

# Aluminum oxide as a multi-function agent for improving battery performance of $\text{LiMn}_2\text{O}_4$ cathode

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## Abstract

Aluminum oxide was used with three different applications to improve battery performance of  $\text{LiMn}_2\text{O}_4$  cathode. Indeed,  $\text{Al}_2\text{O}_3$  was placed beneath, within and upon the electroactive film. In the first application, aluminum oxide was deposited onto the current collector to strengthen connection of the electroactive material with the substrate surface. In the second one,  $\text{Al}_2\text{O}_3$  particles were dispersed within the electroactive film to improve Li intercalation/deintercalation process. And in the last one,  $\text{Al}_2\text{O}_3$  was used as a surface-coating agent to cover the spinel surface to avoid Mn dissolution. The influence of these three approaches on the battery performance of  $\text{LiMn}_2\text{O}_4$  cathode was examined separately and in combination. The results were indicative of the fact that  $\text{Al}_2\text{O}_3$  could be used as a multi-function agent to improve various problems of  $\text{LiMn}_2\text{O}_4$  to achieve an acceptable behavior for battery performance. Indeed, it was demonstrated how combination of different methods using a single agent can lead to superiority improvement of the battery performance. The  $\text{LiMn}_2\text{O}_4$  cathode prepared based on these three approaches exhibits 1000 charge/discharge cycles at room temperature and 400 cycles at an elevated temperature (55 °C), retaining 90% of its initial specific capacity. As  $\text{Al}_2\text{O}_3$  is a simple and low-cost agent, the results are of interest for the practical performance. © 2004 Published by Elsevier B.V.

*Keywords:* Aluminum oxide; Al current collector;  $\text{Al}_2\text{O}_3$  coating;  $\text{LiMn}_2\text{O}_4$ ; Capacity fade

## 1. Introduction

Recent developments of lithium secondary batteries have made them an important type of power sources for portable electronic devices, and even probably a new type of energy source for electric vehicles. The most manufactures already use  $\text{LiCoO}_2$  as cathode material for the fabrication of lithium batteries. However,  $\text{LiCoO}_2$  suffers from some serious disadvantages such as high cost, hazard to the human body and limited sources of cobalt ore. A promising alternative is  $\text{LiMn}_2\text{O}_4$  due to its noticeable advantages such as low cost, low toxicity and relatively high energy density. The main obstacle in commercialization of  $\text{LiMn}_2\text{O}_4$  is severe capacity fades appearing at elevated temperature. Several mechanism responsible for the appearance of capacity fading of  $\text{LiMn}_2\text{O}_4$  such as manganese dissolution [1–3], formation of oxygen deficiency [4], electrolyte decomposition [5], Jahn-Teller distortion [6], cation mixing between lithium and manganese [7], and loss of crystallinity during cycling [8] have been proposed in the literature.

Among different factors claimed to be responsible for the capacity fades of  $\text{LiMn}_2\text{O}_4$ , Mn dissolution is the most important one. Thus, Guyomard and Tarascon have suggested that the easiest way to improve the elevated temperature performance is to fabricate a material with low surface area [9]. However, it is difficult to achieve this situation due to significant roughness of  $\text{LiMn}_2\text{O}_4$  films [10,11]. On the other hand, porosity of the electroactive film can assist the diffusion process leading to better battery performance of the cathode material [12]. There are other factors, which have significant influence on the battery performance, such as particle size and surface morphology. However, it is difficult to control such factors precisely using a conventional solid-state reaction method, which needs long and repeated heat-treatment process.

An applicable method to reduce capacity fades of  $\text{LiMn}_2\text{O}_4$  is surface coating of the spinel to avoid Mn dissolution. Metal oxides are very interesting materials for this purpose to improve cyclability of  $\text{LiMn}_2\text{O}_4$  cathode [13–18], and even to reduce severe capacity fading of  $\text{LiMn}_2\text{O}_4$ -based 5 V cathode materials during high-voltage performances [19]. Indeed, surface treatment of electro-

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active materials with metal oxides to improve both the cyclability and the rate capability of the electrode at room and elevated temperatures have been widely studied by many researchers (cf. recent works [20,21]). Although  $\text{Al}_2\text{O}_3$  is an excellent material for this purpose, less attention has been paid to this interesting agent. For example,  $\text{Al}_2\text{O}_3$  has been widely utilized for surface modification of  $\text{LiCoO}_2$  [22–24], but there is no such extensive investigation devoted to surface modification of  $\text{LiMn}_2\text{O}_4$ . In the content of the present paper, we examine the usefulness of  $\text{Al}_2\text{O}_3$  as a surface coating material and show other applications of this material for improving battery performance of  $\text{LiMn}_2\text{O}_4$  cathode.

## 2. Experimental

### 2.1. Coating of Al current collector

Aluminum plate prepared from pure aluminum (purity better than 99.99%) with geometrical area of  $2\text{ cm}^2$  and thickness of 0.5 mm which, was polished by alumina powder (0.05  $\mu\text{m}$ ) and then washed with acetone in an ultrasonic bath. The  $\text{LiMn}_2\text{O}_4$  films were deposited by radio frequency (rf) magnetron sputtering using a  $\text{LiMn}_2\text{O}_4$  target on the Al current collectors. The  $\text{Al}_2\text{O}_3$ -coated Al current collector was prepared by deposition of a  $\sim 10\text{-nm}$ -thick  $\text{Al}_2\text{O}_3$  by reactive sputtering from an Al target. The coated current collector was annealed at  $400\text{ }^\circ\text{C}$  for 10 h in an  $\text{O}_2$  atmosphere.

The  $\text{LiMn}_2\text{O}_4$  target was prepared by cold pressing and sintering  $\text{LiMn}_2\text{O}_4$  powder at  $800\text{ }^\circ\text{C}$  for 10 h in air. A binder was added to the powders to aid sintering, and the targets were bonded to copper backing plates with indium to the magnetron gun. The targets were sputtered at a working pressure of 20 mTorr with  $\text{Ar}/\text{O}_2 = 3/1$ . A rf power of 100 W was applied to the target. The total amount of the electroactive material deposited was about 40  $\mu\text{g}$ . The apparent thickness of the electroactive material was 500 nm and those of  $\text{Al}_2\text{O}_3$  layers were 10 nm.

### 2.2. Dispersion of $\text{Al}_2\text{O}_3$ particles within $\text{LiMn}_2\text{O}_4$ film

The  $\text{LiMn}_2\text{O}_4$  film containing dispersed  $\text{Al}_2\text{O}_3$  particles was prepared by a chemical process. An amount of the spinel (ca. 1 g) was added to an aqueous solution of aluminum nitrate (10 mM) and mixed for 4 h at room temperature. Then, the precipitation of hydrous aluminum oxide over the  $\text{LiMn}_2\text{O}_4$  particles was performed by adding ammonium hydroxide. The amount of the modifier material can be simply controlled by the ratio of the electroactive material and the metal salt. Then, the resultant product was annealed at  $400\text{ }^\circ\text{C}$  for 5 h in an  $\text{O}_2$ -rich atmosphere. The  $\text{Al}_2\text{O}_3$ -coated  $\text{LiMn}_2\text{O}_4$  particles were deposited onto the Al current collector according to the rf magnetron sputtering procedure described above.

### 2.3. Coating of the $\text{LiMn}_2\text{O}_4$ film with $\text{Al}_2\text{O}_3$

Surface coating of the  $\text{LiMn}_2\text{O}_4$  film was performed by deposition of a thin film of  $\text{Al}_2\text{O}_3$  (ca. 10 nm) by reactive sputtering of an Al target. Then, the  $\text{Al}_2\text{O}_3$ -coated spinel was annealed at  $400\text{ }^\circ\text{C}$  for 10 h in an  $\text{O}_2$  atmosphere.

### 2.4. Materials and apparatus

$\text{LiMn}_2\text{O}_4$  powder was prepared from a commercial sample provided by Merck. The battery performance was investigated in a conventional cell containing a lithium metal anode and the  $\text{LiMn}_2\text{O}_4$  cathodes prepared. It should be noted that most of investigations in this context use carbon-based anodes; however, for this preliminary investigation devoted to battery performance of the cathode, Li metal was employed as anode. The CR2032 coin cells were assembled with the cathodes fabricated. The electrolyte solution was 1 M  $\text{LiPF}_6$  in ethylene carbonate (mp  $35\text{--}38\text{ }^\circ\text{C}$ ) and diethyl carbonate (bp  $125\text{--}126\text{ }^\circ\text{C}$ ). The charge/discharge behaviors of the secondary cells were investigated under galvanostatic condition at a typical rate of C/2 in a potential window between 3.1 and 4.3 V.

Depth profiling by sequential  $\text{Ar}^+$ -ion sputtering and XPS analysis as a common way to determine surface layer thickness and to measure elemental concentrations as a function of the film depth was performed to understand the cathode structure. Indeed, this is a non-destructive technique for this purpose (cf. Refs. [25,26]). Depth profile data were obtained by Ar ion-beam sputtering (4 keV), which is a well-known and reliable method for such investigations. A GBU 1260 X-ray photoelectron spectrometer was employed for this purpose.

## 3. Results and discussion

### 3.1. $\text{Al}_2\text{O}_3$ as an agent for surface modification of current collector

In the first stage of the research, we attempt to investigate the usefulness of  $\text{Al}_2\text{O}_3$  when placed beneath the electroactive material. Using aluminum oxide between the current collector and the electroactive material may have two different advantages: (i) the passive layer formed on the current collector is able to protect it against corrosion; and (ii) this thin layer of aluminum oxide can strengthen connection of the  $\text{LiMn}_2\text{O}_4$  spinel to the Al current collector.

The first effect is obvious due to well-known influence of such passive films to protect metallic substrates against corrosion. Indeed, this is a serious problem for lithium batteries due to their high operating voltage. Although aluminum has been found as an excellent current collector for lithium batteries, however, corrosion of current collector is still important and should be improved. Thus, reducing corrosion of Al current collector by coating its surface with

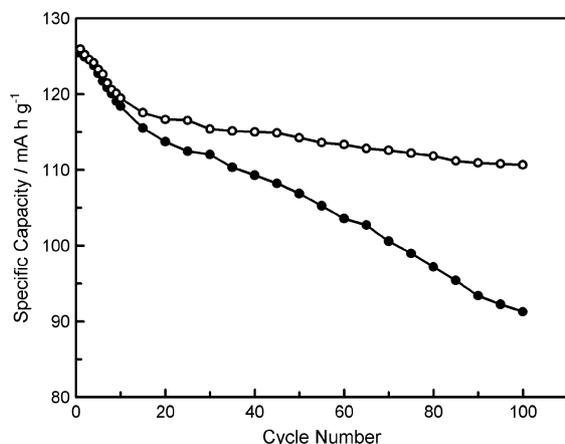


Fig. 1. Cyclability of the  $\text{LiMn}_2\text{O}_4$  cathode material deposited onto an  $\text{Al}_2\text{O}_3$ -coated Al (○) and a bare Al (●) current collector investigated at a C/2 rate ( $T = 22^\circ\text{C}$ ).

$\text{Al}_2\text{O}_3$  is of interest for the practical performance. The influence of the formation of  $\text{Al}_2\text{O}_3$  passive film on Al current collector surface has been described in detail [27,28], though it is irrelevant to the present study. The fluorides generated at high-voltage performance, e.g. 5.5 V vs.  $\text{Li}/\text{Li}^+$ , can react with the aluminum oxide to dissolve the passive layer [29]; however, it is not appropriate for the present system under investigation.

The influence of aluminum substrate has been extensively described in our previous works devoted to fundamental investigation of aluminum substrate for the deposition of various electroactive films [30–34]. This superior property of aluminum is due to the formation of passive aluminum oxide layer on the substrate surface, as this passive layer provides more suitable sites for the deposition of the electroactive material. It is indeed expected, since the own aluminum surface is more rigid than the passive film formed on it; thus, the latter one is capable to swallow the depositing particles. This is similar to the use of a thin ca. 10 nm  $\text{TiO}_2$  underlayer deposited onto Pt current collector, which is common for the preparation of lithium batteries. This effect has been extensively examined for the deposition of conductive polymers on Fe metallic substrate with and without such passive film [35].

Fig. 1 compares cyclability data obtained from battery performances of the  $\text{LiMn}_2\text{O}_4$  spinel deposited onto a conventional and an  $\text{Al}_2\text{O}_3$ -coated Al current collector. The data obtained from repetitive charge/discharge profiles of different cathodes recorded in a potential window of 3.1–4.3 V with a C/2 rate. It is obvious that the battery performance of the  $\text{LiMn}_2\text{O}_4$  cathode can be enhanced by depositing  $\text{Al}_2\text{O}_3$  passive layer on the current collector. According to the data presented below, annealing of the cathode prepared by the deposition of the  $\text{LiMn}_2\text{O}_4$  spinel onto the  $\text{Al}_2\text{O}_3$ -coated current collector leads to interlace of these compounds, which increases stability of the electroactive film deposited. The results indicate that covering the current collector surface

with a thin film of  $\text{Al}_2\text{O}_3$  before the deposition process is an efficient approach to enhance battery performance.

### 3.2. $\text{Al}_2\text{O}_3$ as an incorporating agent

After success of current collector coating with  $\text{Al}_2\text{O}_3$ , it is appropriate to examine the influence of  $\text{Al}_2\text{O}_3$  particles dispersed within the electroactive film deposited. Fig. 2 shows charge/discharge characteristics of the  $\text{LiMn}_2\text{O}_4$  cathodes with and without dispersed  $\text{Al}_2\text{O}_3$  particles. An increase in the specific capacity of  $\text{LiMn}_2\text{O}_4$  as a result of dispersion of  $\text{Al}_2\text{O}_3$  particles within the cathode material is observable. According to the theoretical specific capacity of  $\text{LiMn}_2\text{O}_4$ , i.e.  $148 \text{ mA h g}^{-1}$ , the conventional  $\text{LiMn}_2\text{O}_4$  cathode and the  $\text{LiMn}_2\text{O}_4$  cathode with dispersed  $\text{Al}_2\text{O}_3$  particles have achieved about 84% and 90% of the theoretical capacity, respectively. Such improvement is of great interest for the practical performance. Moreover, the cell voltage of the  $\text{Al}_2\text{O}_3$ -dispersed  $\text{LiMn}_2\text{O}_4$  cathode is slightly higher than that of the conventional  $\text{LiMn}_2\text{O}_4$  cathode. This effect has also been reported in the literature, and might be ascribed to the formation of solid solution of  $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ , though cannot be inspected precisely due its smallness.

In addition, the dispersion of  $\text{Al}_2\text{O}_3$  increases adhesion of the spinel particles. Thus, the  $\text{LiMn}_2\text{O}_4$  cathode with dispersed  $\text{Al}_2\text{O}_3$  exhibits better cyclability in comparison with the conventional  $\text{LiMn}_2\text{O}_4$  cathode. Fig. 3 presents the cyclability of the  $\text{LiMn}_2\text{O}_4$  cathode prepared by dispersion of  $\text{Al}_2\text{O}_3$  particles within the electroactive material. It is obvious that this action improves battery performance in the course of cycling at both room and elevated temperatures.

In general, the enhancement observed in the battery performance of  $\text{LiMn}_2\text{O}_4$  cathode by dispersion of  $\text{Al}_2\text{O}_3$  particles can be attributed to the fact that the existence of  $\text{Al}_2\text{O}_3$  particles acts as contact bridges between the spinel particles. Thus, the interparticle resistance is reduced and the insertion/extraction process can proceed across the

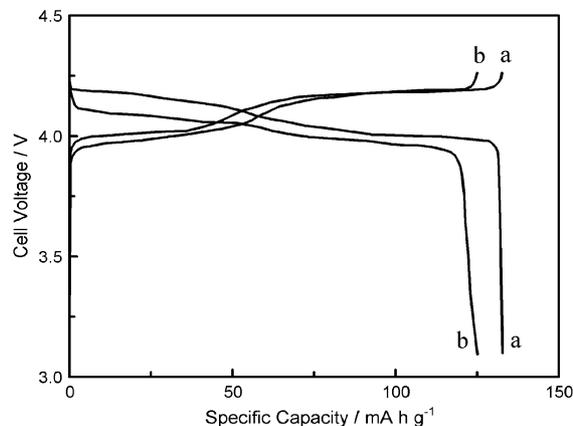


Fig. 2. Charge/discharge profiles of the  $\text{LiMn}_2\text{O}_4$  cathodes with (a) and without (b) dispersed  $\text{Al}_2\text{O}_3$  particles recorded at a C/2 rate.

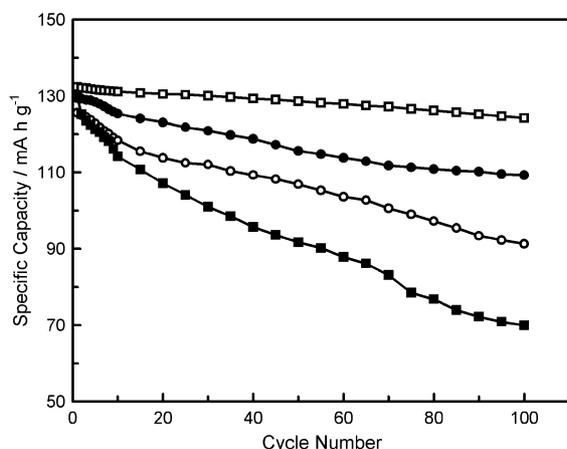


Fig. 3. Cyclability data for the LiMn<sub>2</sub>O<sub>4</sub> cathode with (□) and without (○) dispersed Al<sub>2</sub>O<sub>3</sub> particles at room temperature ( $T=22$  °C) and the LiMn<sub>2</sub>O<sub>4</sub> cathode with (●) and without (■) dispersed Al<sub>2</sub>O<sub>3</sub> particles at an elevated temperature ( $T=55$  °C).

electroactive material mass. It should be emphasized that the metal oxide dispersed cannot originally increase the electrical conductivity of the LiMn<sub>2</sub>O<sub>4</sub> film, due to its higher resistance. Indeed, the porous structure of the Al<sub>2</sub>O<sub>3</sub> provides an opportunity for easier diffusion of Li ions through the electroactive film.

Different factors can be responsible for such modifying properties of the incorporating Al<sub>2</sub>O<sub>3</sub> agent, which should be investigated in detail with a different strategy. However, it is obvious that the presence of Al<sub>2</sub>O<sub>3</sub> between the LiMn<sub>2</sub>O<sub>4</sub> particles has a significant effect to improve battery performance of the LiMn<sub>2</sub>O<sub>4</sub> cathode. This issue has also been addressed in the literature [14].

### 3.3. Al<sub>2</sub>O<sub>3</sub> as a surface coating agent

In the former Sections, generation of the Al<sub>2</sub>O<sub>3</sub> passive film on the current collector and dispersing Al<sub>2</sub>O<sub>3</sub> particles within the electroactive film were described as efficient approaches to enhance battery performance of LiMn<sub>2</sub>O<sub>4</sub> cathode. Now, it is of interest to examine the influence of Al<sub>2</sub>O<sub>3</sub> coating of the spinel surface on its electrochemical behavior. Fig. 4 presents cyclability data for the Al<sub>2</sub>O<sub>3</sub>-coated LiMn<sub>2</sub>O<sub>4</sub> cathode. The results suggest that surface coating of the spinel with a thin film of Al<sub>2</sub>O<sub>3</sub> significantly reduces capacity fades of LiMn<sub>2</sub>O<sub>4</sub> appearing at elevated temperatures.

### 3.4. Combination of three approaches

#### 3.4.1. Depth analysis

To understand further about the structure of the Al<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>-included LiMn<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> multilayers cathode prepared, depth analysis of the electrode was performed. Fig. 5(a) and (b) shows typical depth profiles of the LiMn<sub>2</sub>O<sub>4</sub> cathode without dispersed Al<sub>2</sub>O<sub>3</sub> particles at different

depths. To investigate the influence of annealing treatment on the structure of two thin Al<sub>2</sub>O<sub>3</sub> films attached to both sides of the LiMn<sub>2</sub>O<sub>4</sub> film, the depth analysis was first performed in the absence of dispersed Al<sub>2</sub>O<sub>3</sub> particles (the approach described in Section 3.2). For better resolution, the parts of the depth profiles, which correspond to the lower and upper (10 nm) Al<sub>2</sub>O<sub>3</sub> films deposited beneath and upon the LiMn<sub>2</sub>O<sub>4</sub> material, are illustrated in Fig. 5(a) and (b). As presented in Fig. 5(a) and (b), although the thickness of Al<sub>2</sub>O<sub>3</sub> film is 10 nm, aluminum element was detected in deeper places (approximately up to 30 nm). On the other hand, manganese element was detected within the 10-nm-thick Al<sub>2</sub>O<sub>3</sub> films. The results suggest that annealing process causes diffusion of two compounds within each other. These results indicate that the behaviors of the aluminum oxide films formed beneath and upon the LiMn<sub>2</sub>O<sub>4</sub> are similar.

The depth analysis was also performed to understand the dispersion of the Al<sub>2</sub>O<sub>3</sub> particles within the LiMn<sub>2</sub>O<sub>4</sub> film. To this aim, a LiMn<sub>2</sub>O<sub>4</sub> electrode prepared based on all three approaches was analyzed. Fig. 5(c) displays a typical depth profile to inspect the existence of Al<sub>2</sub>O<sub>3</sub> in three different regions. Similar to the results reported in Fig. 5(a) and (b), gradual changes of aluminum and manganese concentration across two thin films of Al<sub>2</sub>O<sub>3</sub> are observable. In addition, the constant amount of aluminum in middle depth (depth related to LiMn<sub>2</sub>O<sub>4</sub> film) indicates homogeneous dispersion of Al<sub>2</sub>O<sub>3</sub> particles within the electroactive material.

Further investigation showed that this type of Al<sub>2</sub>O<sub>3</sub> distribution is due to thermal treatment of the electrode, as such behavior was not observed for un-heated electrode. In other words, diffusion of Al<sub>2</sub>O<sub>3</sub> into LiMn<sub>2</sub>O<sub>4</sub> and vice versa occurs during thermal treatment of the cathode prepared. It is believed that the thermal treatment process is also accompanied by the formation of solid solution of LiAl<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub>. However, this action cannot be determined

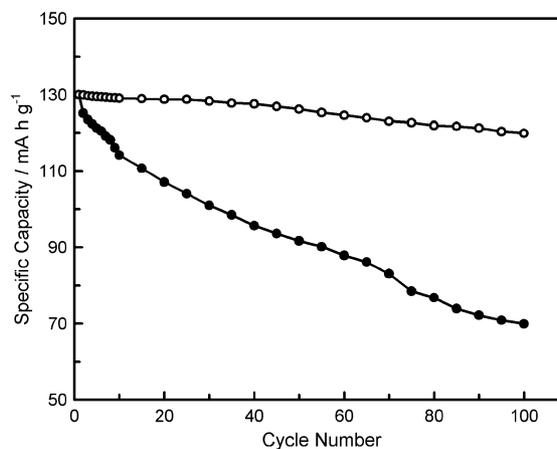


Fig. 4. Cyclability of the Al<sub>2</sub>O<sub>3</sub>-coated (○) and uncoated (●) LiMn<sub>2</sub>O<sub>4</sub> cathodes at an elevated temperature ( $T=55$  °C).

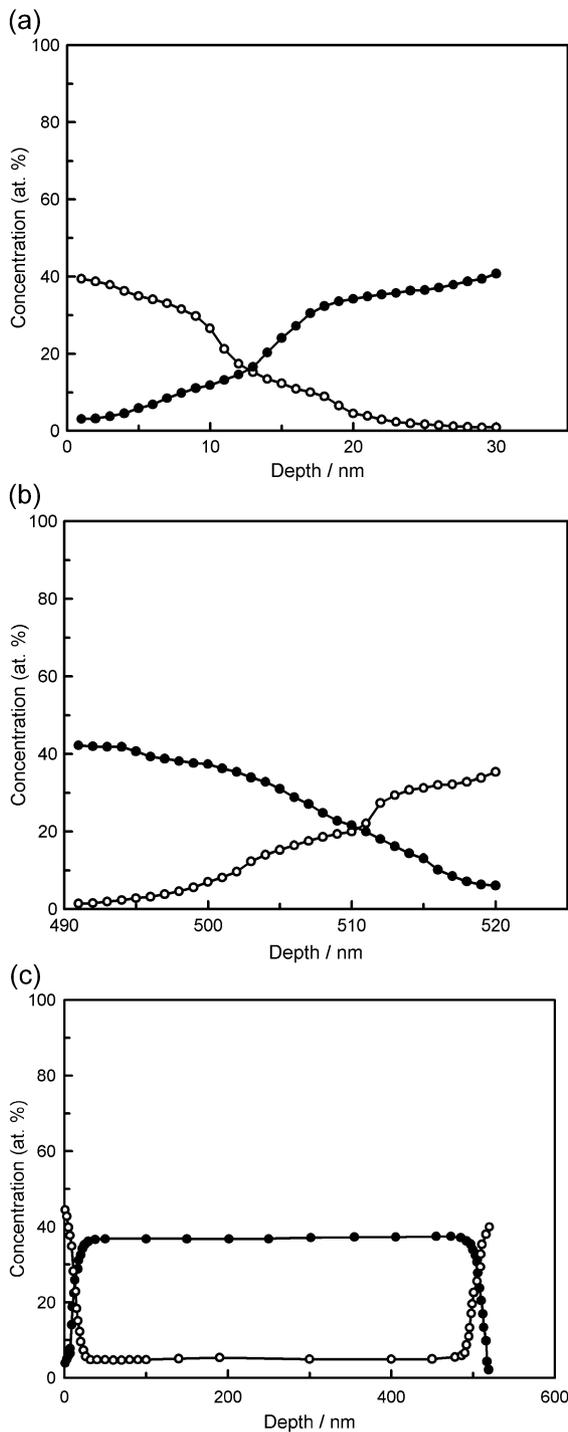


Fig. 5. (a and b) Depth profiles of a LiMn<sub>2</sub>O<sub>4</sub> film coated with 10-nm-thick Al<sub>2</sub>O<sub>3</sub> films deposited on its both sides with structure of Al<sub>2</sub>O<sub>3</sub>/LiMn<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>, respectively. For better resolution, the other parts of the depth profiles were not illustrated. (c) Depth profile of a LiMn<sub>2</sub>O<sub>4</sub> electrode prepared using all three approaches with structure of Al<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>-included LiMn<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>. In the latter case, the depth profile was illustrated as a whole. The symbols (●) and (○) denote manganese and aluminum, respectively.

by XRD, since the amounts Al<sub>2</sub>O<sub>3</sub> agents utilized in three different approaches are very small (even for the case of dispersed Al<sub>2</sub>O<sub>3</sub> particles within LiMn<sub>2</sub>O<sub>4</sub> it is less than 5

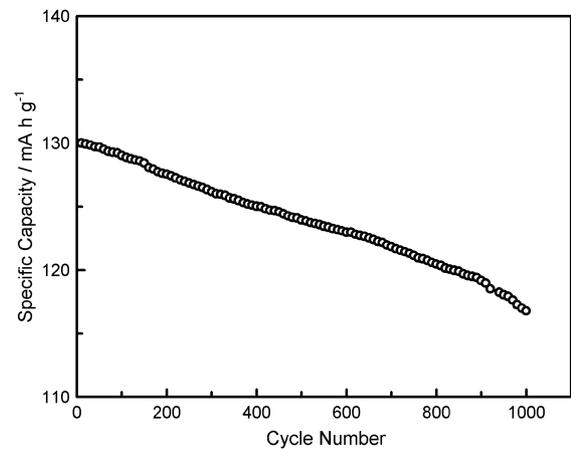


Fig. 6. Long-term cyclability of the LiMn<sub>2</sub>O<sub>4</sub> cathode prepared using all three different approaches, at room temperature.

wt.%). On the other hand, the results obtained from depth analysis of the cathode provide strong evidence for high stability of the electroactive film deposited onto the substrate surface. Indeed, the results are satisfactory to understand the reason for the enhancements achieved for the applied purpose of the present report.

#### 3.4.2. Cyclability

In Sections 3.1, 3.2 and 3.3, the efficiencies of three different approaches using Al<sub>2</sub>O<sub>3</sub> agents were shown separately. Each of the approaches proposed are able to improve battery performance of the LiMn<sub>2</sub>O<sub>4</sub> cathode significantly. Indeed, three different approaches were proposed and classified for improvement of cyclability of the LiMn<sub>2</sub>O<sub>4</sub> cathode in lithium secondary batteries (though one of them has been noted briefly in the literature). However, the improvements achieved separately are similar to those reported in the literature, and cannot guarantee a desirable cyclability of LiMn<sub>2</sub>O<sub>4</sub> for commercialization. At this stage, we just show that combination of three different approaches

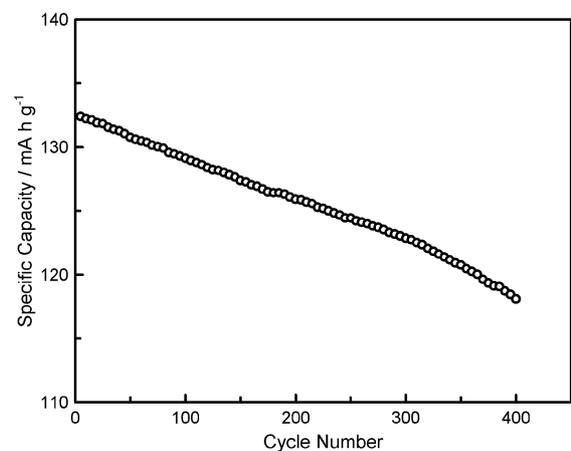


Fig. 7. Long-term cyclability of the LiMn<sub>2</sub>O<sub>4</sub> cathode prepared using all three different approaches, at an elevated temperature ( $T=55\text{ }^{\circ}\text{C}$ ).

proposed has a superior effect to improve cyclability of the  $\text{LiMn}_2\text{O}_4$  cathode.

The results illustrated in Fig. 6 obviously suggest excellent cyclability of the  $\text{LiMn}_2\text{O}_4$  cathode. The  $\text{LiMn}_2\text{O}_4$  cathode prepared based on all three approaches retains about 90% of its initial specific capacity after 1000 charge/discharge cycles. Possibility for performing such number of charge/discharge cycles indicates a good cyclability for lithium secondary batteries.

To investigate  $\text{LiMn}_2\text{O}_4$  as an alternative cathode materials for lithium batteries, it is needed to examine the main problem of  $\text{LiMn}_2\text{O}_4$  cathodes, i.e. capacity fading at elevated temperatures. Similar to excellent cyclability of the  $\text{LiMn}_2\text{O}_4$  cathode prepared using all three approaches (as illustrated in Fig. 6), it exhibited an acceptable cyclability at elevated temperature. The  $\text{LiMn}_2\text{O}_4$  cathode was successfully used for 400 charge/discharge cycles, while it retains 90% of its initial specific capacity (Fig. 7).

As the different approaches are similar and utilize the same modifier agent, combination of them is of interest from commercial point of view, and the cathode can be fabricated by using a single modifier agent. In addition, it is thought that adhesion of  $\text{Al}_2\text{O}_3$  diffused into the  $\text{LiMn}_2\text{O}_4$  film with  $\text{Al}_2\text{O}_3$  particles dispersed within the  $\text{LiMn}_2\text{O}_4$  has a significant effect for higher stability of the  $\text{LiMn}_2\text{O}_4$  film sandwiched between these two  $\text{Al}_2\text{O}_3$  films. A comparative study of the adhesion of the film deposited using modern Pull-off approach (since the classical Scotch tube test is not appropriate for this purpose) [36] was made to understand this issue. The results indicated the adhesion of the cathode material deposited using multi-function  $\text{Al}_2\text{O}_3$  agent is approximately 1.2 times higher than that of conventional  $\text{LiMn}_2\text{O}_4$  film deposited.

#### 4. Conclusion

Three different approaches were proposed to improve battery performance of the  $\text{LiMn}_2\text{O}_4$  cathode by means of  $\text{Al}_2\text{O}_3$  as a multi-function agent. Investigations of these approaches separately indicated that each of them could significantly improve battery performance of the  $\text{LiMn}_2\text{O}_4$  cathode. The novelty of the present work was related to the combination of these approaches, which led to a superior battery performance for the  $\text{LiMn}_2\text{O}_4$  cathode. Indeed, the present study shows that, after significant developments achieved for improving battery performance of  $\text{LiMn}_2\text{O}_4$  cathodes, it is now appropriate to combine different approaches.

#### References

- [1] R.J. Gummow, A. de Kock, M.M. Thackeray, *Solid State Ionics* 69 (1994) 59.
- [2] A. Blyr, C. Sigala, G.G. Amatucci, D. Guyomard, Y. Chabre, J.M. Tarascon, *J. Electrochem. Soc.* 145 (1998) 194.
- [3] X. Sun, H.S. Lee, X.Q. Yang, J. McBreen, *Electrochem. Solid-State Lett.* 4 (2001) A184.
- [4] Y. Xia, T. Sakai, T. Fujieda, X.Q. Yang, X. Sun, Z.F. Ma, J. McBreen, M. Yoshio, *J. Electrochem. Soc.* 148 (2001) A723.
- [5] G.G. Amatucci, C.N. Schmutz, A. Blyr, C. Sigala, A.S. Gozdz, D. Tarascon, J.M. Tarascon, *J. Power Sources* 69 (1997) 11.
- [6] M.M. Thackeray, Y. Shao-Horn, A.J. Kahaian, K.D. Kepler, E. Skinner, J.T. Vaughey, S.J. Hackney, *Electrochem. Solid-State Lett.* 1 (1998) 7.
- [7] J.M. Tarascon, F. Coowar, G. Amatucci, F.K. Shokoohi, D. Guyomard, *J. Electrochem. Soc.* 141 (1994) A826.
- [8] H. Huang, C.A. Vincent, P.G. Bruce, *J. Electrochem. Soc.* 146 (1999) 3649.
- [9] D. Guyomard, J.-M. Tarascon, *J. Power Sources* 54 (1995) 92.
- [10] A. Eftekhari, *Electrochim. Acta* 47 (2002) 4347 (Erratum 48 (2002) 290).
- [11] A. Eftekhari, *Electrochim. Acta* 48 (2003) 2831.
- [12] A. Eftekhari, *Solid State Ionics* 161 (2003) 41.
- [13] Y. Shin, A. Manthiram, *Electrochem. Solid-State Lett.* 5 (2002) A55.
- [14] A.M. Kannan, A. Manthiran, *Electrochem. Solid-State Lett.* 5 (2002) A167.
- [15] J. Cho, G.B. Kim, H.S. Lim, C.-S. Kim, S.I. Yoo, *Electrochem. Solid-State Lett.* 2 (1999) 607.
- [16] S.S. Kim, Y. Kadoma, H. Ikuta, Y. Uchimoto, M. Wakihara, *Electrochem. Solid-State Lett.* 4 (2001) A109.
- [17] A. Eftekhari, *J. Electrochem. Soc.* 150 (2003) A966.
- [18] A. Eftekhari, *J. Power Sources* (in press).
- [19] A. Eftekhari, *J. Power Sources* 124 (2003) 182.
- [20] M.M. Thackeray, C.S. Johnson, J.-S. Kim, K.C. Lauzze, J.T. Vaughey, N. Dietz, D. Abraham, S.A. Hackney, W. Zeltner, M.A. Anderson, *Electrochem. Commun.* 5 (2003) 752.
- [21] Y.-K. Sun, K.-J. Hong, J. Prakash, *J. Electrochem. Soc.* 150 (2003) A970.
- [22] J. Cho, Y.J. Kim, B. Park, *J. Electrochem. Soc.* 148 (2001) A1110.
- [23] J. Cho, Y.J. Kim, T.-J. Kim, B. Park, *Angew. Chem. Int. Ed. (Engl.)* 40 (2001) 3367.
- [24] Y.J. Kim, T.-J. Kim, J.W. Shin, B. Park, J. Cho, *J. Electrochem. Soc.* 149 (2002) A1337.
- [25] V.G. Bhide, S. Salkalachen, A.C. Rastog, C.N.R. Rao, M.S. Hegde, *J. Phys., D, Appl. Phys.* 14 (1981) 1647.
- [26] P.N. Barnes, S. Mukhopadhyay, R. Nekkanti, T. Haugan, R. Biggers, I. Maartense, *AIP Conf. Proc.* 614 (2002) 614.
- [27] K. Kanamura, *J. Power Sources* 81–82 (1999) 123.
- [28] K. Kanamura, T. Umegaki, S. Shiraishi, M. Ohashi, Z. Takehara, *J. Electrochem. Soc.* 149 (2002) A185.
- [29] K. Kanamura, T. Okagawa, Z. Takehara, *J. Power Sources* 57 (1995) 119.
- [30] A. Eftekhari, *Sens. Actuators, B, Chem.* 80 (2001) 283.
- [31] A. Eftekhari, *Talanta* 55 (2001) 395.
- [32] A. Eftekhari, *Synth. Met.* 125 (2001) 295.
- [33] A. Eftekhari, *Mikrochim. Acta* 141 (2003) 15.
- [34] A. Eftekhari, *Sens. Actuators, B, Chem.* 88 (2003) 234.
- [35] A. Eftekhari, *Synth. Met.* (accepted).
- [36] P.A. Steinmann, H.E. Hintermann, *J. Vac. Sci. Technol., A, Vac. Surf.* 7 (1989) 2267.