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Excellent stability of Al-doped $LiMn_2O_4$ prepared by a sol - gel method

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Abstract. $LiAl_xMn_{2-x}O_4$ (x = 0.00, 0.05, 0.10, and 0.15) is synthesized successfully using a sol - gel method at 700 ℃ for 10 h in air. X-ray diffraction (XRD) results indicate the $LiAl_xMn_{2-x}O_4$ has a good crystallinity. Scanning electron microscopy (SEM) images show tiny distinction about the morphology and size for samples. Compared with the pure $LiMn_2O_4$, the Al-doping $LiMn_2O_4$ possesses outstanding cycling capabilitiy, testified by electrochemical measurement, especially for the sample of $LiAl_{0.1}Mn_{1.9}O_4$. The discharge capacity of $LiAl_{0.1}Mn_{1.9}O_4$ delivers up to 113.2mAh g^{-1} at 0.5 C - rate, and the capacity retention is 97.1% after 100 cycles.

Introduction

Among all the cathode materials, Lithium manganese oxide ($LiMn_2O_4$) with spinel structure for LIBs, has given rise to considerable attention by virtue of its low cost, environmental friendliness, abundant manganese resources, high operating potential, good safety and relatively high energy density [1, 2]. So far, many researchers have made a great contribution to improve the electrochemical performance of spinel $LiMn_2O_4$. However, the significant capacity fading during cycling especially at elevated temperature hinders its practical applications on EVs and HEVs. The poor cycling stability is mainly caused by the following three aspects: (i) disproportionation reaction of manganese into the electrolyte solution: $Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$; (ii) the structural transformation from a cubic to tetragonal phase induced the Jahn-Teller distortion on the surface of the spinel structure [3, 4]; (iii) decomposition of the electrolyte. Extensive strategies have been proposed to overcome the problem of capacity decay , so as to improve the cycle performance of $LiMn_2O_4$. Among these strategies, one effective approach is to use a small amount of dopant ions to occupy the position of Mn ions [5].The dopant ions are assumed to occupy the octahedral 16d sites of Mn-ions in the spinel lattice and stabilize the spinel structure [6]. Currently, the Al-substitution of Mn^{3+} has been proved to be a promising way to obtain spinel cathode with longer cycle life, due to abundance, nontoxicity, lightness and cheapness of aluminium [7]. Many researchers have been absorded in synthesizing the $LiAl_xMn_{2-x}O_4$ and the synthesized $LiAl_xMn_{2-x}O_4$ obtained an enhanced electrochemical performance superior to the pure $LiMn_2O_4$ [8].

Synthesized $LiMn_2O_4$ by the sol-gel method possesses several advantages, such as low sintering temperature, short reaction time, narrow particle-size distribution [9]. However, it would be difficult to figure out or prepare an uniform solution with a high oxidation state of manganese ions.

In this paper, a new sol-gel method was used to synthesize an uniform solution with a high oxidation state of manganese ions. And based on the solution, the electrochemical performance of $LiAl_xMn_{2-x}O_4$ is outstanding. In order to systematically understand the effect of different content of doping metal aluminium on the electrochemical performance of $LiMn_2O_4$, then the aims of the work is to explore the electrochemical properties of $LiAl_xMn_{2-x}O_4$ (x = 0.00, 0.05, 0.10, 0.15) prepared by sol - gel method.

Experimental.

The $LiAl_xMn_{2-x}O_4$ (x = 0.00, 0.05, 0.10, 0.15) cathode material was synthesized via the sol-gel method. All the reagents used in the experiment were analytical grade. Lithium nitrate (LiAc), aluminium nitrate ($Al(NO_3)_3·9H_2O$) and manganese acetate ($Mn(Ac)_2·4H_2O$) were thoroughly

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dissolved in a solvant of 80ml ethyl alcohol at a molar ratio of 1.02: x : 2-x (x = 0.00, 0.05, 0.01, 0.15). After the addition of $NH_3 \cdot H_2O$ (25 - 28 wt%), the air was pumped into the homogeneous solution continuously. Then, the acquired black solution was maintained at 85 ℃ under the condition of constant stirring until the formation of black gel. The resultant gel was dried at 85 ℃ for 5h, and then heated at 700 ℃ for 10h in the air followed by cooling down to obtain the final product $LiAl_xMn_{2-x}O_4$.

Cell preparation. Electrochemical tests were performed by the coin cells (2032 type) assembled in an argon glove box. The cathode materials were formed from the active materials, a poly (tetrafluoroethylene) binder and acetylene black in a 84 : 8 : 8 by weight ratio. 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1, vol. %) was used as the electrolyte between lithium metal anode and cathode material.

Measurements. The structure was characterized by powder X-ray diffraction (XRD, Rint - 2000, Rigaku, Japan) using Cu - Kα radiation over the 2θ range of 10° - 80°. A JSM - 6701F scanning electron microscopy (SEM, Japan) was performed to obtain corresponding information about the morphology of the synthesized samples. Electrochemical measurements of the cells were carried out on a LAND CT2001A tester (Wuhan, China) in the voltage range of 3.5 - 4.3V for $LiAl_xMn_{2-x}O_4$/Li cells.

Results and discussion

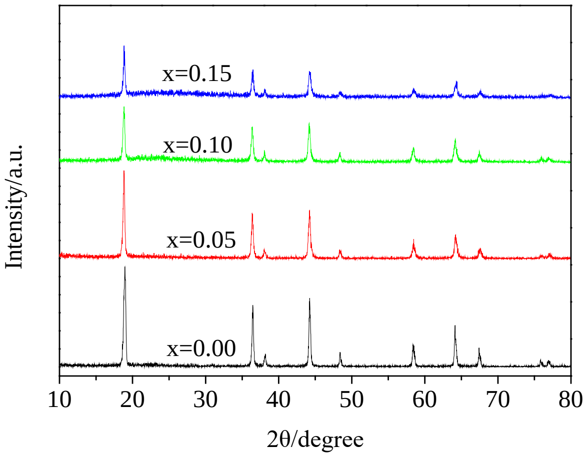

Fig. 1 XRD patterns of $LiAl_xMn_{2-x}O_4$ (x = 0.00, 0.05, 0.10 and 0.15)

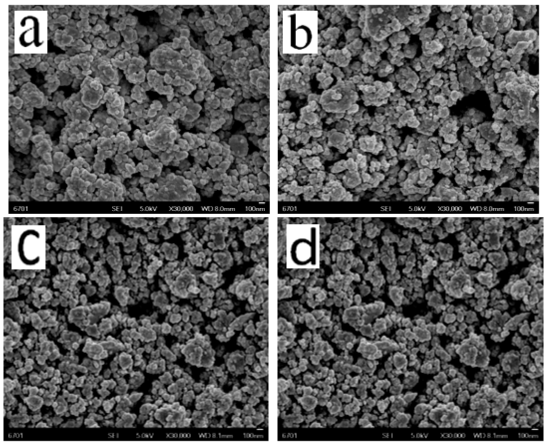

Fig. 2 SEM images of $LiAl_xMn_{2-x}O_4$(a: x= 0.00, b: x = 0.05, c: x= 0.10, d: x= 0.15).

Fig.1 shows XRD patterns of $LiAl_xMn_{2-x}O_4$ (x=0.00, 0.05, 0.10 and 0.15). All of the peaks observed are strong and sharp, which suggest excellent crystallinity. The clear recognizable reflection peaks include eight lattice planes at (111), (311), (222), (400), (331), (511), (440) and (531), which are assigned to the cubic structure of spinel $LiMn_2O_4$ (JCPDS File No. 35 - 0782), with the space group of Fd - 3 m. No impurity phase could be observed in the all samples, which indicates all samples were pure phase spinel structure. The doping of Al has no obvious effect on the spinel structure of the sample, and it plays a supporting role in stabilizing the structure of the material. Therefore, it is confirmed that a suitable amount of Al content is quite necessary for stablizing the spinel structure.

Fig. 2 displays the SEM images of the synthesized $LiAl_xMn_{2-x}O_4$ (x = 0.00, 0.05, 0.10 and 0.15) at the same magnification (× 30,000). It is found that different contents of Al doping have little effect on the micromorphology and size. This is due to the small amount of Al doped in the samples and analogous synthesis processes. All of the samples are composed of small particles or large particles of aggregation, and their average particle size is less than 100nm. The samples with smaller particles are advantageous for the better contact between the interface of electrolyte and electrode materials, which is in favor of the intercalation/deintercalation of lithium ions during the charge-discharge process [10].

Fig. 3 shows the initial galvanostatic charge and discharge curves of $LiAl_xMn_{2-x}O_4$ (x = 0.00, 0.05, 0.10 and 0.15) at 0.5 C - rate. All the samples prepared exhibit two well-defined voltage platforms during the charge-discharge process. The first discharge capacities of $LiAl_xMn_{2-x}O_4$ (x = 0.00, 0.05, 0.10 and 0.15) are given in Fig.3. During the first cycle pure $LiMn_2O_4$ delivers specific discharge capacity of 117.7 mAh g^{-1}, and $LiAl_xMn_{2-x}O_4$ (x = 0.05, 0.10 and 0.15) gives 115 mAh g^{-1}, 113.2 mAh $g^{-1}$and 110.8 mAh g^{-1}, respectively. According to the fore-mentioned data, we can clearly observe the values of the discharge capacity decrease with the increase of the content of Al doping. That is because the valence of aluminum is lower than the average valence of manganese in $LiMn_2O_4$, which leads to the increase of the content of Mn^{4+} in $LiAl_xMn_{2-x}O_4$. Obviously, when Mn^{3+} is partly substituted by Al^{3+}, the capacity of Al-doped $LiMn_2O_4$ decreases with the increase of the content of Mn^{4+}.

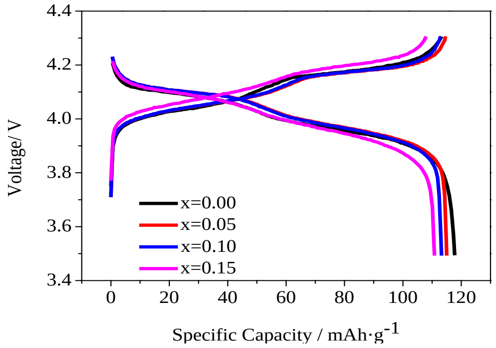

Fig. 3 The initial galvanostatic charge - discharge curves of $LiAl_xMn_{2-x}O_4$ with x = 0.00, 0.05, 0.10 and 0.15 at 0.5 C - rate.

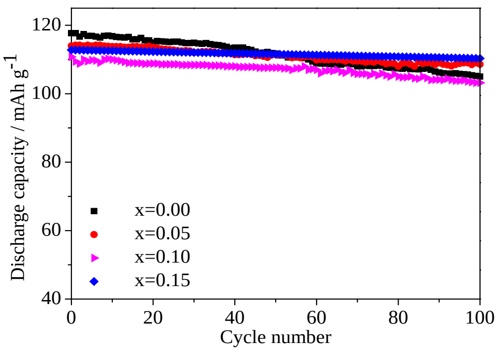

Fig. 4 The cycling performance of $LiAl_xMn_{2-x}O_4$(x = 0.00, 0.05, 0.10 and 0.15) at 0.5 C discharge rate at room temperature (RT).

The cycling performance of all the cathode material is quite significant for their practical applications. The cycling performances of $LiAl_xMn_{2-x}O_4$ (x = 0.00, 0.05, 0.10 and 0.15) at the rate of 0.5 C - rate at RT are showed in Fig. 4. It is overt that the first discharge capacity of undoped sample is maximal. It is consistent with the results in Fig.3. After 100 cycles the capacity retentions are 92% (x = 0.00), 94.96% (x = 0.05) and 97.1% (x = 0.10), and 94.1% (x = 0.15). All the products especially for the Al-doping ones show the excellent cyclabilities. Among them, the $LiAl_{0.1}Mn_{1.9}O_4$ expresses the best cycling behavior. To a certain extent, the introduction of more Al improved the cycle performance availably. Al - doped $LiMn_2O_4$ with better cycleability has great correlation with enhanced structural stability and reduced the Jahn-Teller distortion [11].

Conclusions

The $LiAl_xMn_{2-x}O_4$ with better cycling capabilitiy (x = 0.00, 0.05,0.10, and 0.15) is synthesized successfully using a sol-gel method at 700 ℃ for 10 h in air. (SEM) images indicate different contents of Al doping of the samples have little effect on the micromorphology and size. The samples exhibit the excellent cycling performance at RT, which is really significant for their practical applications. The capacity retentions after 100 cycles at 0.5 C - rate are 92 % (x = 0.00), 94.96 % (x = 0.05), 97.1 % (x = 0.10), and 94.1 % (x = 0.15) at RT, respectively. It suggests that the introduction of Al with the stronger bonding to oxygen is supposed to suppress the Mn^{3+} surface phases, which would undoubtedly enhance the cycling life of $LiMn_2O_4$ and its derivatives.

Acknowledgments

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