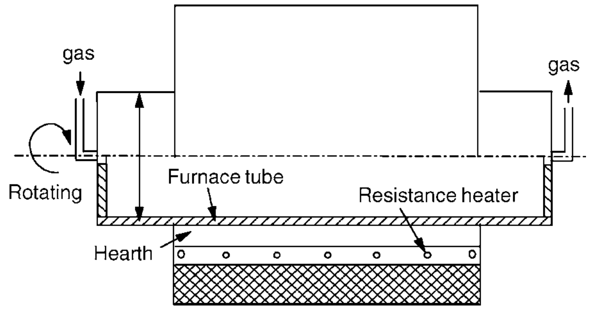

*Figure 1* Schematic of the furnace with a rotary tube.

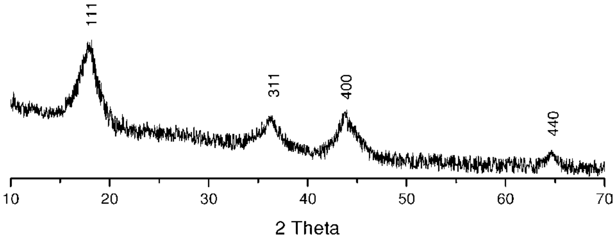

*Figure 2* XRD patterns of mixtures of $LiOH{\cdot}H_2O$, $Al_2O_3$ and $MnO_2$ mechanically alloyed for 5 h exhibiting the peaks of $LiMn_2O_4$ spinel.

The charge/discharge capacity and cycleability of the synthesized powder were investigated in coin cells. The sample powder was mixed with polytetrafluoroethylene (PTFE) as a binder and acetylene black as an electronic conductor at a weight ratio of 80:5:15. The mixture was rolled into films and then dried in vacuum at 120 °C for 20 h. Lithium foil was used as the counter electrode, and 1.0 M $LiPF_6$ dissolved in ethylene carbonate and dimethyl carbonate (1:1 in volume) was used as the electrolyte. The test cells were assembled in an argon glove box. Cells were charged and discharged at 0.30 mA/cm$^2$ within the potential range of 3.0–4.3 V.

Fig. 2 shows the XRD pattern of the powders mechanically alloyed for 5 h. These peaks of the spinel are broader, suggesting spinel amorphization together with a nanoscale crystallite size and a rise in residual mechanical strain. The $LiMn_2O_4$ spinel phase is predominant, which implies that Li—Mn—O spinel was formed during mechanical alloying. On the other hand, the peaks of $MnO_2$, $Al_2O_3$ and LiOH·OH are unidentifiable. During mechanical alloying, plastic $LiOH{\cdot}H_2O$ covers the surface of $MnO_2$ particles and reacts with $MnO_2$ to partially reduce $Mn^{4+}$ ions to $Mn^{3+}$. The process is as follows

$$4LiOH{\cdot}H_2O + 8MnO_2 = 4LiMn^{3+}Mn^{4+}O_4 + 6H_2O + O_2 \qquad (1)$$

Fig. 3 shows XRD patterns of the different $LiAl_{0.1}Mn_{1.9}O_4$ samples calcined at 600 °C and 800 °C. It is confirmed by the XRD patterns that the C600 sample (calcined at 600 °C for 3 h without mechanical alloying and rotary heating) exhibited both spinel Li—Mn—O phase and a trace of $Mn_2O_3$ phase. This impurity phase completely disappears as the calcining temperature is raised to 800 °C (see the XRD pattern of C800 sample). The patterns of MA600 and MAR600 samples (mechanically alloyed for 5 h followed by firing at 600 °C) show pure single spinel phase. Compared with the conventional solid-state reaction, the mechanical alloying decreases the synthesis temperature by introducing nanoscale precursor of Li—Mn—O spinel with structure defects and short diffusion distance.

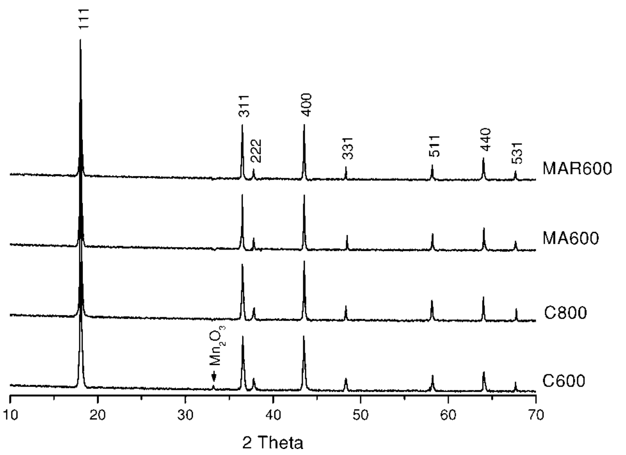

*Figure 3* XRD patterns of C600, C800, MA600 and MAR600 samples.

The lattice constants, which were calculated from XRD data, of the crystal cells of C800, MA600 and MAR600 samples are 0.8232 nm, 0.8202 nm and 0.8198 nm, respectively, showing that there is a slight decrease in lattice constant with decreasing temperature. The crystal lattice constants of MA600 and MAR600 are almost identical. The ionic radius of $Mn^{4+}$ (0.0530 nm) is lower than that of $Mn^{3+}$ (0.0645 nm) and $Mn^{4+}$ is more stable at lower temperature. Thus the lower lattice parameter indicates the $Mn^{4+}$ content in Li—Mn—O spinel is higher. As we know, increasing the $Mn^{3+}$ content during the intercalation process brings Jahn-Teller distortion [14, 15], which results in capacity fading of Li—Mn—O spinel. Therefore, lower temperature synthesis is preferable.

Fig. 4 shows micrographs of MA600 and MAR600 samples. It is significant that the particle size distribution of the MAR600 sample prepared by rotary heating is narrow, and the average size of the powders is 1.57 $\mu$m. In contrast, the particle size of the MA600 sample prepared by static heating is nonuniform with an average size of 2.73 $\mu$m. In terms of average size, the statically heated powders are larger than the powders calcined by rotary heating. In Fig. 4a, there are some big particles (their sizes are over 5 $\mu$m), and inversely, some small particles less than 0.5 $\mu$m also can be observed.

During high temperature synthesizing, when powders mechanically alloyed are static in the furnace, some fine particles sinter together to form coarse particles, and coarser particles grow bigger and bigger with the diminishing of some smaller particles. Thereby, abnormal grain (or particle) growth takes place. In contrast, when the precursor powders are introduced into the rotating furnace, the powders are agitated and exposed to the reaction temperature by means of the rotation of the tube and the associated stirring or tumbling action of the materials. With this movement, the temperatures, crystal structure and chemical composition of these moving powders are all made uniform.

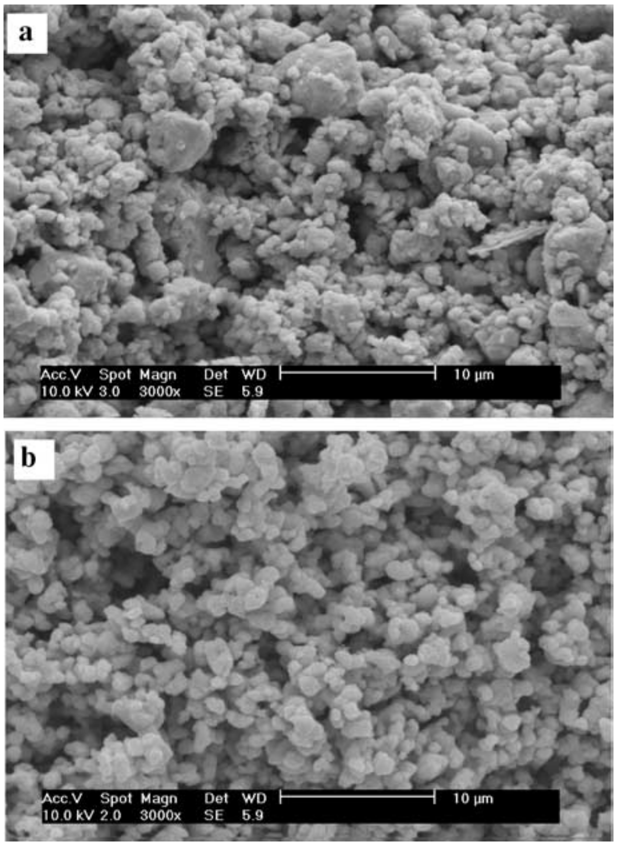

*Figure 4* Micrographs of $LiAl_{0.1}Mn_{1.9}O_4$ powders synthesized at 600 °C for 3 h: (a) the statically heated powders and (b) synthesized powders by rotary heating.

Therefore, the grain (or particle) growth rate within all the powders should be almost the same. Additionally, the stirring, tumbling action associated with interactive grinding among the powders, refines the powders and prevents abnormal grain growth. That is why the products prepared by rotary heating have smaller particle size and much narrows particle size distribution compared with the powders prepared by static heating. The uniform particle size distribution, in a way, implies good quality control in chemical composition and particle size.

The Li/$LiAl_{0.1}Mn_{1.9}O_4$ cells were electrochemically cycled 100 times between 3.0 and 4.3 V at the charging and discharging current density of 0.3 mA/cm$^2$, and the cycle characteristics are shown in Fig. 5. MAR600 exhibits the best cycleability among these three samples. MAR600 delivered an initial charge capacity of 126 mAh/g and a corresponding discharge capacity of 118 mAh/g. The coulombic efficiency for the first cycle was 94%. The discharge capacity was well maintained at 102 mAh/g up to 100 cycles, showing a high reversible capacity and good cycleability. This good cycleability is probably due to the substitution of some Mn—O linkages in the spinel by Al—O. The doped Al cations enhance the stability of the octahedral sites in the spinel skeleton structure [16]. The difference in the electrochemical performances between MA600 and C600 is small and can be ignored. The difference between MA600 and MAR600 may be caused by the particle size distribution. The powders with uniform particle size distribution and smaller particles should have better electrochemical performance. Compared with the conventional solid-state reaction process, the mechanical alloyed precursors can be transferred to Li—Mn—O spinels with a tolerable electrochemical performance at a lower calcining temperature, which suggests competition with those currently developing wet-chemical methods (such as sol-gel, Pechini process, etc. [1, 17, 18]) for low temperature synthesis of Li—Mn—O spinels.

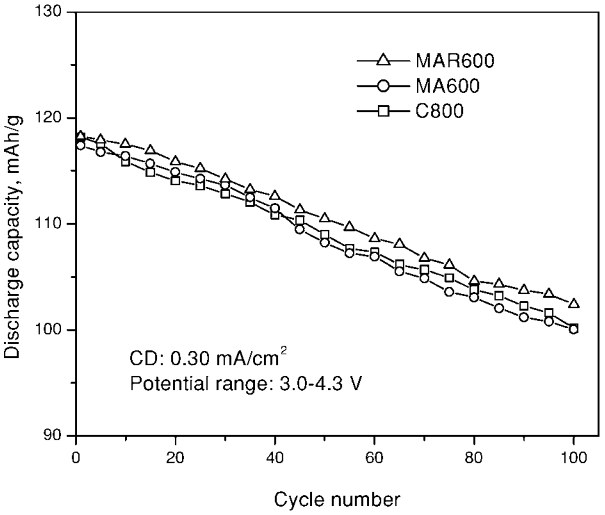

*Figure 5* Discharge capacities of MAR600, MA600 and C800 samples as a function of cycle number.

The present investigation shows that the Al doped $LiMn_2O_4$ powders with narrow particle size distribution, high capacity and good cycle retention were successfully prepared by a solid-state reaction at lower temperature for a shorter heating time (600 °C for 3 h) by employing mechanical alloying and rotary heating. Mechanical alloying ensured the uniform mixing of raw materials at nanoscale together with structure defects and short diffusion distance. The stirring and tumbling movement of the powders in the rotary furnace enhanced the uniformity of temperature, chemical composition and particle size of the powders. The successfully synthesized $LiAl_{0.1}Mn_{1.9}O_2$ materials delivered an initial discharge capacity of 118 mAh/g, and the discharge capacity was well maintained at 102 mAh/g up to 100 cycles, revealing a high reversible capacity and good cycleability.

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