Effect of Al\(^{3+}\) Doping on the Properties of LiMn\(_2\)O\(_4\) Cathode Material

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Abstract. Spinel phase LiAl\(_x\)Mn\(_{2-x}\)O\(_4\) were prepared by a rheological phase reaction method. The samples were characterized by X-ray diffraction, scanning electron microscopy, AC impedance, and galvanostatic charge/discharge profile measurement. These results showed that the LiAl\(_x\)Mn\(_{2-x}\)O\(_4\) had better cycling performance than pure LiMn\(_2\)O\(_4\). Among all the doped samples, the LiAl\(_x\)Mn\(_{2-x}\)O\(_4\) sample showed the best cycling performance, the initial discharge capacity is 132 mAh g\(^{-1}\), and the discharge capacity of 115 mAh g\(^{-1}\) at a rate of 1 C after 100 cycles and capacity retention of 87.1% after 100 cycles (1C=148 mA g\(^{-1}\)). Rate performance and electrochemical impedance spectroscopy measurements showed that the Al-doped spinels had high rate capability and reversible cycling performance.

1. Introduction
LiMn\(_2\)O\(_4\) adopts the spinel structure with space group Fd\(_\text{3}m\), in which manganese occupies the octahedral sites and lithium predominantly occupies the tetrahedral sites of the cubic close-packed oxygen ions, respectively, within a cubic close-packed oxygen array with oxygen ions in 32e sites [1]. Some reports revealed that the spinel LiMn\(_2\)O\(_4\) offers a potentially attractive alternative to the presently commercialized LiCoO\(_2\). The theoretical specific capacity of LiMn\(_2\)O\(_4\) is 148 mAh g\(^{-1}\), and the practical specific capacity approaches 120 mAh g\(^{-1}\). However, a key problem restraining LiMn\(_2\)O\(_4\) from commercialization is its severe capacity and cycling performance fading during cycling. Several factors cause capacity fade of spinel LiMn\(_2\)O\(_4\), as it had been reported by some investigators [2-4]. Such as (i) Mn dissolution of a LiMn\(_2\)O\(_4\) cathode into the electrolyte according to the following reaction: 2Mn\(^{3+}\)\(_{\text{solid}}\) > Mn\(^{4+}\)\(_{\text{solid}}\) + Mn\(^{2+}\)\(_{\text{solutions}}\) then, Mn\(^{2+}\) ions from this reaction, dissolve in the electrolyte solutions, (ii) Jahn–Teller effect arising from the Mn\(^{3+}\) ions, (iii) the high oxidation ability of Mn\(^{4+}\) will lead to a decomposition of the solvents. Furthermore, the cycle life and rate capability of doped LiMn\(_2\)O\(_4\) could be enhanced significantly by cationic substitutions (Co, Cr, Fe, Ga, or Zn) [5] and surface modification (AlPO\(_4\), ZnO, Al\(_2\)O\(_3\) and Bi\(_2\)O\(_3\)) [6].

In this work, we present the synthesis of a Li-Mn-spinel in which Mn ions are partly replaced by Al\(^{3+}\) ions. The structure, morphology, and electrochemical properties of as-synthesis LiAl\(_x\)Mn\(_{2-x}\)O\(_4\) are...
investigated. It shows that LiAl_{x}Mn_{2-x}O_{4} could be suitable for use as cathode in lithium ion battery application.

2. Experimental

All chemicals were of analytical grade and were used without further purification. The LiMn_{2-x}Al_{x}O_{4} was synthesized by using LiAc·4H_{2}O, MnAc_{2}·4H_{2}O, Al (NO_{3})_{3}·9H_{2}O and citric acid, as reactants. The molar ratio of LiAc·4H_{2}O, MnAc_{2}·4H_{2}O, Al (NO_{3})_{3}·9H_{2}O and citric acid was 1: 2-x: x: 3.6. These powders were mixed and thoroughly ground in an agate mortar, and then a few drops of water were added to form a rheological state mixture. The mixture was then heated at 120 °C for 12 h to form a light yellow precursor. The as-prepared samples were obtained by two steps, in which the precursor was heated at 550 °C for 6 h and then was ground to a fine powder and calcined at 800 °C in air for 10 h. The samples with the doping amount x of 0.00, 0.05, 0.10, 0.2 were designated as LMO, LMOAl-0.05, LMOAl-0.1, and LMOAl-0.2, respectively.

Powder X-ray diffraction patterns of the samples were obtained with a Rigaku XRD diffractometer. The morphologies of the samples were observed by using a scanning electron microscope (SEM; LEO 1530VP, Germany).

The electrochemical characterization was performed using CR2032 coin-type test cells. The cell consisted of the LiAl_{x}Mn_{2-x}O_{4} with the composition of 70 wt.% active materials, 20 wt.% carbon black, and 10 wt.-% PVDF, a lithium metal anode separated by a Celguard 2400 microporous film. The electrolyte was 1 mol L^{-1} LiPF_{6} (EC) and (DEC) (1: 1 by volume). The counter and reference electrodes were lithium foil. The model test cells were assembled in a glove box filled with argon gas. Charge-discharge tests were carried out at different current densities in the range of 3.0 V to 4.3 V.

3. Results and discussion

The typical powder XRD patterns of the samples are shown in Fig.1. The patterns of the undoped and doped samples are similar with the structure of spinel. It can be clearly seen that all the diffraction peaks are in agreement with those from the JCPDS 35-0782 card, which corresponds to stoichiometric spinel LiMn_{2}O_{4} with a cubic structure (space group: Fd3m); no other phase or impurities were detected.

Fig.2 shows the SEM photograph of the pristine LiMn_{2}O_{4} and the doped samples LMOAl-0.05, LMOAl-0.1, and LMOAl-0.2, respectively. The four samples are composed of many small polycrystalline particles. The pristine LMO sample consists of aggregates of regular crystallites with a size of 0.2–2 μm in Fig.2a. The non-uniform particles which are agglomerated with the particle size can be observed in Fig.2b–d. The agglomeration and particle size both decreased as the Al content increased, indicating that Al doping can limit the agglomeration of LiMn_{2}O_{4} powders. The decreased size of the Al-doped LiMn_{2}O_{4} particles may increase the electrode–electrolyte contact area and facilitate the transportation of Li ions, which would improve electrochemical performance.

Figure 1. Powder XRD patterns of (a) LMO, (b) LMOAl-0.05, (c) LMOAl-0.1, and (d) LMOAl-0.2.
The typical charge and discharge curves of LMOAl-0.1 electrodes in the voltage range between 4.5 and 3.0 V at a low current density of 1 C at room temperature, as shown in Fig. 3a. From the curves, it can be clearly seen that there are two potential plateaus near 4 V and 4.1 V, which indicates that the insertion and extraction of Li⁺ that occurs in spinel undergo two stages. One of the voltage plateaus, at about 4.0 V, is associated with the removal of Li⁺ from half of the tetrahedral sites, in which Li–Li interactions occur; the other, observed at about 4.1 V, is attributed to the removal of lithium ions from the other tetrahedral sites. The undoped LiMn₂O₄ (LMO) delivers an initial discharge capacity of 126 mAh g⁻¹, but after doping, the initial discharge capacities of the samples LMOAl-0.05, LMOAl-0.1, and LMOAl-0.2 electrodes were 128, 132, and 127 mAh/g, shown in Fig. 3b, respectively. As can be seen, those of the undoped and doped electrodes exhibit excellent cycling stability, and it is obvious that the cycling performance of the LMOAl-0.1 sample was significantly improved. The LMO show a capacity of 1C after 100 cycles: the loss of then initial value was 21.7%. However, the discharge capacity of the LMOAl-0.05, LMOAl-0.1, and LMOAl-0.2 electrodes were 103, 115, and 104 mAh g⁻¹, respectively, so that the loss of capacity is 18.9%, 12.9% and 19.1%. It can be found that LMOAl-0.1 had the best cycling performance among the four samples.

![Figure 2. SEM images of (a) LMO, (b) LMOAl-0.05, (c) LMOAl-0.1, and (d) LMOAl-0.2.](image)

Fig. 3c shows the cycling performances of the LMOAl-0.1 electrode cycled between 4.5 and 3.0 V at various current densities at room temperature. When the current densities are 1, 2, 4, 5, and 10 C, the initial discharge capacities of the LMOAl-0.1 electrode are 125, 117, 108, 96, and 71 mAh/g, respectively. When the current rate was changed from 10 C to 1C, the discharge capacity of LMOAl-0.1 almost returned back to its initial level, Although the discharge capacities decrease with increasing current density, the LMOAl-0.1 electrode displays good capacity retention at different current densities.
Figure 3. Typical charge/discharge curves for selected cycles of (a) LMOAl-0.1; Cycling performance (b) of LMO, LMOAl-0.05, LMOAl-0.1, and LMOAl-0.2; (c) Cycling performance of the LMOAl-0.1 electrode at various current densities; Electrochemical impedance spectra (EIS) of LMO, LMOAl-0.05, LMOAl-0.1, and LMOAl-0.2.

Fig. 3d illustrates the electrochemical impedance spectra of the samples which were recorded in the fresh cell. Two depressed semicircles are observed for both electrodes, the one located in high frequency ranges assigned to surface film resistance and the one located in medium frequency ranges assigned to charge transfer impedance. The kinetics difference of the electrodes was further investigated by modeling AC impedance spectra based on the Randles equivalent circuit. Analysis of the experimental data was performed by fitting equivalent circuits. The charge transfer resistance \( R_{ct} \) was significantly lower for the LMOAl-0.1 electrode (142.8 Ω) compared to that the LMO, LMOAl-0.05, and LMOAl-0.2 electrodes (126, 114 and 182 Ω). The remarkably improved rate properties of the LMOAl-0.1 electrode was due to the suppression of the solid electrolyte interfacial (SEI) layer development and faster kinetics of both the \( \text{Li}^+ \) diffusion and the charge transfer reaction. These facts support that the LMOAl-0.1 electrodes sample has good electrochemical properties suitable for electrode material in lithium ion battery.

4. Conclusion
Single-phase \( \text{LiAl}_{x}\text{Mn}_{2}\text{O}_4 \) spinel materials were synthesized by the rheological phase reaction method. The agglomeration and particle size of the samples decreased with increased Al content. Especially, \( \text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4 \) exhibited excellent cycling stability with a capacity retention of 87.1% at a discharge rate of 1C after 100 cycles. \( \text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4 \) displays higher discharge capacity and best cycling stability. Therefore, the element doping will both enhance the charge/discharge capacity and achieve better cycling stability.
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