

## HEV용 리튬 이차전지 양극물질 $\text{LiMn}_2\text{O}_4$ 에 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ 코팅에 따른 영향

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### Effect of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coating layer on capacity retention of $\text{LiMn}_2\text{O}_4$ as cathode materials of lithium ion secondary batteries for HEV application

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**Key words** :  $\text{LiMn}_2\text{O}_4$ , coating, HEV, sol-gel method

**Abstract** : In these recent years, low cost and stable battery electrode materials have been studied for HV/HEV application. Spinel cathode material  $\text{LiMn}_2\text{O}_4$  is widely studied as a promising cathode material of lithium ion secondary batteries because of it is low cost, easily to be prepared and capable to be operated in high voltage range. In this study,  $\text{LiMn}_2\text{O}_4$  was undergoing surface modification with spinel lithium titanium oxide by sol-gel method in order to enhance its capacity retention. Properties of both unmodified and surface-modified  $\text{LiMn}_2\text{O}_4$  were characterized by XRD, SEM, particle size analyzer while their cycling performance was tested with charge and discharge tester.

#### Nomenclature

LMO : Lithium manganese oxide,  $\text{LiMn}_2\text{O}_4$

LTO : Lithium titanium oxide,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$

XRD : X-ray diffraction

SEM : Scanning electron microscope

### 1. Introduction

Recently  $\text{LiMn}_2\text{O}_4$  has been widely studied as a potential cathode material of lithium ion rechargeable batteries for future HV/HEV application due to it is inexpensive, light weight, easily to be prepared and capable to be operated in high voltage range. However, this  $\text{Fd}_3\text{m}$  spinel structure material has poor cycling efficiency that led by high rate capacity fading during cycling performance<sup>(1)</sup>.

Many research have been done for circumvent the poor cyclability of  $\text{LiMn}_2\text{O}_4$ , such as substitute Mn ions with other 3d transition metals, modify its surface by coating and etc.<sup>(2)-(10)</sup>. Conductivity of  $\text{LiMn}_2\text{O}_4$  is improved by coating high-conducted  $\text{LiCoO}_2$  on its surface to enhance its rate capability<sup>(7)</sup>.  $\text{SiO}_2$  was coated successfully reduce the dissolution of  $\text{Mn}^{2+}$  into electrolyte by reducing the contact of active materials with the electrolyte<sup>(8)</sup>. To stabilize its cycling performance,  $\text{Al}_2\text{O}_3$  was coated

as well<sup>(9)</sup>. Dong-Qiang Liu et al. works reported that  $\text{LiMn}_2\text{O}_4$  was synthesized by sol-gel method and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  sol was synthesized to be coated on  $\text{LiMn}_2\text{O}_4$  surface by sol-gel method<sup>(10)</sup>.

In this study,  $\text{LiMn}_2\text{O}_4$  was synthesized by solid reaction after granulation method, which in the condition to be calcined to obtain high crystalline powder. Then was coated with  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  by sol-gel method in order to enhance its capacity retention.

### 2. Experiment

Stoichiometric amounts of  $\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$  were mixed in a mixer and granulated with spray drying. The well-mixed precursor was calcined at  $750^\circ\text{C}$  for 36 hours in air and sintered at  $850^\circ\text{C}$  for 6 hours in air to form fine powder of a single phase.

Tetrabutyltitanate and lithium acetate were dissolved in a mixture of ethanol and distilled water with the ratio

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of Li:Ti=4:5 to form a clear solution. Then LTO sol was obtained by adding acetic acid. As-prepared LMO was added to sol under stirring. This mixture was stirred until a black gel formed. Finally, this gelatin was dried at 100 °C for 1 hour and fired at 800 °C for 1 hour to obtain the final product.

Properties of obtained final product were analysed with XRD, SEM, and particle size analyzer. Half cell was made to analyse its electrochemical properties within the potential range of 1V~4.3V with constant current of 1mA.

### 3. Results and discussions

#### 3.1 Crystalline phase

Fig. 1 shows the XRD patterns of uncoated LMO and LTO coated LMO with different molar ratios. LMO crystalline phase was presented through XRD studies. Different phases were not observed, which indicates that there is no structural changes of coated LMO. On the other hand, intensity of the main spinel (111) peak decreased after coating process. This revealed that there was LTO coating layer on the LMO surface.

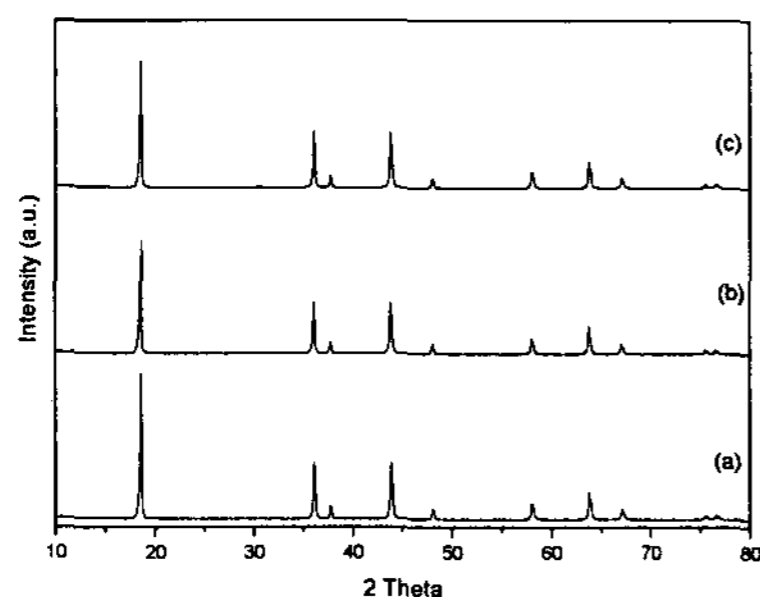


Fig. 1. XRD patterns of (a) uncoated LMO, (b) 2 mol% LTO coated LMO and (c) 5 mol% LTO coated LMO.

#### 3.2 Particle size and microstructure

Fig. 2 shows the average particle size and distribution of uncoated LMO and coated LMO. The uncoated LMO with the average particle size of 5.43 μm, while 2 mol% LTO coated LMO with 13.09 μm and 5 mol% LTO coated LMO with 13.13 μm. These data indicated that the average particle size of these modified-LMO increased with the increasing amount of LTO coating layer due to the agglomeration grains after heat treatment in coating process.

#### 3.3 Morphology

From the particle size data, 5 mol% -coated LMO was only slightly larger than 2 mol%-coated LMO, as this was indicated through SEM images as shown in Fig. 3, both Fig. 3(b) and (c) had no much difference. LTO

coating layer at the surface of LMO was observed, which could confirm that LMO surface was successfully coated with LTO particles. Further confirmation was done with EDX analysis and met great agreement with SEM observation.

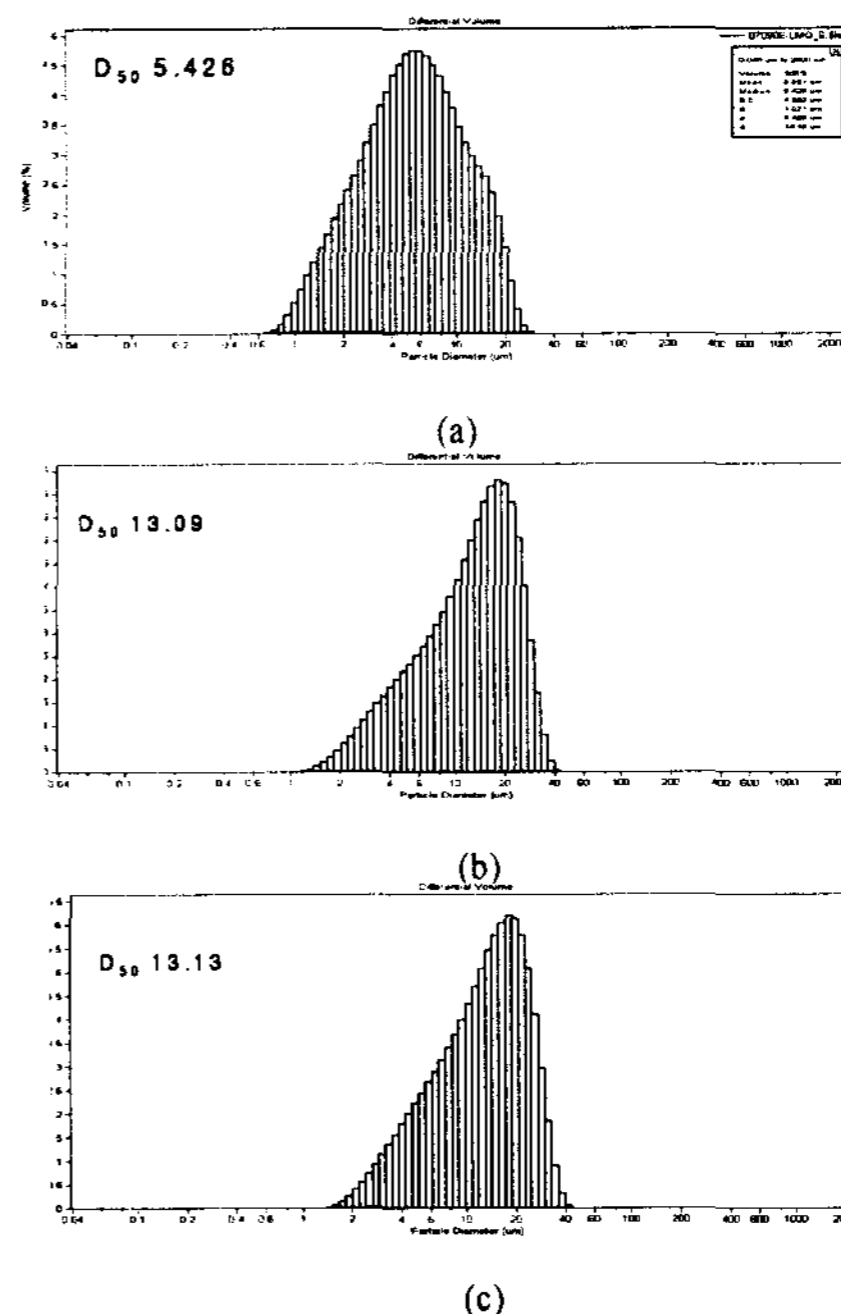
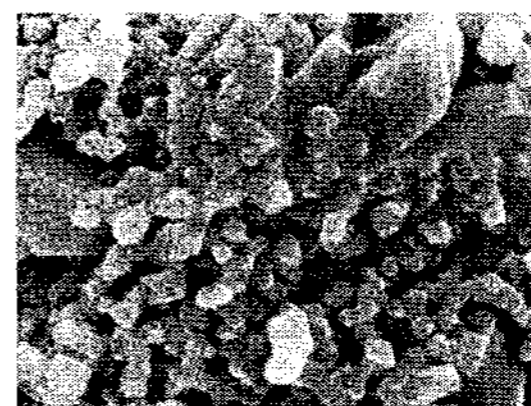


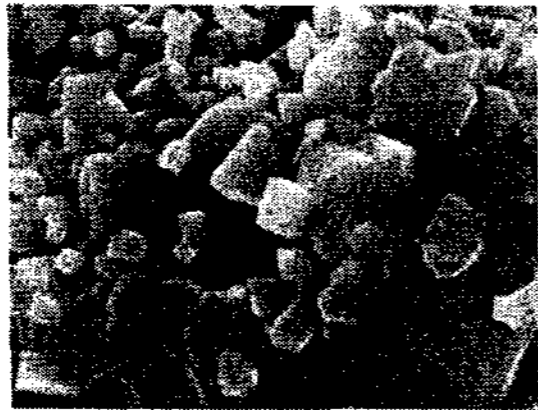
Fig.2. Particle size and distribution of (a) uncoated LMO, (b) 2 mol% LTO coated LMO and (c) 5 mol% LTO coated LMO.



(a)



(b)



(c)

Fig. 3. SEM image of (a) uncoated LMO, (b) 2 mol% LTO-coated LMO, (c) 5 mol% LTO-coated LMO. ( 20kV, X20,000 )

### 3.4 Cycling performance

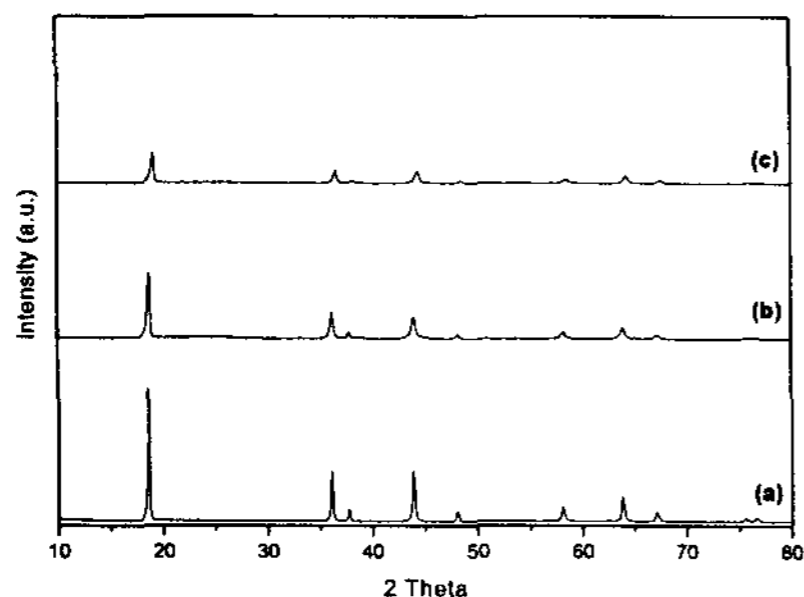


Fig. 4. XRD patterns before charge/discharge test of (a) uncoated LMO, after charge/discharge test of (b) 2 mol% LTO-coated LMO, (c) 5 mol% LTO-coated LMO.

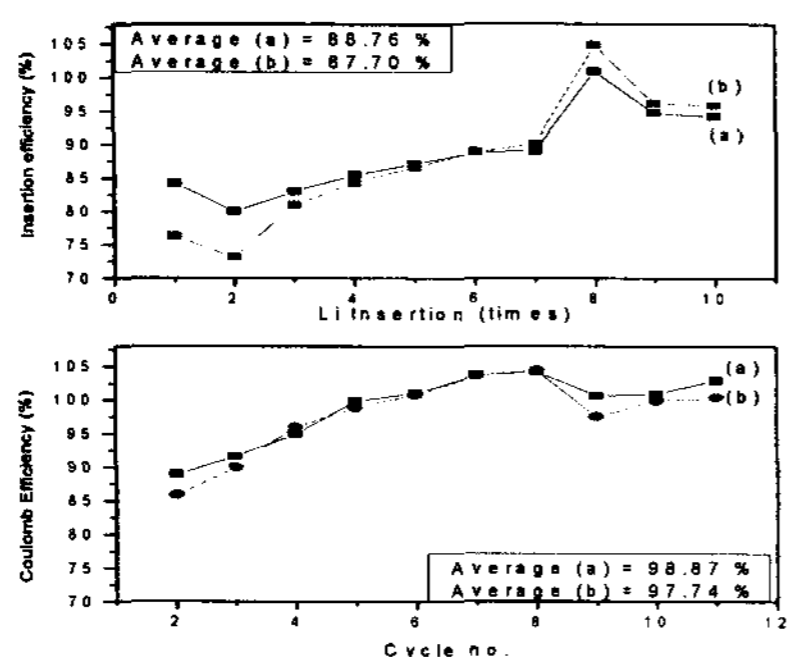


Fig. 5. Lithium efficiency and coulomb efficiency of (a) 2 mol% LTO-coated LMO and (b) 5 mol% LTO-coated LMO.

As shown in Fig. 4, there is no other phases observed, but the spinel structural peak intensities decreased with the increasing amount of LTO coating layer at LMO surface. For further investigation, both lithium ion insertion efficiency and coulomb efficiency were calculated with the charge and discharge data, as shown

in Fig. 5. 2 mol% LTO coated LMO presented better both lithium insertion efficiency and coulomb efficiency, with the average of 88.76% and 98.87%, while 5 mol% LTO coated LMO presented both average values with 87.70% and 97.74%.

These data showed that both coated LMO preformed relatively higher coulomb efficiency than lithium insertion efficiency, which indicated that there were a larger amount of lithium ion extracted from these coated LMO structures during discharging process than the amount of lithium ion inserted back to these structures during charging process. In other words, there are difficulties for lithium ions inserted back to their original locations when they were charged in the tests.

### 4. Conclusion

LTO coating layer on LMO surface successfully reduces the direct contact of LMO with electrolyte, which with the evidence that there had no other phases formed by the consequence of dissolution of manganese ions after the cycling performance.

The disappearing of LMO spinel phase after the cycling performance is suspected to be the effect of granulation, which leads to small specific surface area with agglomerated grains.

Further study is needed to increase coated LMO specific discharge capacity and cycle life, as further experiments are being conducted in our laboratory now.

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