Effect of Al-Doping on Electrochemical Performance of LiMn_2O_4

XINGHUA LIANG*, SHUAIBO ZENG, YUSI LIU, TIANJIAO LIU, LIN SHI and CHAOCHAO YE

Guangxi Science and Technology University, Liuzhou 545006, P.R. China

*Corresponding author: Tel: +86 18648863918; E-mail: lxh304@aliyun.com.cn

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Spinel LiMn_2O_4 and $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ (G^x , $x = 0, 1, 2, 3, 4$) have been synthesized by solid-state method. The synthesized samples were characterized by following methods: X-ray diffraction, scanning electron microscopy. Results showed that $\text{LiAl}_{0.3}\text{Mn}_{1.7}\text{O}_4$ (G^3) was spinel structure which space group was $\text{Fd}3m$. The spinous substances were not observed on its spherical-structured surface. Experimental battery E^x ($x = 0, 0.1, 0.2, 0.3, 0.4$) was assembled by using G^x as cathode electrode, active carbon as conductive agent and Li plate as the anode electrode. The E^x ($x = 0, 0.1, 0.2, 0.3, 0.4$) was characterized by electrochemical impedance spectroscopy, cyclic voltammetry and charge-discharge studies. Results indicated that Al-substitution decreased the internal resistance of E^x . Charge-discharge cycling studies and cyclic voltammetry test showed that Al-substitution substantially improved the capacity retention of the E^x .

Keywords: Lithium ion battery, XRD, SEM, Electrochemical performance.

INTRODUCTION

Spinel LiMn_2O_4 is the most broadly studied cathode material for lithium rechargeable batteries owing to advantages including easy preparation, low cost, non-toxicity, economical and environmental friendly and relatively high energy density¹⁻⁵. The solid-state method, because of its simple processes and easily control and lower requirement in equipment, has been a common way to produce cathode material of lithium ion batteries on a large scale. However, cathode material has not been mixed evenly, which could possibly lead to lower substance purity, Mn_2O_3 being produced and breakdown of the spinel lattice. At the later stage of discharging, on the surface of Mn^{3+} easily takes place the disproportionation reaction⁶⁻⁷: $2\text{Mn}^{3+}(\text{s}) \rightarrow \text{Mn}^{4+}(\text{s}) + \text{Mn}^{2+}(\text{l})$, while the liquid Mn^{2+} dissolves in the electrolyte. It is the reason why the capacity of spinel LiMn_2O_4 fades rapidly in charge-discharge cycle. The structure of spinel could be destroyed and impedance of the battery increases while coulomb effect dwindles under the condition of high temperature and large current charge-discharge process. Above all of these can limit the commercialization of LiMn_2O_4 . In order to solve these problems, people have proposed an effective strategy⁸⁻¹⁰ to substitute Mn^{3+} , which contributes to improve conductivity of the cathode materials as well as the electrochemical performance of the battery. Krins *et al.*¹¹ and Wu *et al.*¹² doping Ti^{4+} greatly improved the electrochemical property of LiMn_2O_4 . Because the binding energy of Cr-O (1142 KJ/mol) is much higher

than that of Mn-O (946 KJ/mol)¹³⁻¹⁵, doping Cr^{3+} propelled the formation of a stable three-dimensional structure and decreasing of the dissolved load of Mn^{2+} , which weakened the Jahn-Teller effect. Even though Thirunakaran *et al.*¹⁶, Wang *et al.*¹⁷ and Lee *et al.*¹⁸ doping Al^{3+} by sol-gel method bettered the stability and cyclic performance of LiMn_2O_4 , the discharge capacity turned out to be 105 mAhg^{-1} after 50 cycles at 0.2 C.

In this paper, we prepared the cathode material of the Al-substitution (G^x) lithium ion battery by solid-state method, which Li plate was used as anode electrode and LiPF_6 concentrated 1 mol L^{-1} (volume proportion of EC/DNC being 1:1) used as electrolyte, Celgard2300 as diaphragm to assemble the battery (E^x). Structure and morphology of the G^x were characterized by XRD and SEM. Cyclic voltammograms and AC impedance were used to analyze the surface state change of E^x electrode after charge-discharge. A higher capacity cathode electrode after storage was given by solid-state method.

EXPERIMENTAL

Atmosphere box furnace (KBF13Q); X ray diffraction (DX-2700); scanning electron microscope (EVO18); vacuum glove box (ZKX-2); high-precise testing system for battery performance (CT3008W); electrochemical workstation (CHI600D).

Lithium acetate (99.9 % pure), manganese acetate (99.9 % pure) and Al_2O_3 (99.9 % pure) were fully mixed with a stoichiometric mole ratio of $\text{Li}:\text{Mn}:\text{Al} = 1.2:(2-x):x$ ($x = 0, 0.1, 0.2, 0.3, 0.4$). Then preheated all of them in the atmosphere furnace

at 450 °C for 4 to 6 h, keeping heating rate below 10 °C min⁻¹. After furnace cooling, increased the temperature to 750 °C and heated them for 50 to 72 h, keeping heating rate below 10 °C min⁻¹. After the furnace cooling again, black G^X (X = 0, 1, 2, 3, 4) can be obtained.

Battery assembly: Cathode paste are formed by mixing G^X (active material) (80 wt. %), active carbon (conductive agent) (10 wt. %) and PVDF-HFP (binder) (10 wt. % polyvinylidene fluoride, PVDF, dissolved in N-methyl-2-pyrrolidone, NMP). The slurry was coated on aluminum foil substrates by doctor blade. Then aluminum foil was dried under the temperature of 80 °C and cut by the tablet machine. Using a piece of lithium metal as anode electrode, LiPF₆ and EC/DNC whose concentration is 1 mol/L (1:1, volume ratio) as electrolyte and Celgard 2300 as diaphragm. The experimental batteries E^X (X = 0, 1, 2, 3, 4) can be assembled in the manual-operation box which was filled with argon gas.

RESULTS AND DISCUSSION

Analysis of X-ray diffraction: Crystal structure of the products were analyzed via X-ray diffraction with CuK_α radiation at a scanning speed of 0.03° s⁻¹, wavelength of 1.5406 Å, tube voltage of 40 kV, tube current of 30 mA. Fig. 1 shows the X-ray diffraction pattern of the G^X powders. It is found that the diffraction peaks at 2θ = 19.14°, 36.15°, 37.91°, 44.80°, 48.19°, 58.35°, 64.80° and 68.96° are corresponding to the 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). It showed that all five groups were spinel-type structure with *Fd3m* space group. Diffraction peaks of Mn₂O₃ were observed at 28.50°, 32.80° in groups of G¹ and G². And there were no diffraction peaks of Mn₂O₃ in groups of G³ and G⁴. Table-1 presented the lattice parameters and full width at half maximum (FWHM) values of (400) peak of the G^X powders. It has been demonstrated that the lower FWHM value of the (400) peak was relative to higher crystallinity of spinel LiMn₂O₄. From Table-1, it is obvious that the Al-substitution had a higher crystallinity than pure LiMn₂O₄. The G^X were relative to higher specific surface area than pure LiMn₂O₄, because of smaller lattice volume.

Fig. 1. X-ray diffraction pattern of the G^X powders. (a) G⁰; (b) G¹; (c) G²; (d) G³; (e) G⁴

Scanning electron microscopy: SEM test was conducted with a microscope magnification of 10000X at a voltage of 20 kV. Its studies reflected the textural and morphological

TABLE-1
LATTICE PARAMETERS OF THE SAMPLES
G^X AND FWHM OF (400) PEAK

Sample	Lattice constant (a) (Å)	Lattice volume (Å ³)	FWHM of (400) peak (°)
G ⁰	8.242	559.8	0.1596
G ¹	8.235	558.4	0.1585
G ²	8.231	557.6	0.1578
G ³	8.228	557.0	0.1576
G ⁴	8.217	554.8	0.1571

characteristics of the G^X. Results suggested that G^X samples had spherical structure with an average diameter size between 50 nm to 500 nm and spinous processes were not observed in Fig. 2. It means that the diaphragm could not be pierced. The structure might avoid short circuit.

Fig. 2. SEM image of G^X powders. (a) G¹; (b) G²; (c) G³; (d) G⁴; (e) G⁰

Electrochemical impedance spectroscopy analysis: Electrochemical impedance spectroscopy was studied with a frequency range of 10 MHz to 100 KHz and amplitude of 5 mV. Fig. 3 was the spectroscopy of E^X in its first process of charge-discharge. It was found that E³ had increased Coulomb effect in the battery because of decreasing internal resistance. Doping Al³⁺ restricted the growth of electrochemical reaction impedance in large current charging-discharging; it greatly enhanced the high current charge-discharge property of the battery.

Cyclic voltammetry: Cyclic voltammetry curve was studied at electrochemical workstation with an initial potential of 3 V and a maximum of 4.4 V. Scanning rate was 0.1 mV s⁻¹ with a sensitivity of 1 × 10⁻⁰⁴. Test temperature was 20 °C. Fig. 4 showed the cyclic voltammetry curves of E^X (X = 0, 1, 2, 3, 4). It indicated two redox peaks of E^X: 3.97 V/3.81 V(E⁰); 3.96 V/3.81 V(E¹); 4.00 V/3.85 V(E²); 3.98 V/3.81 V(E³); 4.00 V/3.84 V(E⁴), which responded to the pair of charge-discharge platforms. Current of E³ at two redox peaks were 6 and 5 mA. The reversible capacity of E³ was also the largest area which was surrounded by two curves. It can also be certified by the charge-discharge curves.

Fig. 3. Electrochemical impedance spectroscopy plots of E^X in initial charge process (E^X , $X = 0, 1, 2, 3, 4$)

Fig. 4. First cyclic voltammograms of E^X . (E^X , $X = 0, 1, 2, 3, 4$)

Analysis of charge-discharge and charge-discharge cycling studies: The charge-discharge test was carried out by Neware battery testing instrument. Current ranges output from -5 mA to $+5$ mA. Both measuring accuracy of current and voltage maintain at $\pm (0.05\% + 0.1\%)$. Tests were carried room temperature. Figs. 5-7 reflected the results under the initial charge-discharge current at 0.1, 0.5 and 1 C. It can be found that specific discharge capacity of cathode materials slowly went down in low current charging-discharging after Al^{3+} doped, however, with the current increasing from 0.1 to 1 C, the discharge capacity of pure LiMn_2O_4 faded faster. Specific discharge capacity of pure LiMn_2O_4 was 35 mAhg^{-1} at 1 C, but E^3 and E^4 were 80 and 82 mAhg^{-1} at 1 C. Figs. 8 and 9 presented cyclic voltammetry curves after 52 cycles at 0.5 C, 1 C. It was indicated that capacities of LiMn_2O_4 without doping Al^{3+} faded obviously at 0.5 C, 1 C. In contrast, capacities of LiMn_2O_4 with doping Al^{3+} didn't fade obviously at the same condition. As a result, doping Al^{3+} can contribute to improve cyclic performance of battery; specific capacities of E^3 became 115 mAhg^{-1} , 90 mAhg^{-1} at 0.5 C, 1 C after 52 cycles.

Conclusion

In the process of synthesizing cathode material G^X ($X = 0, 1, 2, 3, 4$) by solid-state method, doping Al^{3+} had influence on appearance and electrochemical performance of LiMn_2O_4 .

Fig. 5. Charge-discharge curves of E^X ($X = 0, 1, 2, 3, 4$) at 0.1 C in the voltage range of 3.00-4.35 V vs. Li/Li^+

Fig. 6. Charge-discharge curves of E^X ($X = 0, 1, 2, 3, 4$) at 0.5 C in the voltage range of 3.00-4.35 V vs. Li/Li^+

Fig. 7. Charge-discharge curves of E^X ($X = 0, 1, 2, 3, 4$) at 1 C in the voltage range of 3.00-4.35 V vs. Li/Li^+

The synthesized product remained spinel-type. Doping a small quantity of Al^{3+} caused peaks of Mn_2O_3 ; spinous substances were not observed on its spherical-structured surface. In addition, there was great improvement in E^X in its cyclic performance and large current charge-discharge performance. Results of cyclic voltammetry curves suggested that Al^{3+} substituted part of Mn^{3+} restricted the disproportionation reaction at later stage of discharging. Because of increased the current of redox peaks.

Fig. 8. Cyclic performance of E^X ($X=0, 1, 2, 3, 4$) with varying Al^{3+} doping at 0.5 C

Fig. 9. Cyclic performance of E^X ($X=0, 1, 2, 3, 4$) with varying Al^{3+} doping at 1 C

At rate of 0.5 C, 1 C, initial charge and discharge capacities of E^3 were 89 and 80 $mAhg^{-1}$, respectively which turned to be 115 and 90 $mAhg^{-1}$ after 52 cycles.

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