

Effect of MgF₂ coating on the electrochemical performance of LiMn₂O₄ cathode materials

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Received: 14 January 2012 / Revised: 1 March 2012 / Accepted: 10 March 2012 / Published online: 27 March 2012
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Abstract Spinel LiMn₂O₄ cathode materials were coated with 1.0, 3.0 and 5.0 wt.% of MgF₂ by precipitation, followed by heat treatment at 400 °C for 5 h in air. The effects of MgF₂ coating on the structural and electrochemical properties of LiMn₂O₄ cathodes were investigated using XRD, SEM, and electrochemical tests. XRD and SEM results show that no significant bulk structural differences are observed between the coated and pristine LiMn₂O₄. The charge–discharge tests show that the discharge capacity of LiMn₂O₄ decreases slightly, but the cyclability of LiMn₂O₄ is clearly improved when the amount of the MgF₂ coated was increased to 3.0 wt.%. The 3.0 wt.% MgF₂-coated LiMn₂O₄ exhibits capacity retention of 80.1 and 76.7 % after 100 cycles at room temperature (25 °C) and elevated temperature (55 °C) at a rate of 1 C, respectively, much higher than those of the bare LiMn₂O₄ (70.1 and 61.6 %). The improvement of electrochemical performance is attributed to the suppression of Mn dissolution into the electrolyte via the MgF₂ coating layer.

Keywords Lithium ion batteries · Spinel lithium manganese oxide · Surface coating · Magnesium fluoride · Cycling stability

Introduction

In recent years, the development of lithium ion batteries with high power density and high energy density has been accelerated due to the trend of miniaturization of portable electronic devices as well as the development of electric

vehicles (EV/HEV) [1]. Currently, LiCoO₂, LiMn₂O₄, LiFePO₄, LiNi_{0.3}Mn_{0.3}Co_{0.3}O₂, and LiNi_{0.8}Co_{0.15}Al_{0.05} are the main cathode materials for rechargeable lithium ion batteries. Among these, spinel LiMn₂O₄ is regarded as one of the most prospected cathode materials because of its low cost, abundant resource, nontoxicity, easy preparation, and being environmentally friendly [2, 3]. However, the spinel LiMn₂O₄ suffers from irreversible capacity loss during cycling which is especially severe at elevated temperatures. The capacity loss has been ascribed to several factors, including Jahn–Teller distortion in deeply discharged Li_xMn₂O₄ [4], Mn³⁺ dissolution [5], and the electrochemical oxidation of the organic-based electrolyte at the charge state [6].

In order to overcome the capacity fading of LiMn₂O₄, two kinds of method can be employed. One way is substitution of heterogeneous atom into the host LiMn₂O₄ structure, and other one is surface modification. Some studies showed that partial substitution of Mn by Al, Cr, Ni, Zn, Sn, La, Ce, and Zr could increase the stability of the spinel structure and improve the cycling performance of LiMn₂O₄ [7–13], but LiMn₂O₄ still suffers from capacity fading at room and elevated temperatures due to Mn³⁺ dissolution which resulted from some side reactions, which occurred at the interface between the electrode and electrolyte during charge–discharge process [14]. Surface modification of the cathode electrode is an effective way to overcome this problem. Recently, surface modifications with metal oxides such as MgO [15], Al₂O₃ [16], TiO₂ [17], CeO₂ [18], and LBO [19] have been investigated and excellent cyclability was achieved, but most of the metal oxide coatings cannot remain stable under the corrosion of HF [20, 21]. Recently, Sun et al. [20] reported that the AlF₃ coating layer on the surface LiCoO₂ could reduce the formation of LiF films which increased cathode/electrolyte interfacial impedance and also suppressed Co dissolution by preventing LiCoO₂

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surface from HF attack, therefore improving the capacity retention of LiCoO_2 at 4.5 V cutoff cycling.

Usually, MgF_2 is very stable in the electrolyte of Li ion battery. To our best knowledge, it is not seen for improving the electrochemical performance of LiMn_2O_4 by MgF_2 coating. In this work, surface coating of LiMn_2O_4 by MgF_2 was attempted to improve the cyclability. The effect of MgF_2 coating on the electrochemical performances of LiMn_2O_4 at room and elevated temperatures has been investigated.

Experimental

Preparation of spinel LiMn_2O_4

Bare LiMn_2O_4 was synthesized by a modified solid-phase reaction route. First, the precursor Mn_3O_4 was prepared by a hydrolyzation–oxidation method using cheap MnSO_4 as Mn source; then, as-prepared precursor Mn_3O_4 and Li_2CO_3 were mixed homogeneously in a molar ratio of 1:2 and calcined at 750 °C for 20 h to obtain spinel LiMn_2O_4 .

Synthesis of MgF_2 -coated LiMn_2O_4

To prepare MgF_2 -coated LiMn_2O_4 , NH_4F and MgCl_2 were separately dissolved in distilled water. LiMn_2O_4 powder was incorporated into the MgCl_2 solution followed by the slow addition of NH_4F solution. The weight ratio of MgF_2 to LiMn_2O_4 powder was fixed to 1.0, 3.0, and 5.0 wt.%, respectively. The mixed solution was constantly stirred at room temperature for 5 h and then filtered using distilled water. The obtained MgF_2 -coated LiMn_2O_4 powder was heated at 400 °C for 5 h.

Physical characterizations

The phase identification of the samples was performed with a diffractometer (D/Max-3 C, Rigaku, Japan) using $\text{CuK}\alpha$ radiation ($\lambda=1.54178$ Å) and a graphite monochromator at 36 kV and 20 mA. The scanning rate was 8°/min and the scanning range of diffraction angle (2θ) was $10^\circ \leq 2\theta \leq 75^\circ$. The morphology of the sample was observed using scanning electron microscopy (SEM; JSM-5600LV, JEOL, Japan) and field emission scanning electron microscope (FE-SEM; LEO1525, Germany). Energy-dispersive spectroscopy (EDS) was obtained in conjunction with SEM to roughly determine the element content of powders together with SEM in large field of view.

Electrochemical characterizations

The cathode electrode studies were prepared by a doctor blade coating method with a slurry mixed with 80 wt.% of

cathode active material, 5 wt.% of acetylene black, 5 wt.% of graphite conductor, and 10 wt.% of polyvinylidene fluoride binder in *N*-methyl-2-pyrrolidone solvent. This mixture was then applied onto an etched aluminum foil current collector and dried at 110 °C for 12 h in a vacuum oven. The coated cathode foil was then pressed and then cut into circular discs of 10 mm in diameter.

The button cells were assembled using 2025 stainless steel coin-type containers in an argon-filled glove box. Lithium was used as the anode and reference electrode; 1 M LiPF_6 with 1:1 ratio of ethylene carbonate and dimethyl carbonate (EC/DMC) was used as the electrolyte and a thin polypropylene film acted as the separator. Charge–discharge measurements were carried out in Neware battery test system BTS-XWJ-6.44S-00052 (Newell, Shenzhen, China) in the voltage range of 3.0 and 4.4 V at room temperature (25 °C) and elevated temperature (55 °C). The cyclic voltammogram experiments were carried out at a scan rate of 0.05 mV s^{-1} between 3.0 and 4.4 V using CHI 660A electrochemical workstation (Chenhua, China).

Results and discussion

Structure and morphology analysis

To determine the effect of MgF_2 coating on the crystal structure of LiMn_2O_4 , X-ray powder diffraction was carried out on the bare and coated spinel materials. Figure 1 shows the XRD patterns of the bare and MgF_2 -coated LiMn_2O_4 samples. All of the diffraction peaks correspond to a well-defined cubic spinel structure with space group $\text{Fd}\bar{3}\text{m}$, being in good agreement with JCPDS card 88-1749. It implies that the bulk structure of LiMn_2O_4 remains unchanged after surface modification. No diffraction peaks belonging to

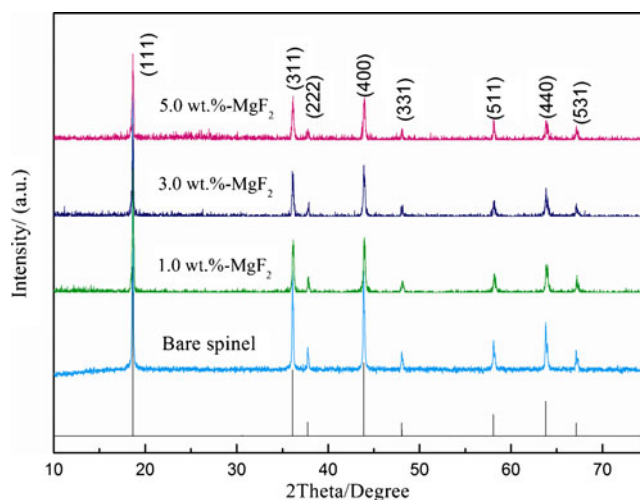


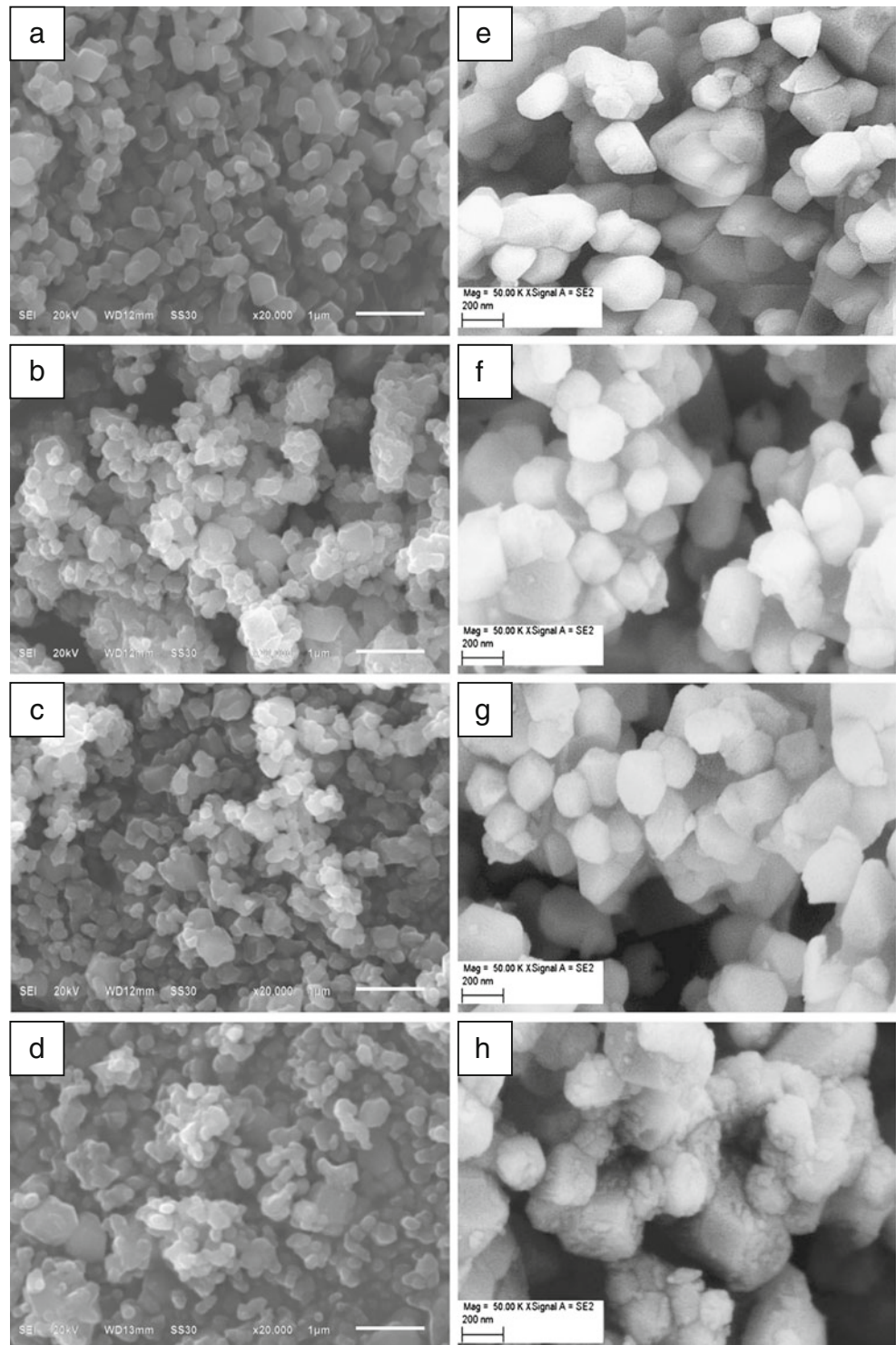
Fig. 1 X-ray diffraction patterns of the bare and MgF_2 -coated LiMn_2O_4 samples

MgF₂ are detected for the MgF₂-coated LiMn₂O₄ powders. This indicates that the surface coating layer was only a thin film and existed as an amorphous phase. It is probably because the coating sources were heat-treated at 400 °C, which is not high enough for the formation of a crystalline coating phase. Apparently, this result corresponds with the works reported by Seung-Taek Myung et al. and Hyunjung

Lee et al., in which most of the coating layers are amorphous [22, 23].

Furthermore, the lattice constant *a* of uncoated and 1.0, 3.0, and 5.0 wt.% MgF₂-coated LiMn₂O₄ samples are 0.825, 0.824, 0.824 and 0.824 nm, respectively. Earlier reports have indicated that substitution of metal ions from Mn³⁺ in LiMn₂O₄ causes significant changes in lattice parameters [24,

Fig. 2 SEM images of **a** the bare, **b** 1.0 wt.%, **c** 3.0 wt.%, and **d** 5.0 wt.% MgF₂-coated LiMn₂O₄ samples and FE-SEM images of **e** the bare, **f** 1.0 wt.%, **g** 3.0 wt.%, and **h** 5.0 wt.% MgF₂-coated LiMn₂O₄ samples



25]. The radius of Mg^{2+} and Mn^{3+} is 0.078 and 0.065 nm, respectively. Therefore, if Mn^{3+} ions were substituted for Mg^{2+} ions in crystal lattice, the lattice parameter of the substituted spinel material would be apparently changed. Small changes in the lattice parameter for all samples show that MgF_2 coating does not enter the spinel structure but is just presented on the surface of LiMn_2O_4 .

The surface morphology of the bare LiMn_2O_4 and MgF_2 -coated LiMn_2O_4 particles are presented in Fig. 2. It can be seen that the particle size of bare spinel is about 200 nm, and there is no visible size difference between the bare and the MgF_2 -coated LiMn_2O_4 particles. On the other hand, the surface morphology of the particles is changed after being coated by MgF_2 (shown in Fig. 2e–h). The surface of the 1.0 wt.%- MgF_2 coated sample is almost the same as the bare one. When the amount of MgF_2 coating increases to 5.0 wt.%, most of the surface of the sample is covered by the coating layer. The coated particles are apt to agglomerate, and the edges and corners become blurred because of the presence of the MgF_2 coating layers. Of course, the agglomeration of the MgF_2 -coated LiMn_2O_4 particles can reduce the contact between spinel particles and electrolyte and thus decrease Mn^{3+} dissolution.

Figure 3 displays the SEM image and the corresponding EDS maps of Mg and F for the 3.0 wt.% MgF_2 -coated spinel powder. As can be seen in the images, the distribution of Mg and F on the powder surfaces is fairly uniform, respectively. Thus, it can be confirmed that the surface of LiMn_2O_4 was successfully coated with MgF_2 particles.

Electrochemical performance

Figure 4 shows the initial charge and discharge curves of bare and 1.0, 3.0, and 5.0 wt.% of MgF_2 -coated LiMn_2O_4 samples at a discharge rate of 0.5 C between 3.0 and 4.4 V (vs Li/Li^+) at room temperature. It can be obviously seen that the LiMn_2O_4 samples with and without MgF_2 coating have similar charge–discharge profiles and exhibit two charge–discharge plateaus in the potential region of 4.0–4.2 V, which are ascribed to the remarkable characteristics of a well-defined spinel LiMn_2O_4 . The voltage plateaus indicate that the insertion and extraction of lithium ions occur in two states [26]. The first voltage plateau at about 4.0 V is associated with the removal of lithium ions from half of the tetrahedral sites. The second voltage plateau observed at around 4.1 V is ascribed to the removal of lithium ions from the remaining tetrahedral sites. Compared with the base one, the MgF_2 -coated LiMn_2O_4 samples show lower capacity. The discharge capacity decreases slightly with increasing the amount of MgF_2 coating to 3.0 wt.% but reduces remarkably to 105.8 mAh g^{-1} when the amount of MgF_2 coating increases to 5.0 wt.%. It is probably because MgF_2 coating is electrochemically inactive. The MgF_2 layer may both increase the contact resistance

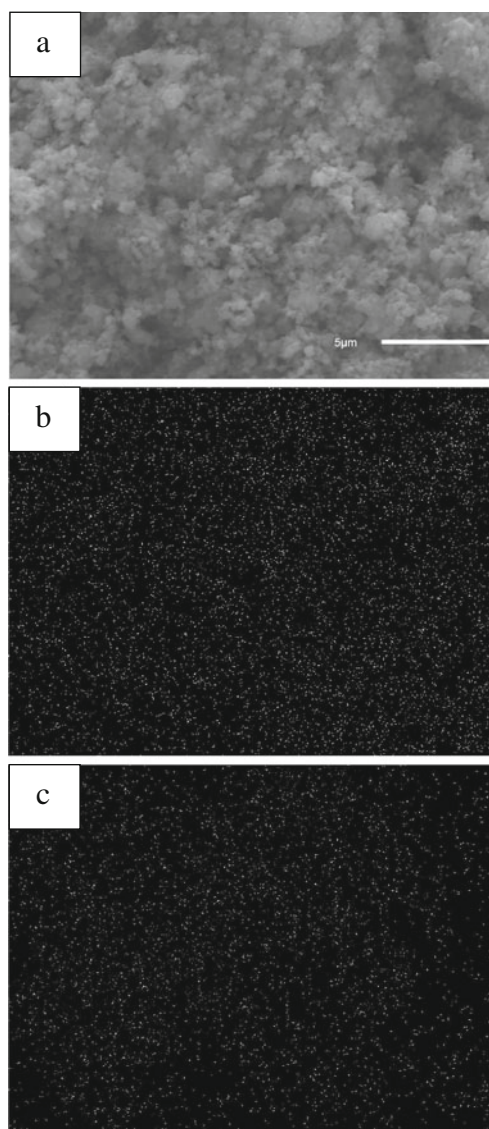


Fig. 3 SEM image of 3.0 wt.% MgF_2 -coated LiMn_2O_4 (a) and the corresponding EDS mapping of Mg (b) and F (c)

between particles and the charge transfer resistance between the cathode and the electrolyte.

The effect of modification on the capacity retention of the bare LiMn_2O_4 was investigated as a function of the MgF_2 coating content. The cycling efficiencies and discharge capacities of the bare and MgF_2 -coated LiMn_2O_4 at 0.5 C between 3.0 and 4.4 V at room temperature are presented in Figs. 5 and 6, respectively. It can be seen from Fig. 5 that all the samples show high cycling efficiency. Comparatively, the cycling efficiency of 3.0 wt.% MgF_2 -coated sample is higher than the other three samples, and it can hold relatively steady upon cycling. The first cycle discharge capacities, 100th cycle discharge capacities, and capacity retention ratios for MgF_2 -coated and uncoated LiMn_2O_4 are summarized in Table 1. As can be seen in Fig. 6 and Table 1, the discharge capacity of the bare LiMn_2O_4 fades from 127.1 to

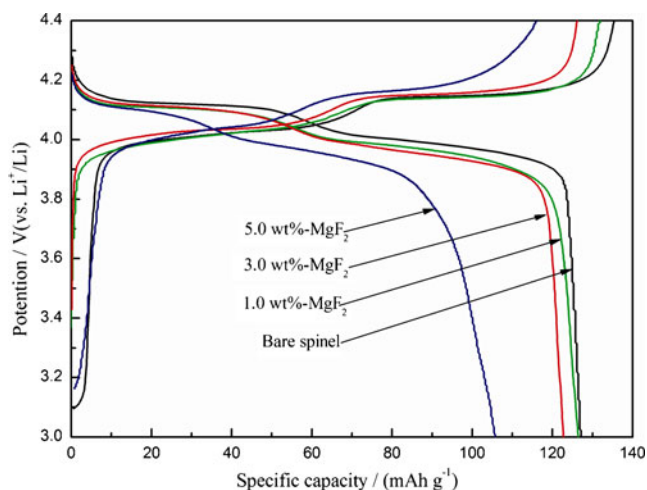


Fig. 4 Initial charge–discharge curves of the bare and MgF₂-coated LiMn₂O₄ cycled at 0.5 C between 3.0 and 4.4 V

96.2 mAh g⁻¹ after 100 cycles. On the contrary, all of the MgF₂-coated samples exhibit excellent capacity retention, and the capacity retention after 100 cycles is observed to be dependent on the coating amount of MgF₂. For example, the capacity retentions are 77.3 % for 1.0 wt.%, 85.2 % for 3.0 wt.%, and 80.2 % for 5.0 wt.% MgF₂ coating, respectively. The 3.0 wt.% of MgF₂ coating is apparently the most effective in improving the cycling performance of LiMn₂O₄. With a low MgF₂ coating amount, the LiMn₂O₄ surface may not be protected efficiently and result in inferior cycling performance. When the MgF₂ content increases from 3.0 to 5.0 wt.%, the cycling performance gets worse. This manifests that the MgF₂ coating can facilitate the diffusion of lithium ions for the appropriate content. As MgF₂ increases beyond the optimal coating content, the excess insulating MgF₂ will hinder the transportation of lithium ions, leading to the

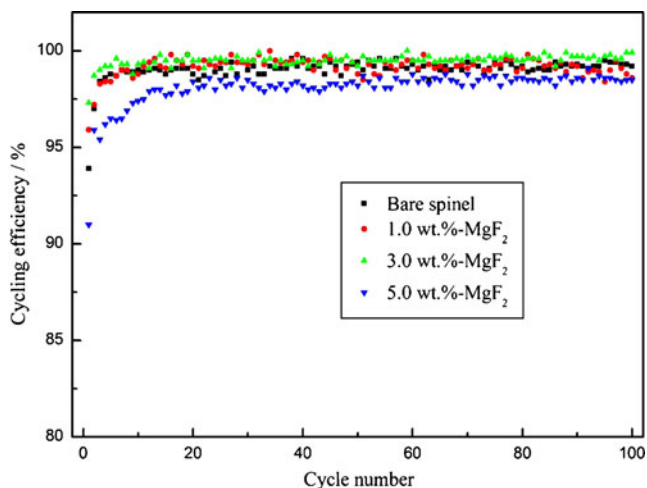


Fig. 5 Cycling efficiency of the bare and MgF₂-coated LiMn₂O₄ cycled at 0.5 C between 3.0 and 4.4 V at room temperature

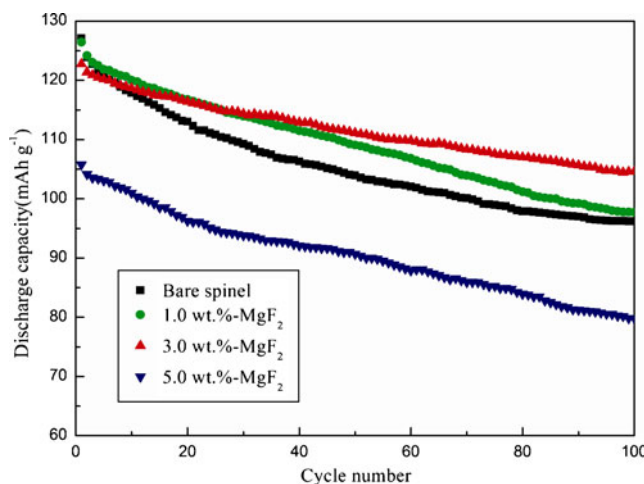


Fig. 6 Cycling performances of the bare and MgF₂-coated LiMn₂O₄ cycled at 0.5 C between 3.0 and 4.4 V at room temperature

evident decay of the capacity. Therefore, 3.0 wt.% MgF₂-coated LiMn₂O₄ is the optimum composition to enhance the stability and cycling performance of LiMn₂O₄.

The electrochemical cycling performance of the bare and the 3.0 wt.% MgF₂-coated LiMn₂O₄ at a current rate of 1 C between 3.0 and 4.4 V at room temperature (25 °C) and elevated temperature (55 °C) are shown in Fig. 7, and the corresponding discharge capacity values are listed in Table 2. As shown in Fig. 7a, the initial discharge capacity of the bare LiMn₂O₄ is 124.0 mAh g⁻¹ at room temperature, and it declines to 86.9 mAh g⁻¹ after 100 cycles. While the 3.0 wt.% MgF₂-coated LiMn₂O₄ shows a little lower initial discharge capacity of 118.8 mAh g⁻¹ than the bare sample, the capacity gradually reduces in the first 20 cycles and then keeps a nearly stable value. The discharge capacity is 95.1 mAh g⁻¹ after 100 cycles. Therefore, it can be concluded that the 3.0 wt.% MgF₂-coated LiMn₂O₄ is an attractive method for improving the performance of LiMn₂O₄ because MgF₂ coating provides the interface not only with a chemically stable but also a highly Li⁺-conducting barrier layer which can effectively reduce the chemical reaction between the charged active materials and the electrolyte.

Figure 7b shows the electrochemical cycling performance of the bare and the 3.0 wt.% MgF₂-coated LiMn₂O₄

Table 1 Capacities and capacity retention rates of the bare and MgF₂-coated LiMn₂O₄ at 0.5 C at room temperature

Cathode materials	Initial discharge capacity at 0.5 C (mAh g ⁻¹)	100th discharge capacity at 0.5 C (mAh g ⁻¹)	Capacity retention rate at 0.5 C (%)
Bare spinel	127.1	96.2	75.7
1.0 wt.% MgF ₂	126.4	97.7	77.3
3.0 wt.% MgF ₂	122.7	104.6	85.2
5.0 wt.% MgF ₂	105.8	84.8	80.2

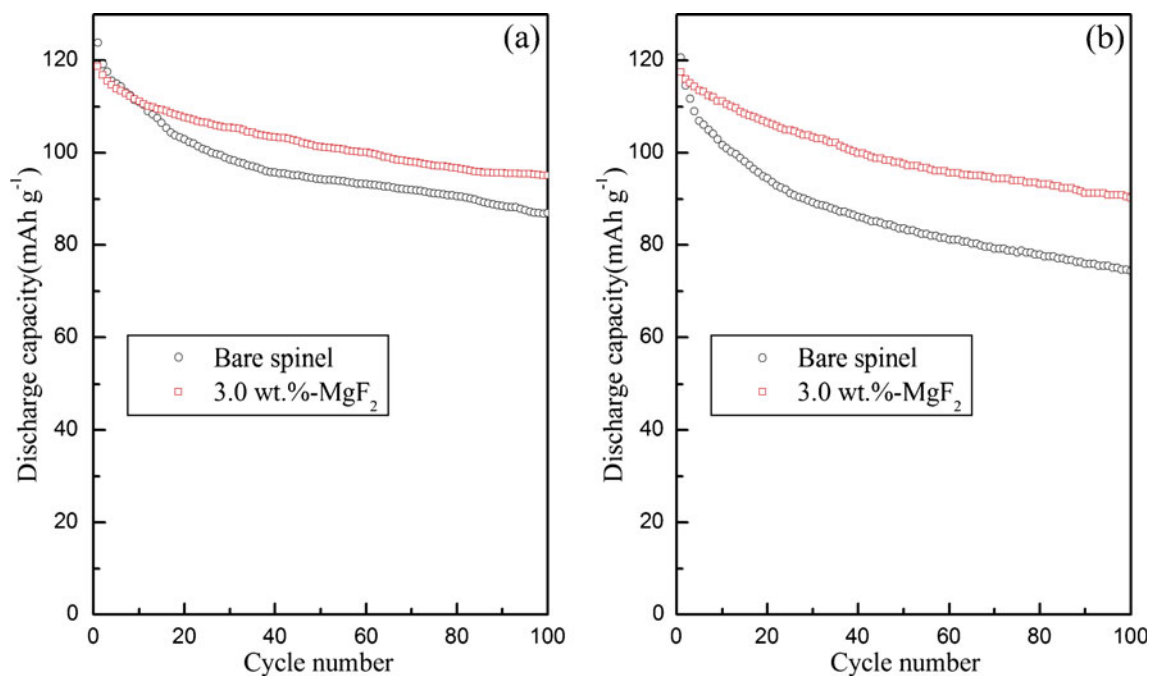


Fig. 7 Cycling performances of the bare and 3.0 wt.% MgF₂-coated LiMn₂O₄ cycled between 3.0 and 4.4 V at **a** room temperature (25 °C) and **b** elevated temperature (55 °C)

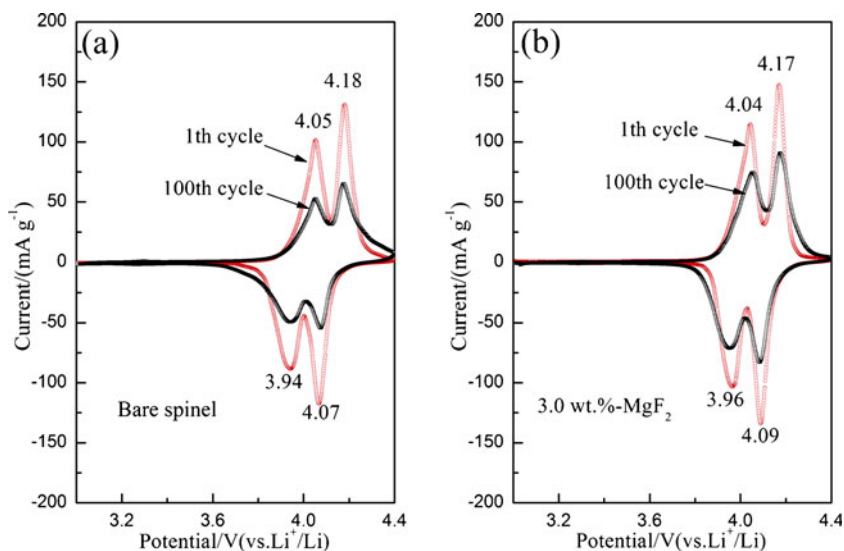
at elevated temperature (55 °C). Generally speaking, the major issue with spinel LiMn₂O₄ materials is their poor electrochemical performance at elevated temperature owing to Mn³⁺ dissolution into the electrolyte [5]. Obviously, surface modification is an effective technology for improving the cyclability of LiMn₂O₄ at elevated temperature. As can be seen in Fig. 7b, the discharge capacity of the bare LiMn₂O₄ fades from 120.7 to 74.7 mAh g⁻¹ with a retention of 61.9 % after 100 cycles between 3.0 and 4.4 V at 1 C at 55 °C. However, the discharge capacity of the 3.0 wt.% MgF₂-coated spinel electrodes clearly shows an improved cycling behavior compared with the bare one in the same conditions. The discharge capacity of the 3.0 wt.% MgF₂-coated LiMn₂O₄ fades from 117.5 to 90.2 mAh g⁻¹ with a retention of 76.7 % of its initial capacity. Therefore, it is proposed that MgF₂ coating is also an effective way in improving the elevated temperature capacity retention of LiMn₂O₄.

The typical cyclic voltammograms of bare LiMn₂O₄ and MgF₂-coated LiMn₂O₄ electrodes were carried out using lithium as a counter and reference electrode in the potential range between 3.0 and 4.4 V at a scan rate of 0.05 mV s⁻¹. Two cells were freshly cycled and were then used for the galvanostatic charge–discharge studies at room temperature. After the completion of the 100th cycle, the two cells were again characterized by cyclic voltammogram. Figure 8 represents the cyclic voltammogram profiles of the bare and 3.0 wt.% MgF₂-coated LiMn₂O₄. Two pairs of oxidation and reduction peaks appear around 4.0 and 4.15 V; the split of the redox peaks into two couples indicates that the electrochemical intercalation and de-intercalation reactions of lithium ion proceed in two steps. Three obvious features can be observed from Fig. 8a, b. First, both the oxidation and reduction peaks in the 3.0 wt.% MgF₂-coated LiMn₂O₄ are sharper than those of the bare LiMn₂O₄, indicating a quick electrode reaction after MgF₂ modification. Second, the intervals

Table 2 Capacities and capacity retention rates of the bare and 3.0 wt.% MgF₂-coated LiMn₂O₄ at 1 C at room and elevated temperature

Cathode materials	Initial discharge capacity at 25 °C (mAh g ⁻¹)	100th discharge capacity at 25 °C (mAh g ⁻¹)	Capacity retention rate at 25 °C (%)	Initial discharge capacity at 55 °C (mAh g ⁻¹)	100th discharge capacity at 55 °C (mAh g ⁻¹)	Capacity retention rate at 55 °C (%)
Bare spinel	123.96	86.94	70.14	120.69	74.33	61.59
3.0 wt.% MgF ₂	118.78	94.47	79.53	117.51	90.16	76.73

Fig. 8 Cyclic voltammetric curves of initial and 100th cycle for **a** the bare and **b** 3.0 wt.% MgF₂-coated LiMn₂O₄ cycled between 3.0 and 4.4 V at a scan rate of 0.05 mV s⁻¹ at room temperature



between the oxidation and the corresponding reduction potentials of the 3.0 wt.% MgF₂-coated LiMn₂O₄ are less than those of the bare LiMn₂O₄, implying that the polarization is decreased after MgF₂ coating. Therefore, 3.0 wt.% MgF₂ coating can effectively improve the kinetic properties of LiMn₂O₄. Additionally, the oxidation and reduction peaks related to 3.0 wt.% MgF₂-coated LiMn₂O₄ electrode are much more steady compared to the peaks of the bare electrode after 100 cycles. These differences indicate that 3.0 wt.% MgF₂-coated LiMn₂O₄ electrode is of better reversibility than bare spinel electrode. As a result, MgF₂ coating is very helpful to stabilize the structure of LiMn₂O₄ during charge–discharge process.

Conclusions

LiMn₂O₄ was successfully prepared by Mn₃O₄ as a precursor, and then it was modified by a different ratio MgF₂. All of the bare and MgF₂-coated LiMn₂O₄ samples have well-defined cubic spinel structure which indicated that the MgF₂ layer was only coated on the surface rather than diffused into the crystal interior. The 3.0 wt.% MgF₂-coated LiMn₂O₄ exhibits better capacity retention of 85.2 % after 100 cycles compared with the 75.7 % capacity retention for the pristine LiMn₂O₄ at room temperature at a rate of 0.5 C. Even at higher currents corresponding to 1-C rate at an elevated temperature (55 °C), the capacity retention of 3.0 wt.% MgF₂-coated LiMn₂O₄ is found to be 76.7 %, which is significantly higher than the bare LiMn₂O₄. The improved performance of the surface-coated sample is because the MgF₂ coating on the surface of LiMn₂O₄ can prevent direct contact between the LiMn₂O₄ particles and electrolyte and therefore reduce the dissolution of Mn³⁺ and the oxidation of electrolyte.

Acknowledgements This work was financially supported by the National Natural Science Foundation of China under project no. 20871101, Joint Fund of Natural Science of Hunan Province and Xiangtan City under project no. 09BG005, and Project of Condition Research of Hunan Province under project no. 2010TC2004 Colleges.

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