

Electrochemical characteristics of Al₂O₃-coated lithium manganese spinel as a cathode material for a lithium secondary battery

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Abstract

Al₂O₃-coated spinels were investigated with respect to their electrochemical characteristics. A Al₂O₃ coating on commercial LiMn_{2-x}M_xO₄ (Nikki, Japan, M = Zr) was prepared by using the sol–gel method. AA analysis showed that manganese and lithium dissolution occurred during the coating process. XRD patterns show that increase in the lattice parameter of Al₂O₃-coated spinels is related to formation of a solid solution on the surface of active materials. Impedance results revealed that Al₂O₃-coated spinel has electronic resistance. However, the cell performance was enhanced with the Al₂O₃ coating. Al₂O₃ is regarded as a coating material for stable cycling performance. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

The layered oxides, LiCoO₂, LiNiO₂ and spinel LiMn₂O₄ have been the most widely studied as 4 V cathode materials. Among these, spinel lithium manganese oxide (LiMn₂O₄) has been extensively investigated as a cathode material for a lithium secondary battery because of its low cost, easy preparation and environmental advantages. Early LiMn₂O₄ cathodes suffered from poor cycling efficiency at room temperature. However, the substitution of a small amount of dopant ion at the Mn sites has been proposed as a successful route for improving the cycling stability of LiMn₂O₄. The enhanced cycling stability has been attributed to the structure stabilization by a smaller volume change [1] during charge–discharge as well as to suppression of cation mixing [2]. A lot of work has been directed toward the stabilization of the spinel structure. In previous reports, researchers such as Amatucci et al. have proposed a surface treatment by using organic and inorganic compounds to decrease reactivity of the interface between the electrode and electrolyte [3]. Recently, a metal oxide-coated LiCoO₂ cathode [4–6] has shown relatively good capacity retention without decrease in the original capacity. As for the Li⁺ extraction

reaction, Hunter [7] and Feng et al. [8] postulated that the redox-type reaction occurs predominantly with the spinel. This mechanism is based on a disproportionation surface reaction: 2Mn³⁺ → Mn²⁺ + Mn⁴⁺. We report the preparation of Al₂O₃-coated spinel by using chloride compounds which may dissolve the spinel a little during the coating process. Therefore, it is quite possible that raw materials treated with an acidic sol solution generate a new surface after the coating process. We investigated the electrochemical characteristics and structural properties of Al₂O₃-coated spinel.

2. Experimental procedures

A sol precursor for coating was prepared by mixing ethyl-alcohol and AlCl₃·6H₂O (Junsei, Japan) and then LiMn_{2-x}M_xO₄ (Nikki, Japan, M = Zr, reversible capacity: 100 mAh/g) was immersed to sol precursor. To protect dissolution of manganese attributable to the low pH of the sol precursor, the immersion time was adjusted by a few seconds. After drying at 80 °C, the powder obtained was calcinated at 500 °C for 3 h. After being washed with water, they were filtered and then dried at 80 °C.

The thermal behavior of the sol precursor was examined by thermogravimetric analysis (TGA). The chemical composition of powder obtained was measured by using

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atomic absorption spectroscopy (AAS). The morphology was observed using field emission scanning electron microscopy (FE-SEM). Elemental distribution (Al) on the spinel was investigated by an Electron Probe Microanalyzer (EPMA). XRD measurements were done by means of a diffractometer using Cu K α radiation. Electrochemical voltage spectroscopy (EVS) and impedance spectroscopy were used to determine the dominant factor for electrochemical properties. Active material (86%) was mixed with acetylene black (AB, 9%) and polyvinylidene fluoride (PVdF, 5%) using acetone. The slurry was spread on the aluminum foil, followed by pressing and drying. The electrolyte was a mixture (1:1:1, v/v/v) of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) containing 1 M LiPF₆ salt. Electrochemical behavior was determined in a LiMn_{2-x}M_xO₄ (M = Zr)/MCMB graphite (as anode) cell sealed in a metallized plastic bag. Charge–discharge test was performed galvanostatically at a C/2 rate (3.0–4.2 V) in a multi-channel battery tester.

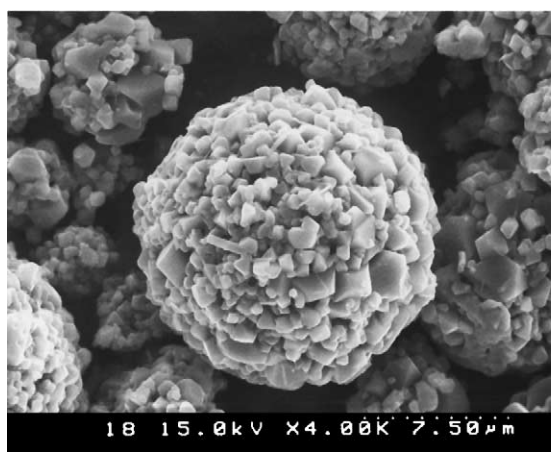
3. Results and discussion

3.1. pH and TGA of sol precursor

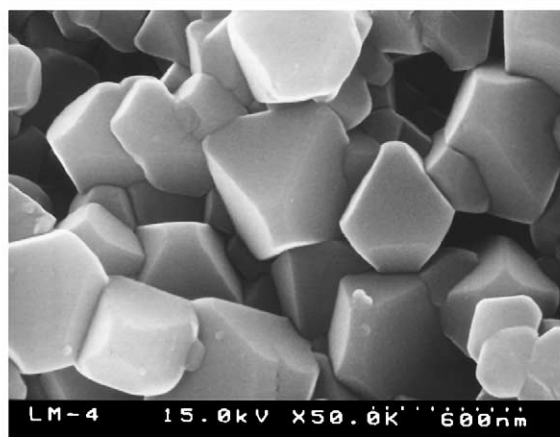
A pH of sol precursor containing aluminum chloride was measured. Upon increasing the aluminum chloride concentration (0.355–1.07 M), pH decreased from –0.221 to –0.840. From the color change of the solution after a long immersion or mixing with the raw material, the dissolution of spinel can be observed with the naked eye. Although the spinel powder was immersed in precursor for a short time (a few seconds), it is expected that the dissolution reaction of the spinel by acid can take place on the surface of the spinel. From the TGA result of the sol precursor, it was

Table 1
Al₂O₃ weight percentage of samples

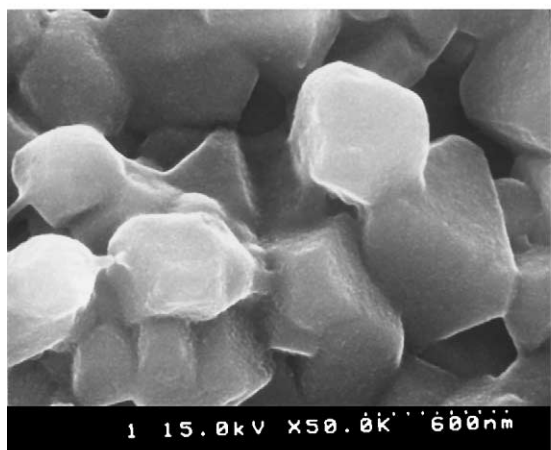
	Al ₂ O ₃ (1)	Al ₂ O ₃ (2)	Al ₂ O ₃ (3)	Al ₂ O ₃ (4)
Al ₂ O ₃ (%)	0.56	1.27	1.61	2.11



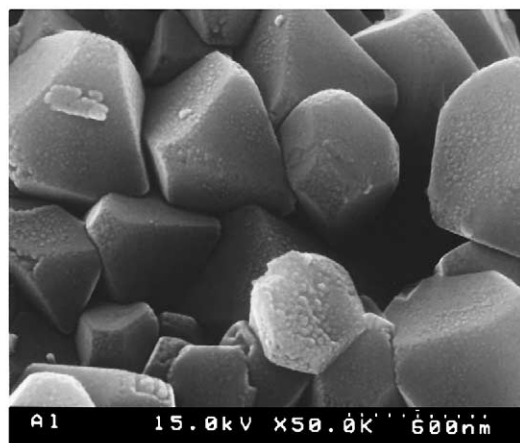
(a)



(b)



(c)



(d)

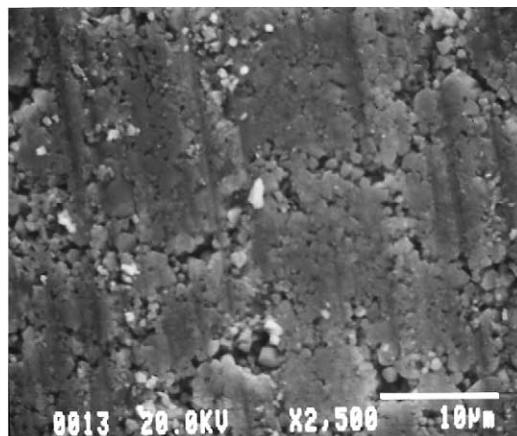
Fig. 1. SEM micrograph of spinel with Al₂O₃ coating process: (a) image obtained at $\times 4000$ (bare powder); (b) image obtained at $\times 50000$ (bare powder); (c) image of powder coated with sol precursor; (d) image after calcination (at 500°C).

revealed that below 400 °C, there was a weight loss due to the decomposition process of the chloride compound. The weight loss of the specimens stopped at temperatures above 450 °C.

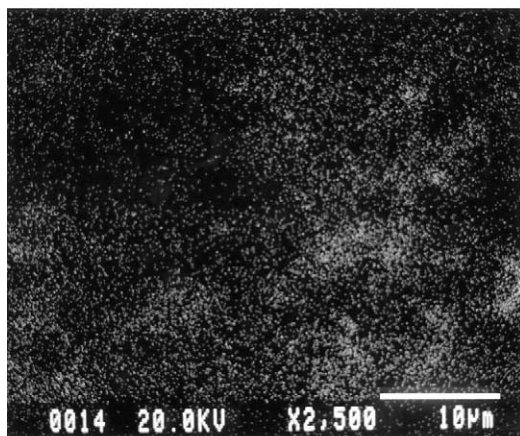
3.2. Variation of the morphology and composition after Al_2O_3 coating

Fig. 1 shows an SEM micrograph of the spinel with the coating process: (a) image obtained at $\times 4000$ (bare powder); (b) image obtained at $\times 50\,000$ (bare powder); (c) powder coated with sol precursor; (d) powder after calcination (at 500 °C). Fig. 1(a) and (b) indicate that the bare powder possesses agglomerated particles (about the size of 10 μm) and that agglomerated particles were composed of small particles about 500–600 nm. The surface of powder (angular feature) is smooth. As shown in Fig. 1(c) and (d), spinel powder is covered with nano sized aluminum oxide after heating at 500 °C.

Fig. 2 shows EPMA (Electron probe micro analyzer) results obtained on Al_2O_3 -coated spinel powder. As can be



(a)



(b)

Fig. 2. SEM micrograph and EPMA image of Al_2O_3 -coated spinel. (a) SEM micrograph of Al_2O_3 -coated spinel. (b) EPMA image of Al for Al_2O_3 -coated spinel.

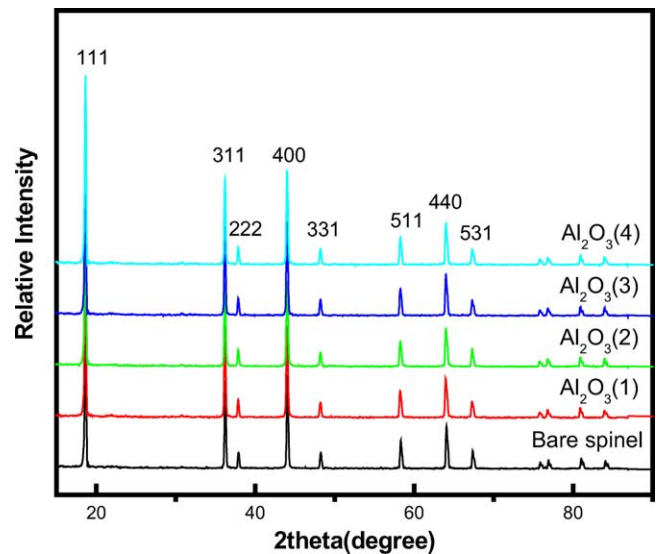


Fig. 3. X-ray diffraction patterns of bare spinel and Al_2O_3 -coated spinels.

seen in the EPMA image, it was found that the distribution of aluminum on the powder is fairly uniform.

A list of the samples analyzed by AAS is given in Table 1. The weight percentage of Al_2O_3 in the Al_2O_3 -coated spinel is measured to be about from 0.56 to 2.11%. The ratio (Li/Mn) of before and after coating is observed (in examples for the bare and Al_2O_3 (4) sample). Before coating, the ratio of Li/Mn was 0.554. However, after coating, Li/Mn ratio is present as 0.540. We presume that dissolution of Mn and Li occurred during the coating process because of the too low pH of the sol precursor.

3.3. Structure variation according to amount of Al_2O_3 coating

With an Al_2O_3 proportion from 0.56 to 2.11%, it is noted that neither new phases nor peak broadening is observed (Fig. 3). This is due to a small amount of amorphous Al_2O_3 and a relatively low heating temperature (500 °C) which did not severely change the original structure of the spinel.

Variations of lattice parameter between the fully charged and the initial state are listed in Table 2. In the case of bare spinel, the lattice parameter (a) has decreased from 8.215 to 8.100 Å ($\Delta a = 0.115$ Å) with charge. Al_2O_3 -coated spinels have a larger lattice constant than bare spinel in the initial state and have a larger lattice change between the initial and

Table 2
Lattice constant variation between initial and full charged state

Sample (Å)	Bare spinel	Al_2O_3 (1)	Al_2O_3 (2)	Al_2O_3 (3)	Al_2O_3 (4)
Initial state	8.215	8.227	8.225	8.227	8.221
Fully charged state	8.100	8.070	8.079	8.088	8.070
Δa	0.115	0.157	0.148	0.137	0.157

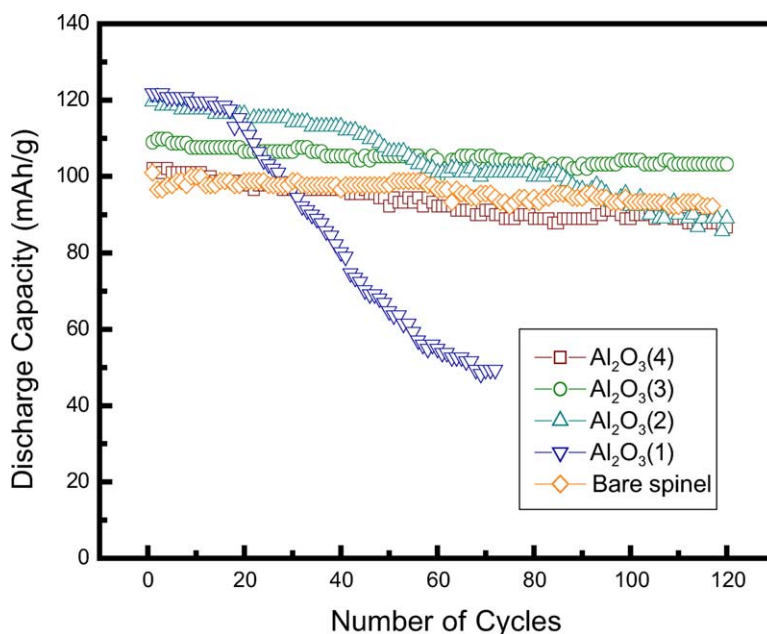


Fig. 4. Cycle performance of bare spinel and Al_2O_3 -coated spinel vs. MCMB cell.

fully charged state. This result may be caused by the solid solution formed on the surface of the spinel [3] or by a subtle structure variation induced by the sol precursor coating and heating.

3.4. Electrochemical characteristics of Al_2O_3 -coated spinel

Fig. 4 compares the cycle performance of Al_2O_3 -coated spinel and bare spinel at $C/2$ rate, in the 3.0–4.2 V range. In the case of the Al_2O_3 -coated spinel, the reason for the increase of the initial discharge capacity is unclear, but may be caused by structural changes which have a direct relation to the solid solution formed on spinel or expansion of contracted crystal lattices (Table 2) by coating and heating (at 500 °C).

The discharge capacity of sample Al_2O_3 (1) rapidly faded after 20 cycles due to a defective surface caused by the acidic and low viscous sol precursor coating. Even the discharge capacity of the Al_2O_3 (2) drops from 120 to 90 mAh/g with increasing cycles. However, Al_2O_3 (3) and Al_2O_3 (4) show similar or improved cell performance compared to the bare spinel. The reason for this phenomenon with Al_2O_3 content is unclear but may be associated with the penetration depth of acid species into spinel by sol precursor coating. By controlling pH and viscosity which were strongly affected by the aluminum chloride content, as well as the amount of Al_2O_3 , after over 100 cycles, it is expected that high initial capacity and stable cycle performance would be obtained.

The EVS profile is given in Fig. 5. The main lithium deintercalation peaks (1, 2) and intercalation peaks (3, 4) are observed at the range of 3.0–4.3 V. Compared to the bare spinel, peaks of Al_2O_3 (1) are sharp and have no special

shifting. Higher peak intensity of Al_2O_3 (1) corresponds to enhanced discharge capacity by the coating. From the decrease in the peak after 20 cycles, it can be seen that fading of the discharge capacity occurs mostly at the first step (peak 1, 4). In order to evaluate the electrochemical characteristics with an Al_2O_3 coating, AC impedance spectroscopy was carried out. There are two semi-circles that indicate surface film resistance and charge transfer resistance, respectively.

By employing an equivalent circuit (Fig. 6) of the spinel/MCMB cell to simulate impedance data, charge transfer resistance (R_{ct}) and surface film resistance (R_{film}) were calculated at potential marked in Fig. 5. The Charge transfer resistance and film resistance data are listed in Table 3.

In the case of Al_2O_3 (1), the resistance of the second circle (R_{ct}) is higher than that of the bare one except for '1'. This seems to indicate that Al_2O_3 as coating material has electronic resistance. However, the diameter of the first circle (resistive element of electrolyte–electrode interface) is smaller than that of the bare spinel. These results may be due to the surface change by coating or decrease of particle-to-particle resistance in the composite electrode by coating.

Table 3
Impedance fitting results for bare spinel and Al_2O_3 (1) vs. MCMB cell

Resistive element (Ω)	1	2	3	4
Bare spinel				
R_{ct}	1.343	1.315	1.199	1.143
R_{film}	1.247	1.415	1.434	1.476
Al_2O_3 (1)				
R_{ct}	1.266	1.374	1.281	1.182
R_{film}	1.098	1.210	1.261	1.261

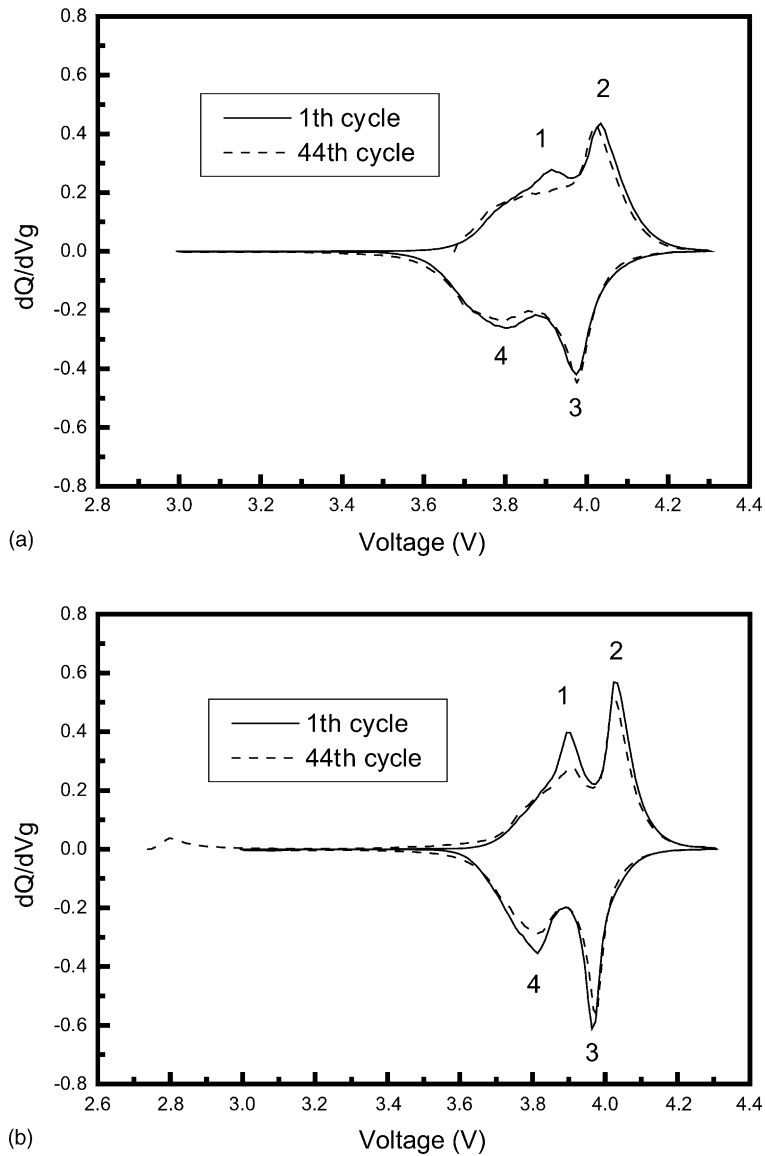


Fig. 5. EVS of bare spinel and Al₂O₃ (1) with cycling: (a) bare spinel/MCMB; (b) Al₂O₃ (1)/MCMB.

4. Conclusions

The SEM showed homogeneous contact between the bare spinel and coating material. AAS results of the Al₂O₃-coated manganese spinel revealed that small amounts of manganese and lithium dissolution occurred during the coating process. Increase in the lattice parameter of the Al₂O₃-coated manganese spinels is related to changes in the original spinel structure. The initial capacity of these Al₂O₃-coated samples is higher than that of the bare spinel, which is due to structural change, which occurred with Al₂O₃ coatings. Impedance spectra provide evidence for an increase in polarization from the Al₂O₃-coated sample. However, Al₂O₃-coated samples have improved interfacial properties between the electrolyte and electrode. From the charge–discharge characteristics and impedance results,

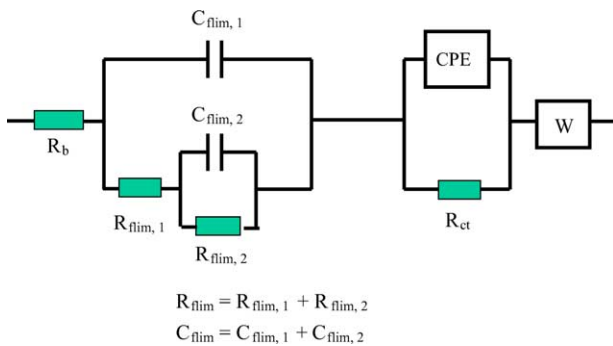


Fig. 6. Equivalent circuit proposed for spinel/MCMB cell.

the Al₂O₃ coating and coating process are regarded as an interesting method for yielding stable cycling performance.

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