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The Synthesis and Electrochemical Property of Spinel Cathode Material $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ for Lithium-Ion Batteries

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Novel spinel $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ as cathode material for Li-ion battery was prepared through two-step solid-state reaction and treatment by Li-Mn-Co-O material on the surface of $Li_{1.05}[Mn_{1.99}Gd_{0.01}]O_4$ particles. The physical and electrochemical properties of the materials were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), cyclic voltammetry (CV) and charge-discharge test. The novel material showed improved electrochemical properties compared with the pristine $LiMn_2O_4$, especially at elevated temperature. The initial discharge capacity of the $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ was 128.0 mAh g^{-1} with a fading rate of 0.041% per cycle at 25°C. Moreover, the cycle ability was improved more evidently at 55°C, the retentions ratio of capacity was up to 91% for the novel material after 100 cycles.

Keywords: Lithium-ion battery; Cathode material; Spinel; Solid-state reaction

1. INTRODUCTION

Over the past decades, lithium cobalt oxide, with its excellent electrochemical performance, has become the standard cathode material in commercial lithium-ion batteries. However, the high cost and toxicity of cobalt may eventually limit the development of lithium-ion batteries market. Therefore, it is crucial to search the substitutions for it.

Depending on the lower cost of manganese, the spinel $LiMn_2O_4$ has been realized as the promising alternative to $LiCoO_2$. It was lower toxicity and more environmentally compatible [1-9]. However, the capacity and cycle ability of $LiMn_2O_4$ are still desired to be improved, particularly at elevated temperatures. Investigations have showed that the $LiMn_2O_4$ suffered from a rapid capacity fading, especially at high temperatures, which was attributed to the phase transition from cubic to tetragonal phase upon 3V cycling or the dissolution of manganese in the electrolyte [10-14]. This reaction began at the spinel/electrolyte interface and sped up at high temperatures. Many research groups had attempted to reduce the capacity fading of $LiMn_2O_4$ by surface treatment to avoid Mn dissolution [15-28]. Metal oxides are effective materials for this purpose such as ZnO, CeO_2, MgO, Al_2O_3. In addition, $LiCoO_2$ [29,30], $LiCu_xMn_{2-x}O_4$ [31], $LiNi_{1-x}Co_xO_2$ [32], $Li_4Ti_5O_{12}$ [33] were also tried as surface treatment materials of $LiMn_2O_4$ to enhance the uniformity of the surface coverage. But most of the reported improve the cycle ability at the cost of capacity. On the other hand, the demand for rechargeable batteries with high specific capacity makes it necessary to improve the specific capacity of $LiMn_2O_4$. It was reported that doping of $LiMn_2O_4$ lattice with rare-earth elements like La, Nd in the 16d sites can improve electrical properties of cathode materials greatly and stabilize the structure of $LiMn_2O_4$ [34-40]. It can be deduced that better electrochemical properties could be achieved if $LiMn_2O_4$ is modified with both doping and surface treatment.

In this study, the spinel cathode material $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}\text{-}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ was synthesized using a two-step solid-state method, which was easy to control. To improve the cycle ability, the surface of spinel material was treated by the mixed compounds of manganese, cobalt and lithium. Meanwhile, as previous work from our laboratory [41], rare-earth element of Gd was introduced into $LiMn_2O_4$ materials for higher capacity. It combined the modifying, doping and two-step solid-state synthesized method to stabilize the spinel structure of $LiMn_2O_4$, the cycle ability and capacity of which were expected to improve under room and high temperature.

2. EXPERIMENTAL

2.1. Materials preparation

The compound $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ was prepared by high temperature solid-state method in air. First, a stoichiometric mixture of Li_2CO_3 (CR), MnO_2 (CMD) and Gd_2O_3 (AR) for the nominal composition of $Li_{1.05}[Mn_{1.99}Gd_{0.01}]O_4$ was ground by ball grinding, then the mixture were calcined at 800°C for 3h. The obtained $Li_{1.05}[Mn_{1.99}Gd_{0.01}]O_4$ powder was continuously mixed with the compounds of Li_2CO_3 (CR), MnO_2 (CMD) and Co_3O_4 (AR) (cationic ration of Li: Mn: Co = 1.05: 1.8: 0.2), targeting for a final composition of $Li_{1.05}[Mn_{1.99}Gd_{0.01}]O_4$: Li-Mn-Co-O = 1: 0.1. Then the mixtures were ground thoroughly. Finally, the object product was got by a second time calcination: 850°C for 5h and then 600°C for 10h in air atmosphere. Meanwhile, the pristine $LiMn_2O_4$, $Li_{1.05}Mn_{1.99}Gd_{0.01}O_4$ and $Li_{1.05}Mn_{1.8}Co_{0.2}O_4$ were prepared for the purpose of comparison with one-step solid-state method, which was calcined at 850°C for 8h and 600°C for 10h in air. These spinel powders were confirmed by X-ray diffraction analysis followed.

To prepare the composite cathodes, the as-synthesized compounds was mixed with the conductive acetylene black and polytetrafluoroethylene (PTFE) emulsion with a weight ratio of 80: 10: 10, which formed a uniform paste, separately. The electrode sheet was obtained by rolling the paste into a 0.10-0.15 mm thick membrane and then pressing onto a nickel foil. At last, the assembly was dried under a vacuum at 120°C for about 12 h.

The powder microelectrode was prepared by etching the tip of a platinum microdisc electrode (diameter 30 μm) in a hot mixed solution of hydrochloric acid and nitric acid for about 5 min to form a microcavity [8]. The sample was filled into the microcavity by the gently grinding in the powder on the surface of flat plate.

2.2. Material characterizations

The crystallinity and phase of the prepared products were performed by powder X-ray diffraction (XRD) with Cu Kα radiation in a Lab-X6000 X-ray diffractometer. Scanning electron micrographs were obtained under Quanta 200 scanning electron microscope. The cyclic voltammetry (CV) was carried out with a microelectrode technique. Coin-type cell (CR 2016) was constructed for electrochemical characterization. The cell consisted of a cathode, a pure lithium metal as anode and a reference electrode, which were separated by a porous polypropylene film. The electrolyte was EC-DMC/1M $LiClO_4$. Constant-current charge-discharge tests at room and elevated temperature were used to measure the electrochemical properties and all tests were conducted in an argon-filled dry box.

3. RESULTS AND DISCUSSION

3.1. Structural analysis and morphology of samples

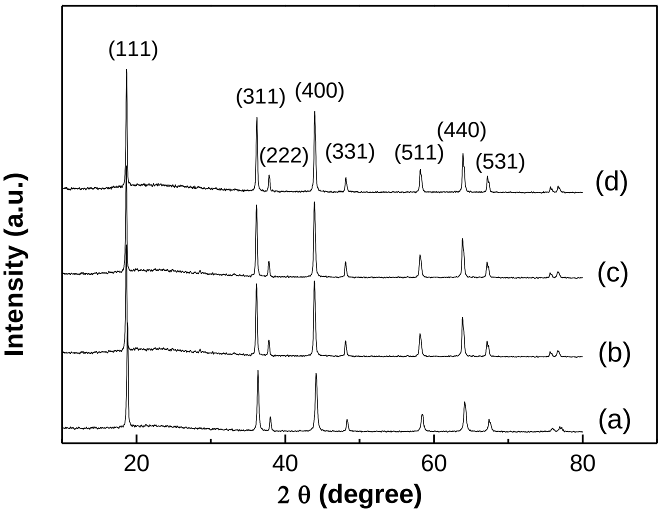


Figure 1. The XRD patterns: (a) pristine $LiMn_2O_4$; (b) $Li_{1.05}Mn_{1.8}Co_{0.2}O_4$; (c) $Li_{1.05}Mn_{1.99}Gd_{0.01}O_4$ and (d) $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$

The preparation process of the $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}$-$(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ material was as follows: Firstly, the basic conformation of spinel $Li_{1.05}[Mn_{1.99}Gd_{0.01}]O_4$ is formed via calcinating at high-temperature (800°C) for a short time. Then the mixed compounds of manganese, cobalt and lithium can be modified on the surface of $Li_{1.05}[Mn_{1.99}Gd_{0.01}]O_4$ particles through grinding. The second high-temperature (850°C) heat treatment may induce the mixed compounds to complete a solid-state reaction and the inner structure of spinel $Li_{1.05}[Mn_{1.99}Gd_{0.01}]O_4$ to be more integrated. A low-temperature (600°C) treatment is performed in order to make the surface structure more stable. Since the reaction takes place from the surface layer, the interface between surface layer and $Li_{1.05}[Mn_{1.99}Gd_{0.01}]O_4$ particles may react firstly, which will form the transition-layer. And the extent of reaction will pervade around the interface gradually. The final product $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ may be obtained.

The XRD patterns of the as-synthesized materials were presented in Fig. 1. All the samples were identified as well-defined spinel phases with a space group *Fd3m*, in which Li^+ ions occupied the tetrahedral (8a) sites; Mn^{3+}, Mn^{4+}, Gd^{3+} and Co^{3+} ions resided at the octahedral (16d) sites; and O^{2-} ions were located at (32e) sites. The XRD patterns for $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$, $Li_{1.05}Mn_{1.99}Gd_{0.01}O_4$ and $Li_{1.05}Mn_{1.8}Co_{0.2}O_4$ powders exhibited the same peaks with pristine $LiMn_2O_4$ without any impurity phases. In addition, the relevant intensities of the (311), (400) and (440) peaks for $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ were higher than that of pristine $LiMn_2O_4$, which showed better crystallization.

The lattice constants of the products were summarized in Table 1. From the statistic results, it could be seen that the novel spinel materials had a larger lattice parameter value (a = 8.23927 Å) comparing with pristine $LiMn_2O_4$. The results illustrated that the novel spinel materials with Li-Mn-Co-O modified had been successfully fabricated and possessed better crystallinity. Simultaneously, we found that lattice parameter value of $Li_{1.05}Mn_{1.99}Gd_{0.01}O_4$ was the largest as speculated due to the ionic radius increases in the order of Co^{3+}, Mn^{3+} and Gd^{3+}. And $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ was secondary, which illustrated that Gd^{3+} played major role in lattice parameter value.

Table 1. The lattice parameters for compounds

Cathode Materials	Lattice parameter, *a* (Å)	d-spacing (111) (Å)	Relative standard deviation of a (%, n=3)
$LiMn_2O_4$	8.20707	4.73835	2.34
$Li_{1.05}Mn_{1.8}Co_{0.2}O_4$	8.18236	4.71085	3.58
$Li_{1.05}Mn_{1.99}Gd_{0.01}O_4$	8.24022	4.75813	3.22
$Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$	8.23927	4.75694	2.15

Fig. 2 displayed the surface morphology of the as-prepared $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ and pristine $LiMn_2O_4$ powders obtained through the scanning electron microscopy (SEM). It could be found from the Fig. 2(b), the small particles of about 2 μm diameter covered on the surface of the main materials. Since the small particles, the smooth surface presented in pristine $LiMn_2O_4$ was altered for $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ (Fig. 2a). It may be due to the two-step solid-state synthesized method and modifying of Li-Mn-Co-O material and it was expected to reduce the capacity fading especially at elevated temperature.

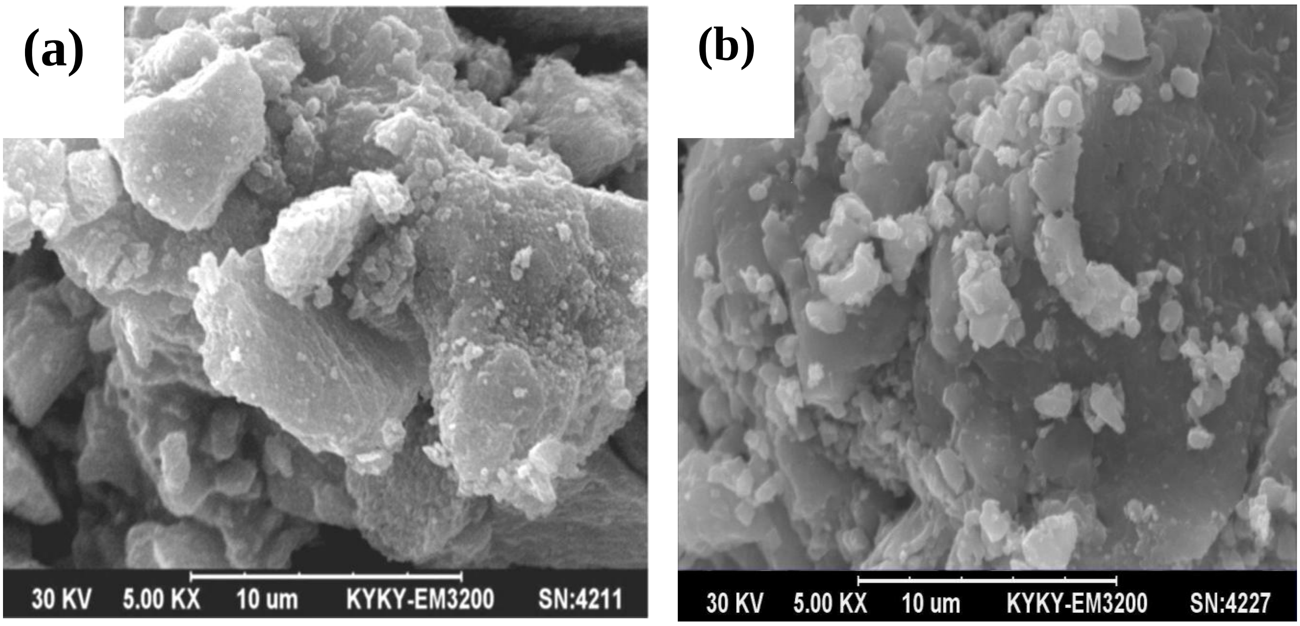


Figure 2. SEM images of (a) pristine $LiMn_2O_4$ and (b) $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$

3.2. Electrochemical properties

The cyclic voltammograms (CVs) of the $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}$-$(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ and pristine $LiMn_2O_4$ powders were shown in Fig. 3. The studies were carried out at a scan rate of 0.05 mV s^{-1} using microelectrode technique. It could be found that the two CV curves showed similar peak shape with two couples of redox peaks at around 4.05/3.95 V and 4.18/4.05 V, which were typical for spinel $LiMn_2O_4$ [34,42]. The redox peaks were split into two couples, indicating that the lithium-ion intercalation and de-intercalation reactions proceeded in two steps. In addition, as shown in Fig. 3, the variation of CV peaks for $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ was slighter than that for pristine $LiMn_2O_4$ after 10 cycles, which indicated that the cycle ability of $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ was improved largely, which is an important issue to development large-scale batteries.

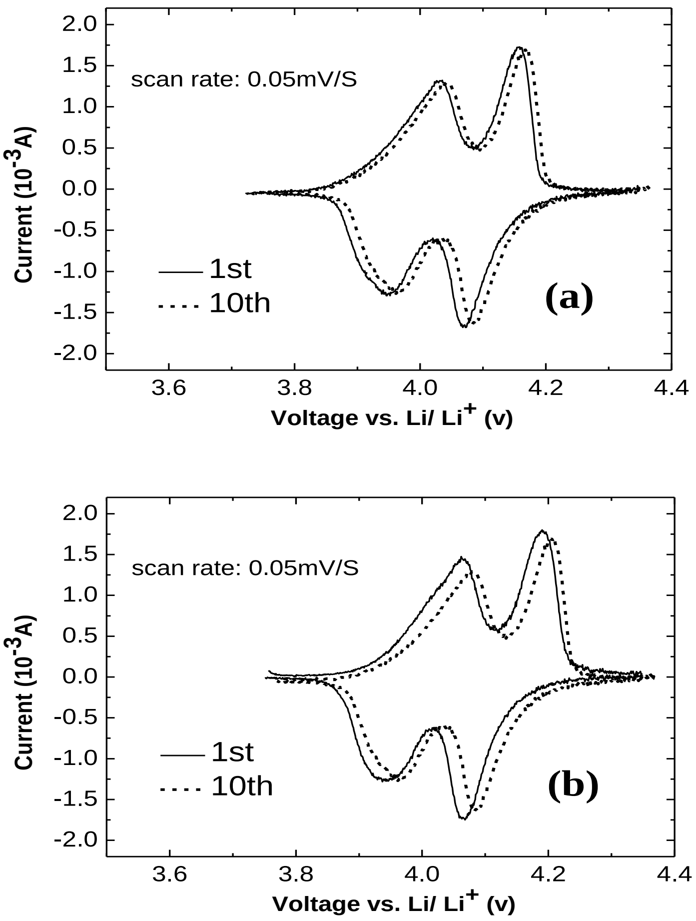
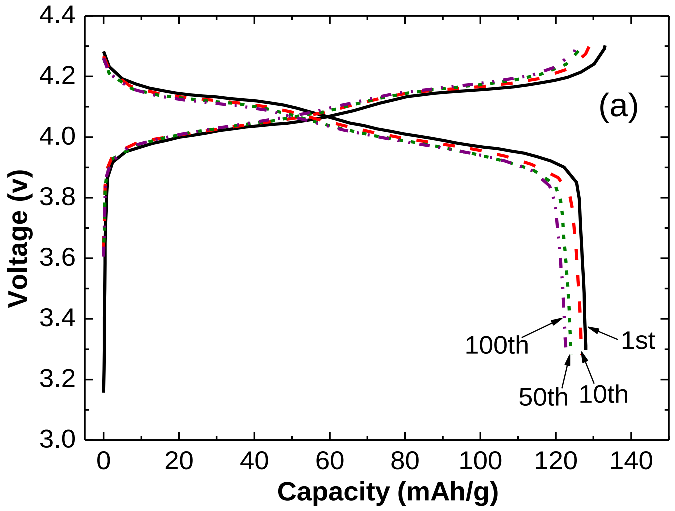


Figure 3. The CVs in 3.75–4.35V range at 25 °C with a rate of 0.05 mV s $^{-1}$: (a) $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$; (b) pristine $LiMn_2O_4$



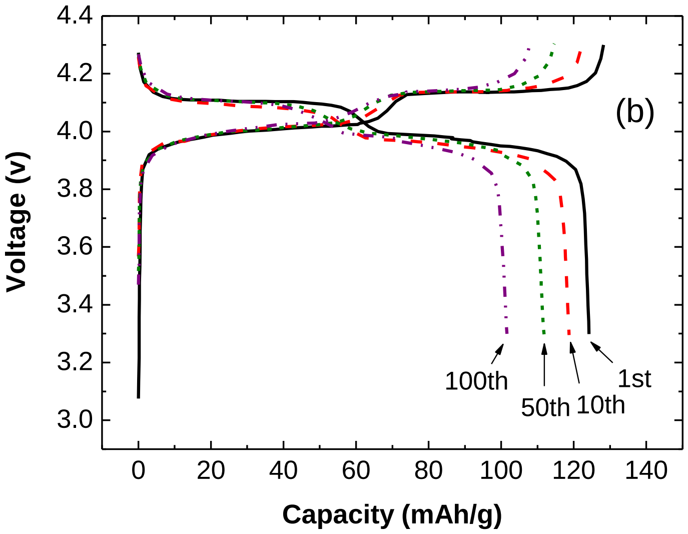
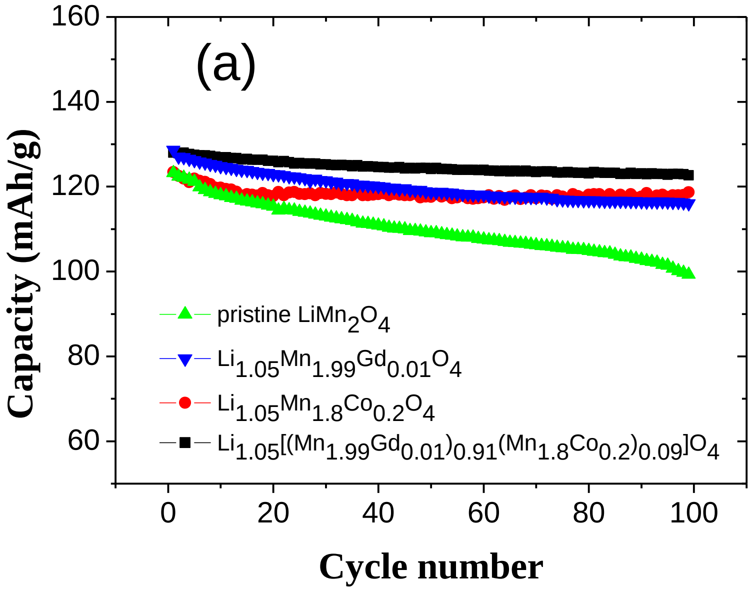


Figure 4. The charge–discharge curves in the voltage of 3.3–4.3V at 25°C: (a) $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$; (b) pristine $LiMn_2O_4$

In order to investigate the electrochemical behavior of as-received novel materials. The charge–discharge curves of $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ and pristine $LiMn_2O_4$ material, between 3.3 and 4.3V at 25°C were illustrated in Fig. 4. They both showed two same plateaus distinctly, which were the characteristic voltage profile of a spinel $LiMn_2O_4$. It could be seen that the coated material exhibited much better capacity retention than the pristine $LiMn_2O_4$. The discharge capacity for the $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ was 128.0, 126.9 and 122.7 mAh/g at the 1st, 10th and 100th cycles, respectively; the fading rate of capacity was 0.041% per cycle.



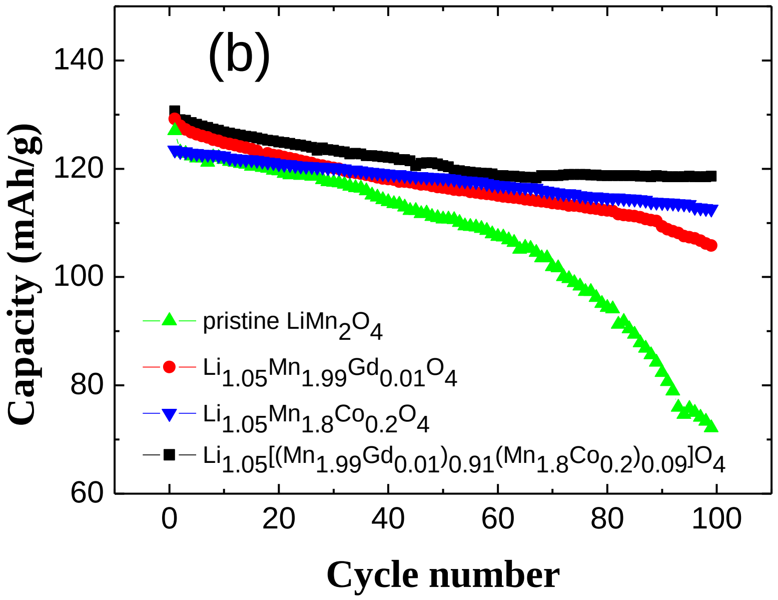


Figure 5. The cycling performance of $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$, $Li_{1.05}Mn_{1.99}Gd_{0.01}O_4$, $Li_{1.05}Mn_{1.8}Co_{0.2}O_4$ and pristine $LiMn_2O_4$ with a constant current density of 0.5C: (a) 25°C; (b) 55°C

For the pristine $LiMn_2O_4$ material, the relevant discharge capacity was 123.2, 118.0 and 99.3 mAh/g at the 1st, 10th and 100th cycles, respectively; the capacity fading rate was about 0.194% per cycle. These improvements on cycle stability might be attributed to the two-step solid-state synthesized method and modified by Li-Mn-Co-O material, avoiding the dissolution of Mn^{2+}. The results were similar to the references [25, 43, 44].

The cycling performance of lithium-ion battery with different cathode materials at 25°C and 55°C was illustrated as Fig. 5. The Figures showed the variation of discharge capacity of materials as a function of cycle number of the cell. These cells cycled with a constant current density of 0.5C between 3.3 and 4.3 V. At room temperature (Fig. 5a), the capacity fading after 100 cycles was about 20% for the pristine $LiMn_2O_4$, while only 4% for the novel spinel material $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$.

In the spinel phase, lithium insertion/extraction from/into 8a sites of the tetrahedral occurs at 4 V; correlating with the Mn^{3+}/Mn^{4+} oxidation/reduction process. However, the amount of inserted/extracted lithium decreases gradually with cycling. In order to prevent it, $LiMn_2O_4$ has been doped by partial substitution for Mn^{3+} by several cations such as Li, Fe, Ti, Ge, Co, Cr, Ni, and Zn [45]. Hua [46] reported that a high content of Li can lead to low capacity and excellent rechargeability. Furthermore, others reported that doping of $LiMn_2O_4$ lattice with rare-earth elements like La, Nd in the 16d sites can improve electrical properties of cathode materials greatly [37,38]. It also can be illustrated from Fig.5 (a) in our work, compared with pristine $LiMn_2O_4$, the first discharge capacity of $Li_{1.05}Mn_{1.8}Co_{0.2}O_4$ was not higher, but the novel spinel material

$Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co0_{.2})_{0.09}]O_4$ showed higher special capacity, owing to the doping of Gd element. So we think that substitution effect of Gd could cause the increase of first discharge capacity.

As an evident characterization for spinel material, the capacity losing was more serious at 55°C for pristine $LiMn_2O_4$ (Fig. 5b), the capacity retention ratio of which was only 58% over 100 cycles. However, the capacity retentions ratio of novel spinel material was as high as 91%, which was also better than the just doped material $Li_{1.05}Mn_{1.99}Gd_{0.01}O_4$. It suggested that the cycle stability was greatly improved for spinel material after modifying, doping and two-step solid-state synthesized method, especially at high temperature.

Moreover, Table 2 shows the comparison of electrochemical performances with previous literatures about modified cathode materials. As can be seen from it, surface treatment with metal oxides [16,20] and doping of $LiMn_2O_4$ lattice with rare-earth elements [47-49] were efficient ways to improve the cycling stability and discharge capacities. The initial discharge capacity of $LiNi_{0.5}Mn_{1.5}O_4$ [47] was the highest, whereas the capacity faded rapidly without surface modified. The capacity retentions ratio of the $LiCoO_2$-coated $LiMn_2O_4$ [50] was excellent, but the initial discharge capacity of which was less than 110 mAh/g. The novel material prepared through both doping and surface treatment in this work showed the best cycling stability under room and high temperature. Meanwhile, synthesizing by two-step solid-state method for the novel material was easy to control, whereas other methods reported as Table 2 were complex or hard to reproduce.

Table 2. The comparison of electrochemical performances for different spinel cathode materials

Cathode materials	25 °C		55-60 °C		Rate (C)	Voltage (V)	Synthesis method	Ref.
	The initial discharge capacities (mAh/g)	The capacity fading per cycle (%)	The initial discharge capacity (mAh/g)	The capacity fading per cycle				
ZnO-modified $LiMn_2O_4$	/	/	121	0.05	1.0	3.0-4.4	Rheological phase reaction method	[16]
2%CeO_2-modified $LiMn_2O_4$	101	0.10	117	0.45	0.5	3.0-4.0	Solid-state reaction following a Pechini method	[20]
$LiNi_{0.5}Mn_{1.5}O_4$	131.1	0.148	/	/	0.5	3.0-4.9	Rapid hydrothermal and post-calcination	[47]
$LiMn_{1.96}Ni_{0.04}O_4$	84	0.08	/	/	0.5	3.2–4.35	Spray-drying method	[48]
$Li_{1.02}Co_{0.1}Ni_{0.1}Mn_{1.8}O_4$	118	0.19	/	/	0.3	3.3-4.3	Sol–gel method	[49]
5% $LiCoO_2$-coated $LiMn_2O_4$	<110	0.05	113	0.15	0.5	3.3-4.4	Micro-emulsion process	[50]
pristine $LiMn_2O_4$	123.2	0.239	127.0	0.42	0.5	3.3-4.3	Two-step solid-state synthesized method	This work
$Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}$-$(Mn_{1.8}Co_{0.2})_{0.09}]O_4$	128.0	0.041	130.7	0.09	0.5	3.3-4.3	Two-step solid-state synthesized method	This work

4. CONCLUSIONS

Novel spinel cathode material $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ for Li-ion battery was synthesized by a simply two-step solid-state method. XRD data showed that the as-synthesized material exhibited the same peaks as pristine $LiMn_2O_4$ without any impurity phases. From the SEM, the smaller particles could be seen on the surface of novel materials that different from the smooth surface presented in pristine $LiMn_2O_4$. Moreover, the novel material exhibited improved electrochemical properties especially at elevated temperature. At room temperature, the capacity fading of the material $Li_{1.05}[(Mn_{1.99}Gd_{0.01})_{0.91}(Mn_{1.8}Co_{0.2})_{0.09}]O_4$ was 0.041% per cycle. Furthermore, the capacity retentions ratio of the novel material was greatly improved compared with the pristine $LiMn_2O_4$ at 55°C, which could be up to 91% after 100 cycles. These improvements were attributed to the existence of the combined effects of modifying, doping and two-step solid-state synthesized method, which prevented the dissolution of Mn and stabilized the spinel structure.

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References

1. H.J. Choi, K.M. Lee, G.H. Kim, J.G. Lee, *J. Am. Ceram. Soc.*, 84 (2001) 242.
2. M.Y. Song, D.S. Ahn, H.R. Park, *J. Power Sources*, 83 (1999) 57.
3. Y.P. Fu, Y.H. Su, C.H. Lin, S.H. Wu, *J. Mater. Sci.*, 41 (2006) 1157.
4. S.R. Das, S.B. Majumder, R.S. Katiyar, *J. Power Sources*, 139 (2005) 261.
5. S.R. Das, I.R. Fachini, S.B. Majumder, R.S. Katiyar, *J. Power Sources*, 158 (2006) 518.
6. N. Santander, S.R. Das, S.B. Majumder, R.S. Katiyar, *Surf. Coat. Technol.*, 177 (2004) 60.
7. Y Huang, J Li, D Jia, *J. Mater. Sci.*, 41 (2006) 4163.
8. X.H. Hu, X.P. Ai, H. X. Yang, Sh. X. Li, *J. Power Sources*, 74 (1998) 240.
9. Y. Xia, N. Kumada, M. Yoshio, *J. Power Sources*, 90 (2000) 135.
10. R.J. Gummow, A. Dekock, M.M. Thackeray, *Solid State Ion.*, 69 (1994) 59.
11. G.G. Amatucci, C.N. Schmutz, A. Blyr, C. Sigala, A.S. Gozdz, D. Larcher, J.M. Tarascon, *J. Power Sources*, 69 (1997)11.
12. B. Banov, Y. Todorov, A. Trifonova, A. Momchilov, V. Manev, *J. Power Sources*, 68 (1997) 578.
13. A.D. Robertson, S.H. Lu,W.F. Averill,W.F. Howard, *J. Electrochem. Soc.*, 144 (1997) 3505.
14. A. Blyr, C. Sigala, G. Amatucci, D. Guyomard, Y. Chabre, J.M. Tarascon, *J. Electrochem. Soc.*, 145 (1998) 194.
15. J. Cho, G.B. Kim, H.S. Lim, C.S. Kim, S.I. Yoo, Electrochem. *Solid State Lett.*, 2 (1999) 607.
16. H.W. Liu, C.X Cheng, Z.Q. hu, K.L. Zhang, *Mater. Chem. Phys.*, 101 (2007) 276.
17. D.Q. Liu, X.Q. Liu, Z.Z. He, *J. Alloy. Compd.*, 436 (2007) 387.
18. X.F. Li, Y.L. Xu, *Electrochem. Commun.*, 9 (2007) 2023.
19. J. Tu, X.B. Zhao, J. Xie, G.S. Cao, D.G. Zhuang, T.J. Zhu, J.P. Tu, *J. Alloy. Compd.*, 432 (2007) 313.
20. H.W. Ha, N.J. Yun, K. Kim, *Electrochim. Acta*, 52 (2007) 3236.

21. D. Guyonard, J.M. Tarascon, *J. Electrochem. Soc.*, 140 (1993) 3071.
22. G.G. Amatucci, A Blyr, C. Sigala, P. Alfonse, J.M. Tarascon, *Solid State Ion.*, 104 (1997) 13.
23. J.S. Gnanaraj, V.G. Pol, A. Gedanken, D. Aurbach, *Electrochem. Commun.*, 5 (2003) 940.
24. S.W. Lee, K.S. Kim, H.S. Moon, H.J. Kim, B.W. Cho, W.I. Cho, J.B. Ju, J.W. Park, *J. Power Sources*, 126 (2004) 150.
25. J.L. Shui, B. Lin, W.L. Liu, P.H. Yang, G.S. Jiang, C.H. Chen, *Mater. Sci. Eng. B*, 113 (2004) 236.
26. H.W. Chan, J.G. Duh, S.R. Sheen, *Surf. Coat. Technol.*, 116 (2004) 188.
27. Z. Zheng, Z. Tang, Z. Zhang,W. Shen,Y. Lin, *Solid State Ion.*, 148 (2002) 317.
28. J. Cho, T.J. Kim, Y.J. Kim, B. Park, *Chem. Commun.*, 1074 (2001).
29. S.C. Park, Y.M. Kim, Y.M. Kang, K.T. Kim, P.S. Lee, J.Y. Lee, *J. Power Sources*, 103 (2001) 86.
30. Z. Liu, H.Wang, L. Fang, J.Y. Lee, L.M. Gan, *J. Power Sources*, 104 (2002) 101.
31. H.W. Chan, J.G. Duh, S.R. Sheen, S.Y. Tsai, C.R. Lee, *Surf. Coat. Technol.*, 200 (2005) 1330.
32. S.C. Park, Y.M. Kim, S.C. Han, S. Ahn, C.H. Ku, J.Y. Lee, *J. Power Sources*, 107 (2002) 42.
33. D.Q. Liu, X.Q. Liu, Z.Z. He, *Mater. Chem. Phys.*, 105 (2007) 362.
34. J. Tu, X.B. Zhao, D.G. Zhuang, G.S. Cao, T.J. Zhu, J.P. Tu, *Physica. B*, 382 (2006) 129.
35. S.T. Yang, J.H. Jia, L. Ding, M.C. Zhang, *Electrochim. Acta*, 48 (2003) 569.
36. H.W. Liu, K.L. Zhang, *Mater. Lett.*, 58 (2004) 3049.
37. Y.T. Xie, R.D. Yang, Y. Lan, Q. Lu, K.H. Dai, P. He, *J. Power Sources*, 168 (2007) 272.
38. R. Singhal, S.R. Das, M.S. Tomar, O. Ovideo, S. Nieto., R.E. Melgarejo, R.S. Katiyar, *J. Power Sources*, 164 (2007) 857.
39. R.E. Melgarejo, M.S. Tomar, S. Bhaskar, P.S. Dobal, R.S. Katiyar, *Appl. Phys. Lett.*, 81 (2002) 2611.
40. M.S. Tomar, R.E. Melgarejo, A. Hidalgo, S.B. Majumder, R.S. Katiyar, *Appl. Phys. Lett.*, 83 (2003) 341.
41. X.J. Sun, X.H. Hu, Y. Shi, S.X. Li, Y.Q. Zhou, *Solid State Ion.*, 180 (2009) 377.
42. H. Huang, C. Wang, W.K. Zhang, Y.P. Gan, L. Kang, *J. Power Sources*, 184 (2008) 583.
43. B.J. Hwang, R. Santhanam, C.P. Huang, Y.W. Tsai, J.E. Lee, *J. Electrochem. Soc.*, 149 (2002) A694.
44. Z.S. Zheng, Z.L. Tang, Z.T. Zhang, W.C. Shen, *J. Inorg. Mater.*, 17 (2002) 999.
45. Y.Y. Xia, H. Takeshige, H. Noguchi , M. Yoshio, *J. Power Sources*, 56 (1995) 61.
46. G. Hua, *J. Electrochem. Soc.* 143 (1996) 178.
47. E.Q. Zhao, L. Wei, Y.D. Guo, Y.J. Xu, W.C. Yan, D.Y. Sun, Y.C. Jin. *J. Alloy. Compd.*, 695 (2017) 3393.
48. H. M. Wu. J. P. Tu. X. T. Chen. Y. Li, X. B. Zhao. G. S. Cao. *J. Solid State Electrochem.*, 11 (2007) 173.
49. B.J. Hwang, R. Santhanam, S.G. Hu, *J. Power Sources*, 108 (2002) 250.
50. Z.L. Liu, H.B. Wang, L. Fang, J.Y. Lee, L.M. Gan, *J. Power Sources*, 104 (2002) 101.