

# Improvement of Cycling Stability of $\text{LiMn}_2\text{O}_4$ Cathode by $\text{Al}_2\text{O}_3$ Surface Coating for Li-Ion Batteries

H. ŞAHAN\*, H. GÖKTEPE, F. KILIÇ DOKAN, A. AYDIN, S. VEZİROĞLU AND Ş. PATAT  
Department of Chemistry, Faculty of Science, Erciyes University, 38039 Kayseri, Turkey

The effect of the  $\text{Al}_2\text{O}_3$  coating on the charge–discharge cycling performance of spinel powder ( $\text{LiMn}_2\text{O}_4$ ) was investigated in the range of 3.5–4.5 V at 1C. The  $\text{Al}_2\text{O}_3$  coating on the surface of the spinel powder was carried out using the solution method, followed by 500 °C for 6 h in air. Powder X-ray diffraction pattern of the  $\text{Al}_2\text{O}_3$ -coated spinel  $\text{LiMn}_2\text{O}_4$  showed that the  $\text{Al}_2\text{O}_3$  coating medium was not incorporated in the spinel bulk structure. Scanning electron microscopy results showed that the  $\text{Al}_2\text{O}_3$  coating particles were homogeneously distributed on the surface of  $\text{LiMn}_2\text{O}_4$  powder particles. The  $\text{Al}_2\text{O}_3$ -coated  $\text{LiMn}_2\text{O}_4$  retained 92.3% of its original capacity after 30 cycles, showing much better cycle ability than the bare lithium manganese oxide. The improvement of electrochemical performance is attributed to suppression of  $\text{Mn}^{2+}$  dissolution into electrolyte via  $\text{Al}_2\text{O}_3$  layer.

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## 1. Introduction

Cubic spinel  $\text{LiMn}_2\text{O}_4$  is of great interest for the replacement of  $\text{LiCoO}_2$  in Li-ion batteries due to its high voltage, natural abundance, low cost, and environmental benignity [1]. However,  $\text{LiMn}_2\text{O}_4$  exhibits serious capacity fading during charge and discharge. In order to overcome this capacity fading problem, two kinds of methods can be employed. One way is the substitution of mono-, di-, or trivalent cations in  $\text{LiMn}_2\text{O}_4$  to decrease  $\text{Mn}^{3+}$  ions which cause disproportion reactions. The other one is to coat the  $\text{LiMn}_2\text{O}_4$  particles with various protective layers. Some studies showed the substitution of Mn ions at 16d sites with ions with a valence  $\leq +3$  to give doped spinels  $\text{Li}_x\text{M}_y\text{Mn}_{2-y}\text{O}_4$  ( $\text{M} = \text{Li}, \text{Al}, \text{Co}, \text{Ni}, \text{Fe}, \text{Cr}, \text{Zn},$  and  $\text{Mg}$ ), which could enhance the cycling stability at room temperature [2, 3]. Although this approach has improved the structural stability, it seriously reduces initial capacity, depending on the kind of substituted metals (M) and their content.

Recently, surface modifications with oxides such as  $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$  [4],  $\text{Cr}_2\text{O}_3$  [5] have been investigated and shown excellent cycle ability. These studies considered that the presence of oxide coating can minimize the contact area of  $\text{LiMn}_2\text{O}_4$ /electrolyte interface and suppress dissolution of manganese. This study examines the effect on the electrochemical cycling performance of  $\text{LiMn}_2\text{O}_4$  by coating its surface with the  $\text{Al}_2\text{O}_3$  via solution method. The treatment is expected to affect the cycleability. The preparation, structure and electrochemical performance of the surface-treated  $\text{LiMn}_2\text{O}_4$  cathode materials are discussed in comparison with the bare one. To the best of our knowledge, this is first time that such coating has been attempted as a means to improve the electrochemical performance of  $\text{LiMn}_2\text{O}_4$  cathode material.

## 2. Experimental

Bare  $\text{LiMn}_2\text{O}_4$  was prepared by a glycine-nitrate combustion process [6]. Synthesis of acetyl–alumoxane: pseudobohemite (20.0 g, 333 mmol) was slowly added to a vigorously stirring mixture of acetic acid (51.0 mL, 667 mmol) in water (200 mL). The resulting slurry was decanted after 10 min and then centrifuged at 6000 rpm for 1 h to yield a clear viscous solution. Removal of the volatiles in vacuum ( $10^{-2}$  Torr) at 90 °C results in clear, white granules. The granules were dissolved in water and dried for 24 h at 80 °C to yield a clear glassy material. The acetate–alumoxane is soluble in water and slightly soluble in ethanol [7]. Al-oxide modifying (1.6 wt%) on  $\text{LiMn}_2\text{O}_4$  material was carried out in acetyl–alumoxanes aqueous solution. The bare  $\text{LiMn}_2\text{O}_4$  powder was added to the solution to obtain a suspension. The suspension was stirred vigorously with a magnetic stirrer for 3 h at 50 °C to make it dispersed homogeneously and then dried in an oven at 100 °C to evaporate the water. After that, the obtained powder was further heated in a muffle furnace at 500 °C for 5 h and then cooled to room temperature.

Samples were verified by X-ray diffraction (XRD, Bruker AXS D8, using  $\text{Cu } K_\alpha$  radiation). The morphology and microstructure of samples were observed by scanning electron microscopy (LEO 440). Thermogravimetry (TG) and differential thermal analysis (DTA) measurements were conducted by the Perkin–Elmer (Diamond) high temperature thermal analyzer with 5–20 mg samples and a heating rate of 10 °C/min from 50 to 700 °C in air.

The electrochemical performance was investigated by galvanostatic charge/discharge experiments. Two-electrode teflon cell was used to evaluate the electrochemical properties of both uncoated and  $\text{Al}_2\text{O}_3$ -coated  $\text{LiMn}_2\text{O}_4$  electrodes. The electrochemical cells consisted of Li-metal sheet as a counter electrode and 1 M  $\text{LiPF}_6$  in ethylene carbonate/diethyl carbonate

\*corresponding author; e-mail: halil@erciyes.edu.tr

(EC/DEC, 1:1 vol.%) as a liquid electrolyte. Cell construction and sealing were carried out in an argon-filled glove box. Galvanostatic cycling was performed between 3.4 and 4.5 V with 1C on an MLab Multi Channel battery tester.

### 3. Results and discussion

The chemical analysis of the base and surface-treated lithium manganese oxide indicated that the stoichiometry of the elements was very close to the targeted formula. To determine the effect of  $\text{Al}_2\text{O}_3$  coating on the crystal structure of  $\text{LiMn}_2\text{O}_4$ , the X-ray powder diffraction was carried out for uncoated and coated spinel materials.

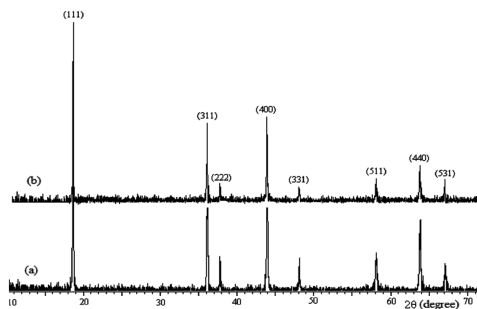


Fig. 1. X-ray diffraction patterns of (a) the bare  $\text{LiMn}_2\text{O}_4$  and (b) the  $\text{Al}_2\text{O}_3$ -coated  $\text{LiMn}_2\text{O}_4$ .

The XRD patterns of the base and  $\text{Al}_2\text{O}_3$  coated  $\text{LiMn}_2\text{O}_4$  are presented in Fig. 1. The XRD pattern of the base  $\text{LiMn}_2\text{O}_4$  powder in Fig. 1a shows that the material is pure spinel phase with space group of  $Fd3m$ . There is no significant change in the XRD pattern for the coated spinel material in Fig. 1b, compared with the base one. Calculated lattice parameters by Win-Metric program were  $a = 8.237 \text{ \AA}$  and  $a = 8.236 \text{ \AA}$ , respectively, for the base and  $\text{Al}_2\text{O}_3$  coated materials. Almost no change in the lattice parameter for both samples indicated that the  $\text{Al}_2\text{O}_3$  coating medium was not incorporated into the spinel structure but is just presented on the surface of  $\text{LiMn}_2\text{O}_4$ . The presence of  $\text{Al}_2\text{O}_3$  was not detected by XRD. Absence of  $\text{Al}_2\text{O}_3$  related peak in Fig. 1a,b is due to the little amount of  $\text{Al}_2\text{O}_3$  (1.6 wt%) in the  $\text{Al}_2\text{O}_3$  coated final product.

To work out the possible chemical composition of the coating layer, thermal gravimetric examination for the precursor powder of coating material, obtained from evaporation of solution of alumoxanes xerogel, was carried out in Fig. 2. A drastic weight loss is seen to  $300^\circ\text{C}$  due to evaporation of absorbed and bonded water from the precursor. Then, minor decrease in the weight is seen between  $300^\circ\text{C}$  and  $400^\circ\text{C}$ , which is attributed to decomposition of acetates. No obvious change is observed at above  $500^\circ\text{C}$ . Therefore, it is confirmed that the calcination temperature for coating was enough to produce  $\text{Al}_2\text{O}_3$ .

The surface morphology change of  $\text{LiMn}_2\text{O}_4$  after coating with  $\text{Al}_2\text{O}_3$  is presented in Fig. 3. It is seen that

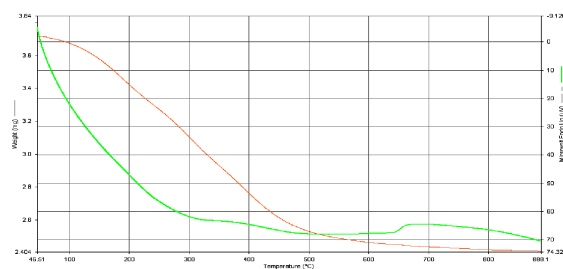


Fig. 2. Thermal gravimetric curve of the precursor powder as the coating medium obtained from evaporation of aqueous solution of acetyl-alumoxanes.

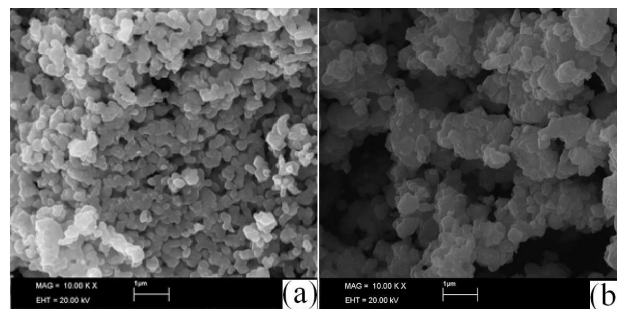


Fig. 3. SEM images of (a) the bare  $\text{LiMn}_2\text{O}_4$ , (b)  $\text{Al}_2\text{O}_3$ -coated  $\text{LiMn}_2\text{O}_4$ .

the particle size of uncoated- $\text{LiMn}_2\text{O}_4$  particles is about 200 nm, and there is no size difference between the bare and the  $\text{Al}_2\text{O}_3$ -modified  $\text{LiMn}_2\text{O}_4$  particles. On the other hand, the surface morphology of the uncoated  $\text{LiMn}_2\text{O}_4$  particles is smooth, as shown in Fig. 3a,c, but it becomes rough and aggregated after coating with  $\text{Al}_2\text{O}_3$  (Fig. 3b). Figure 4 shows the continuous charge and discharge profiles of the bare and surface treated  $\text{LiMn}_2\text{O}_4$  performed at room temperature.

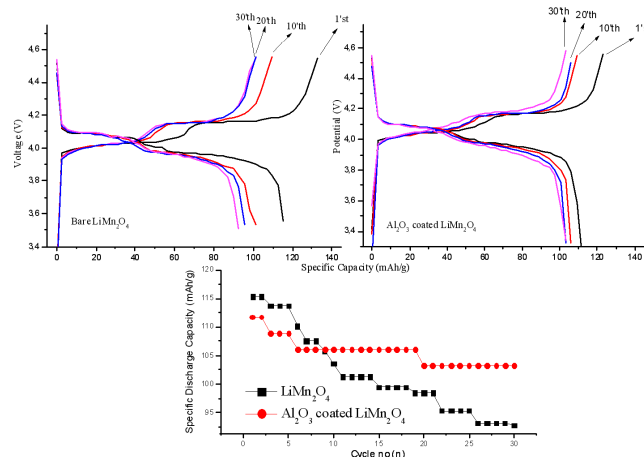


Fig. 4. Charge-discharge curves and cycling performances of the bare  $\text{LiMn}_2\text{O}_4$  and  $\text{Al}_2\text{O}_3$  modified  $\text{LiMn}_2\text{O}_4$ .

From Fig. 4, we can find that the surface-modified  $\text{LiMn}_2\text{O}_4$  cathode material displays lower discharge capacity ( $111.8 \text{ mAh g}^{-1}$ ) than the bare one. This can be explained that the  $\text{Al}_2\text{O}_3$  layer forms a barrier for the movement of Li ions, which hinders the extraction and insertion of Li ions from the spinel and results in the low initial specific capacity of the cathode. As seen in Fig. 4, after 30 cycles the discharge capacity of the bare  $\text{LiMn}_2\text{O}_4$  faded from 115.4 to 92.4  $\text{mAh g}^{-1}$  with the capacity fade of 19.6% of its initial capacity.

However, under the same conditions, the discharge capacity of the  $\text{Al}_2\text{O}_3$ -coated spinel electrodes clearly shows an improved cycling behavior compared with the bare one. The  $\text{Al}_2\text{O}_3$ -coated  $\text{LiMn}_2\text{O}_4$  exhibits maximum discharge capacity of  $111.8 \text{ mAh g}^{-1}$ , but after 30 cycles only 7.7% capacity loss was obtained and the discharge capacity still maintained at  $103.2 \text{ mAh g}^{-1}$ . This cycling behavior of the  $\text{Al}_2\text{O}_3$ -coated  $\text{LiMn}_2\text{O}_4$  indicates the impact of  $\text{Al}_2\text{O}_3$  coating significantly which improved the cycling performances at room temperature. The  $\text{Al}_2\text{O}_3$  coating prevents the direct contact between the spinel and the electrolyte and therefore reduces the dissolution of manganese and the oxidation of electrolyte.

#### 4. Conclusions

The  $\text{LiMn}_2\text{O}_4$  material were successfully coated with 1.6 wt.%  $\text{Al}_2\text{O}_3$  by a sol-gel process. The  $\text{Al}_2\text{O}_3$  coating did not result in change in the host structure of  $\text{LiMn}_2\text{O}_4$  and no impurity such as  $\text{Al}_2\text{O}_3$  were detected. The discharge capacity of the  $\text{Al}_2\text{O}_3$  coated spinel electrode shows an improved cycling behavior compared with the bare one. The improved performance of the sur-

face coated cathode sample is ascribed to  $\text{Al}_2\text{O}_3$  coated on the surface of  $\text{LiMn}_2\text{O}_4$ , which suppresses dissolution of  $\text{Mn}^{3+}$  ions in the cathode material. Therefore,  $\text{Al}_2\text{O}_3$  surface modification is an effective way to improve the electrochemical performance of  $\text{LiMn}_2\text{O}_4$  cathode material.

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