The Synthesis and Performance of Spinel $LiMn_2O_4$ Doping Ce^{4+} for Li-ion Batteries Cathode Materials

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Abstract: Spinel $LiCe_xMn_{2-x}O_4$ ($x=0\sim0.5$) as cathode materials for Li-ion batteries were synthesized by solid state method and characterized by XRD and charge-discharge test. The $LiCe_{0.03}Mn_{1.97}O_4$ displayed better reversibility and cycle cability at room and high temperature.

Key words: spinel LMn_2O_4; doping; Li-ion batteries; rare earth
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With the developing of the society, the spinel LMn_2O_4 has shown a great foreground for application as the cathode materials for Li-batteries, because of its many advantages[1]. The obstruction for commercial application of spinel LMn_2O_4 is its fast capacity fading with charge/discharge cycling[2]. Doping is an effective method[3].

In this paper, describe the synthesis and performance of spinel LMn_2O_4 doping Ce^{4+} with CeO_2. The electrochemical performances have been studied.

1 Experiment

The Li_2CO_3 (99.5%), MnO_2 (96%) and CeO_2 (99.99%) were mixed in some ratios and ball milled using agent for 4 h. After drying these were preheated at 500 ℃ for 16 h and cacined at 750 ℃ for 24 h all in the air. Through nature cooling, the samples of $LiCe_xMn_{2-x}O_4$ ($x=0\sim0.05$) as cathode materials were gained.

2 Result and Discussion

The typical powder XRD patterns of the prepared products are shown in Fig. 1.

The diffraction peaks of all materials correspond to spinel phase. The $LiCe_{0.03}Mn_{1.97}O_4$ was most aculeted than others. At the same time Ce peak was observed and as the amount of doping increasing. In theory, the $LiCe_{0.03}Mn_{1.97}O_4$ maybe have highest capability than others. The charge-discharge curves of $Li/LiCe_xMn_{2-x}O_4$ ($x=0\sim0.05$) as cathode batteries when cycled 20 curves between 3.0 and 4.3 V 0.2 C at room temperature were presented in Fig. 2. The dates was the same to the before analyzes. the discharge capability of spinel LMn_2O_4 that initial capability reached to 124 mAh/g had most fading as the charge-discharge cycles. The sample $x=0.05$ had low capability maybe much amount CeO_2 distory the crystal structure. Indicated the substitution becoming more difficult when the amount of dopant increased. The materials doped 0.03 that its initial capability was close to the capability of spinel LMn_2O_4 had the highest capability and displayed better reversibility and cycle capability.

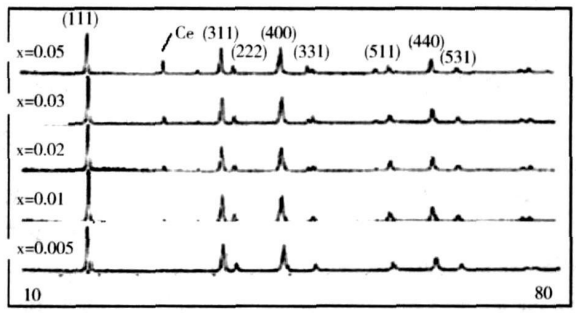

Fig. 1 X-ray diffraction patterns for $LiCe_xMn_{2-x}O_4$ ($x=0\sim0.05$)

The charge-discharge dates of $LiCe_{0.03}Mn_{1.97}O_4$ cycled 100 curves at 25 ℃ and cycled 25 curves at 55 ℃ are showed in Fig. 3. The capability at high temperature was lower than its at room temperature. Specially, the capability of $LiCe_{0.03}Mn_{1.97}O_4$ through 100 cycles at room temperature was 107 mAh/g, through 25 cycles at high temperature remain 100 mAh/g. Indicated that the material had better cycle capability at high or room

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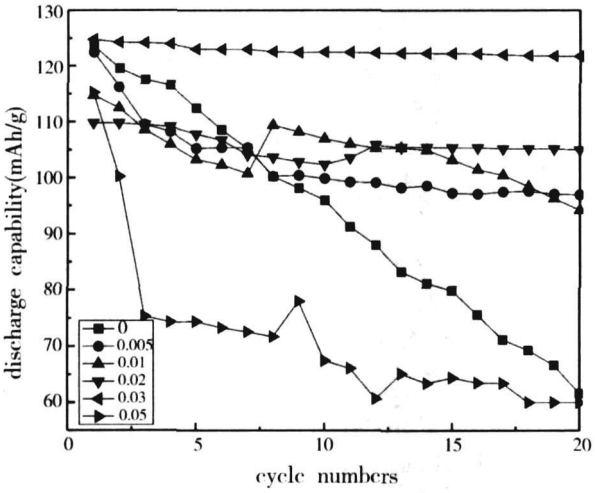

Fig. 2　The cycle curves of the materials $LiCe_xMn_{2-x}O_4$ (A x = 0.005, B x = 0.01, C x = 0.02, D x = 0.03, E x = 0.05)

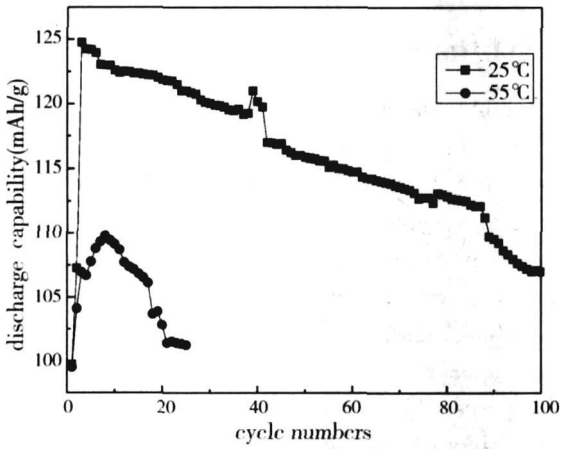

Fig. 3　The capacity curves of the $LiCe_{0.03}Mn_{1.97}O_4$ at different temperature

temperature. Because of The special electro-character of CeO_2[4]. Some CeO_2 doped in crystal lattice stayed the structure, others surplus CeO_2 remained in materials improved its performance when charge-discharge cycles.

3　Conclusion

The spinel $LiCe_xMn_{2-x}O_4$ ($x = 0 \sim 0.05$) were synthesized by solid method. But the testing dates displayed that some CeO_2 still was found in the materials. And the cathode material $LiCe_{0.03}Mn_{1.97}O_4$ exhibited excellent reversibility and capability along with long charge-discharge cycles at room (25 ℃) and high temperature (55 ℃). The dates indicted that some radios CeO_2 doped in the crystal lattice were helpful for the stability of materials, others milled with sample also helpful for improving the electrochemsitry because of the special characters of rare earth.

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正极材料尖晶石 $LiMn_2O_4$ 掺杂 Ce^{4+} 的合成与性能研究

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摘　要：由高温固相法合成了锂离子电池正极材料尖晶石 $LiCe_xMn_{2-x}O_4$ ($x = 0 \sim 0.5$)，并经 XRD和电化学等测试。实验结果表明，材料 $LiCe_{0.03}Mn_{1.97}O_4$ 在常温和高温下都具有较好的循环性能和电化学性能。

关键词：尖晶石 $LiMn_2O_4$；掺杂；锂离子电池；稀土

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