

The elevated temperature performance of LiMn_2O_4 coated with $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($X = 0.2$ and 1)

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Abstract

The surface coating of LiMn_2O_4 using a gel precursor of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($X = 0.2$ and 1) prepared from a solution-based chemical process was attempted in order to enhance the electrochemical performances of LiMn_2O_4 at elevated temperature. After the surface of LiMn_2O_4 was coated with $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($X = 0.2$ and 1) coating solution and heated at 750°C , the surface of LiMn_2O_4 was covered with fine $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($X = 0.2$ and 1) particles. $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($X = 0.2$ and 1)-coated LiMn_2O_4 showed an excellent capacity retention at 65°C compared to pure LiMn_2O_4 . While pure LiMn_2O_4 retained 81% of the initial capacity after storage in the discharged state at 65°C for 300 h, LiCoO_2 -coated LiMn_2O_4 showed no capacity loss. The improvement of storage performance at 65°C is attributed to the suppression of electrolyte decomposition and the reduction of Mn dissolution resulting from encapsulating the surface of LiMn_2O_4 with LiCoO_2 . The surface coating with $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ also enhanced the high temperature cycle performance of LiMn_2O_4 . Consequently, It is proposed that the surface encapsulation of LiMn_2O_4 with fine $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($X = 0.2$ and 1) particles improve its high temperature performance. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

LiMn_2O_4 is a very promising cathode material with economical and environmental advantages over the layered compounds such as LiCoO_2 and LiNiO_2 . Especially, the good thermal stability of LiMn_2O_4 is a positive factor for its use in batteries for electric vehicle [1]. However, LiMn_2O_4 shows severe capacity fading with cycling at room and high temperatures. It was reported that the capacity fading mechanism at room temperature was related to the Jahn–Teller distortion caused by Mn^{3+} Jahn–Teller ions [2]. The cycling performance of LiMn_2O_4 at room temperature was enhanced by the partial substitution of Mn in LiMn_2O_4 with transition metals (Co, Cr, Ni, Fe, Ti, and Zn) [3–8].

Despite the improvement of cycle stability at room temperature, LiMn_2O_4 has still suffered from significant capacity fading at elevated temperature [4,9]. These problems are associated with Mn^{2+} dissolution [10]. Mn dissolution is induced by HF acid, which is generated by secondary

chemical reactions from temperature-enhanced electrolyte decomposition. In order to solve the dissolution problem, earlier studies have been focused on a chemical modification of LiMn_2O_4 by a partial substitution of Mn with transition metals or by a partial substitution of O with F [11–13]. These attempts were effective to a certain extent for improving the cycle life at 50 – 60°C . Based on the fact that the dissolution of Mn occurs on the surface of LiMn_2O_4 particle, the study to separate the catalytic surface of LiMn_2O_4 from the electrolyte was investigated. It was reported that LiMn_2O_4 was coated with an inorganic lithium boron oxide glass (LBO) for the protection of the electrolyte from the catalytic effects of LiMn_2O_4 [14]. However, LBO-coated LiMn_2O_4 showed poor cyclic property at elevated temperatures due to the tendency of the spinel to form solid solutions with the borate compounds. Therefore, it can be speculated that a new coating material that is stable at high temperature and has no catalytic effect is needed for improving the elevated temperature property of LiMn_2O_4 . In our pervious work, the surface of LiMn_2O_4 was successfully coated with fine LiCoO_2 particles by applying the modified Pechini process as a coating method and its cycling property at 65°C was

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enhanced significantly because LiCoO₂ has an excellent elevated temperature performance [15,16].

In the current work, the storage property at 65 °C of LiCoO₂-coated LiMn₂O₄ was examined and LiNi_{0.8}-Co_{0.2}O₂-coating was attempted in order to minimize the use of expensive cobalt. The electrochemical properties of LiNi_{1-x}Co_xO₂-coated LiMn₂O₄ were characterized.

2. Experimental

2.1. Preparation of LiNi_{1-x}Co_xO₂-coating solution and coating of LiMn₂O₄

Sun and co-workers reported that the fine LiMn₂O₄ powder was synthesized by a chemical process using aqueous solution of metal acetates [17,18]. In this work, the use of gel precursor of LiNi_{1-x}Co_xO₂ ($X = 0.2$ and 1) was attempted in order to coat the surface of LiMn₂O₄. Stoichiometric amounts of lithium-acetate (Li(CH₃COO)·2H₂O, 98% Aldrich), cobalt-acetate tetrahydrate (Co(CH₃COO)₂·4H₂O, 99% Aldrich) and nickel-acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O, 99% Aldrich) were mixed in distilled water at 50–60 °C. An aqueous solution of glycolic acid (HOCH₂CO₂H, 70% Aldrich) as a chelating agent was then added to this mixture. Ammonium hydroxide was slowly added to this solution until a pH of 6.5–7.0 was achieved. Then, this solution was thoroughly mixed in refluxing system for 6 h at 80–90 °C. The resultant solution was evaporated at about 80 °C until the concentration of the resultant solution reached 0.7–1 mol/l. Commercial LiMn₂O₄ powder was then added to this coating-solution with a constant stirring. The powder in the coating-solution was screened with a centrifuge to remove the remaining coating solution. The screened powder was dried in a vacuum oven and was calcined for 6 h at 750 °C in oxygen atmosphere.

2.2. Characterization of LiNi_{1-x}Co_xO₂-coated LiMn₂O₄ ($X = 0.2$ and 1)

The morphology change of the coated-material was observed with a scanning electronic microscope (SEM, Philips SEM515, Holland). The amount of coating material in the coated-samples was determined by energy dispersive analysis of X-rays (EDAX) and inductively coupled plasma (ICP).

In order to fabricate the cathode electrode, 88 wt.% of spinel powder was mixed with 7 wt.% of acetylene black, added to a solution of 5 wt.% of polyvinylidene fluoride (PVDF) in *N*-methyl-2-pyrrolidinone (NMP), and spread on Al foil. After the electrode was dried at 140 °C for 2 h in vacuum (10⁻³ Torr), it was compressed. Coin cells were assembled in an argon filled glove-box using a Li metal as a counter electrode and a 1 M LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC) (EC:DEC = 1:1 by

volume) as an electrolyte. The cells were cycled between 3.0 and 4.3 V at room temperature and 65 °C to analyze the electrochemical response. In order to analyze the electrochemical impedance response, a Solatron 1255 frequency response analyzer was used in conjunction with the Solatron 1286 electrochemical interface. The coated area of the electrodes was controlled to be 1 cm². After the electrode attained an equilibrium potential (4.1 V), the electrochemical impedance measurements were carried out by applying an ac voltage of 5 mV over the frequency range from 1 mHz to 100 kHz. In order to investigate the dissolution behavior of Mn into the electrolyte, as-received LiMn₂O₄ (0.11 g) and LiCoO₂-coated LiMn₂O₄ (0.11 g) were immersed in LiPF₆(EC:DEC) electrolyte (10 ml) for 24 h at 65 °C and then the immersed lithium manganese oxides were separated from the electrolyte with a filter paper. The electrolytes passed through the filter paper were analyzed with ICP to determine the dissolved Mn content.

3. Results and discussion

3.1. Structural and electrochemical characterization of LiCoO₂-coated LiMn₂O₄

Fig. 1 shows the surface morphology change of LiMn₂O₄ after coating with LiCoO₂. While the surface morphology of as-received LiMn₂O₄ (Fig. 1(a) and (b)) was smooth and round, the surface of LiCoO₂-coated LiMn₂O₄ after coating and heating was covered with fine particles as shown in Fig. 1(c) and (d). Our previous work demonstrated that the particle on the surface of coated LiMn₂O₄ was LiCoO₂ with selected area diffraction (SAD) patterns of TEM [15]. In order to analyze the composition of the coated material on the surface of LiMn₂O₄, EDAX analysis was performed. EDAX result of Table 1 shows that 2.19 at.% of cobalt exists on the coated LiMn₂O₄.

The discharge curves of as-received LiMn₂O₄ and LiCoO₂-coated LiMn₂O₄ are shown in Fig. 2. Both materials show the nearly same discharge capacity of 115 mAh/g irrespective of LiCoO₂-coating. The capacity changes of as-received LiMn₂O₄ and LiCoO₂-coated LiMn₂O₄ stored in the discharged state and charged state at 65 °C are shown in Figs. 3 and 4, respectively. While as-received LiMn₂O₄ showed 19% of capacity loss after storage in the discharged state at 65 °C for 300 h, LiCoO₂-coated LiMn₂O₄ showed no capacity loss (Fig. 3). LiCoO₂-coated LiMn₂O₄ also exhibited excellent capacity retention after storage in the charged

Table 1
EDAX analysis of LiCoO₂-coated LiMn₂O₄ powder

	Atomic%
O	37.95
Mn	59.86
Co	2.19

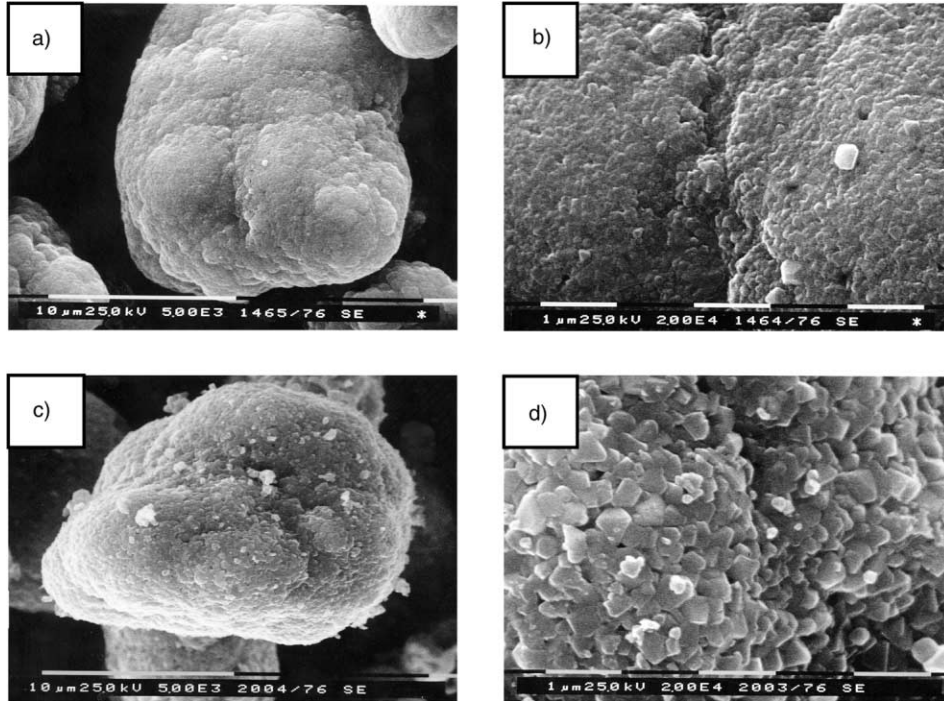


Fig. 1. Surface morphologies of (a and b) as-received LiMn_2O_4 and (c and d) LiMn_2O_4 -coated with LiCoO_2 .

state at 65°C for 300 h although the capacity of as-received LiMn_2O_4 drastically decreased with time at 65°C (Fig. 4).

Tarascon et al. reported that the reason for the capacity loss of LiMn_2O_4 at high temperature was due to the dissolution of Mn [10]. In order to investigate the behavior of Mn dissolution at high temperature, the surface changes of as-received LiMn_2O_4 and LiCoO_2 -coated LiMn_2O_4 after storing at 65°C for 80 h are shown in Fig. 5. As shown in Fig. 5(a) and (b), many pores were found on the surface of as-received LiMn_2O_4 , which is speculated to be induced by Mn dissolution. However, in the case of LiCoO_2 -coated LiMn_2O_4 (Fig. 5(c) and (d)), the surface covered with fine LiCoO_2 particles showed no pore after high temperature

storage. From these results, it can be supposed that Mn dissolution is restrained from LiCoO_2 -coated LiMn_2O_4 . Mn ion content dissolved into the electrolyte was analyzed with ICP in order to confirm the decrease of Mn dissolution in LiCoO_2 -coated LiMn_2O_4 . Table 2 shows that the amount of Mn ion dissolved from LiCoO_2 -coated LiMn_2O_4 is smaller than that from as-received LiMn_2O_4 distinctively as expected in Fig. 5. Mn dissolution is caused by HF acid of which formation is controlled by chemical reaction from the electrolyte decomposition [13,19]. The electrolyte decomposition by the catalytic activity of LiMn_2O_4 forms the passivation film on the surface of cathode. Therefore, the cause of the decrease of Mn dissolution in LiCoO_2 -coated LiMn_2O_4 can be investigated by analyzing the passivation films formed on the surface of cathode with EIS experiment. Fig. 6 compares the EIS profiles of as-received LiMn_2O_4 and LiCoO_2 -coated LiMn_2O_4 before and after storing in the discharged state at 65°C for 300 h, respectively. Both electrodes were initially cycled for five times and EIS measurements were carried out. And then, EIS spectra were obtained again after both samples were discharged at 3.0 V

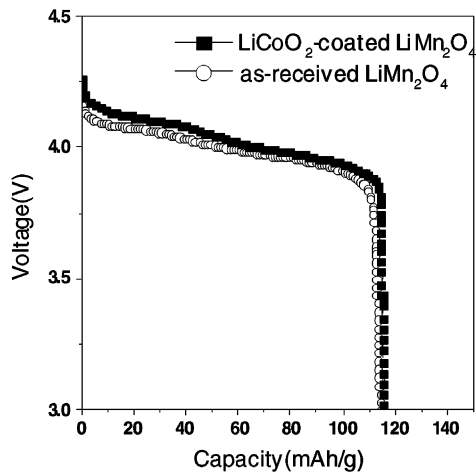


Fig. 2. Discharge curves of as-received LiMn_2O_4 and LiCoO_2 -coated LiMn_2O_4 at the rate of 24 mAh/g between 3.0 and 4.3 V.

Table 2

ICP analyses of $\text{LiPF}_6(\text{EC}:\text{DEC})$ electrolytes where as-received LiMn_2O_4 and LiCoO_2 -coated LiMn_2O_4 have been immersed for 24 h at 65°C , respectively

	LiMn_2O_4	LiCoO_2 -coated LiMn_2O_4
Li ($\mu\text{g}/\text{ml}$)	3890	4760
Mn ($\mu\text{g}/\text{ml}$)	1330	215
Co ($\mu\text{g}/\text{ml}$)		9.4

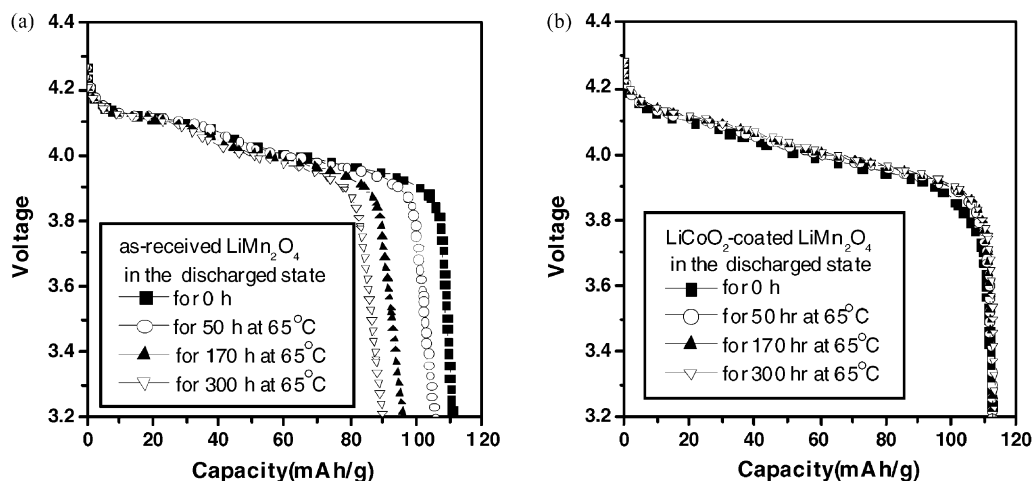


Fig. 3. Capacity variation of (a) as-received LiMn_2O_4 and (b) LiCoO_2 -coated LiMn_2O_4 with storage time in the discharged state at 65°C .

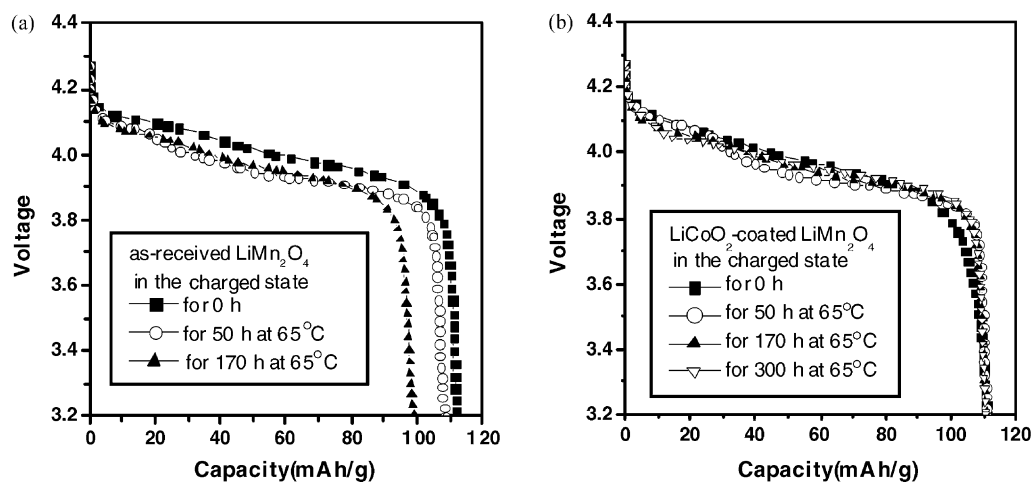


Fig. 4. Capacity variation of (a) as-received LiMn_2O_4 and (b) LiCoO_2 -coated LiMn_2O_4 with storage time in the charged state at 65°C .

and stored at 65°C for 300 h. All the EIS profiles of Fig. 6 consisted of two arcs and all the arcs were enlarged after the storage at 65°C for 300 h. It was reported that the first arc in the high frequency range might correspond to the passivation film formed by the reaction between the oxide and electrolyte and the interfacial impedance of the Li anode, and the second arc in the low frequency range might contain the contribution of the contact resistance between inter-particles [20]. As shown in Fig. 6, the enlargement of the first arc of LiCoO_2 -coated LiMn_2O_4 was suppressed in comparison with that of as-received LiMn_2O_4 . It means that the formation of passivation film on the surface of LiMn_2O_4 is restrained by coating its surface with LiCoO_2 because LiCoO_2 has weaker catalytic activity than LiMn_2O_4 . Therefore, it can be concluded that the high temperature storage property of LiCoO_2 -coated LiMn_2O_4 is improved because the suppressed formation of passivation film on the surface prohibits the HF acid generation which cause the dissolution of Mn ion. This high temperature performance of LiCoO_2 -coated LiMn_2O_4 meets that of the presently commercialized LiCoO_2 .

3.2. Electrochemical characterization of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -coated LiMn_2O_4

In order to minimize the use of expensive cobalt in coating of LiMn_2O_4 , $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -coated LiMn_2O_4 was attempted in this work. Fig. 7 shows the surface of LiMn_2O_4 was coated with $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ uniformly. The amounts of Ni and Co on the coated LiMn_2O_4 were 2.24 and 0.61 at.%, respectively (Table 3). Fig. 8 compares the changes of discharge capacity of as-received LiMn_2O_4 , LiCoO_2 -coated LiMn_2O_4 , and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -coated LiMn_2O_4 with cycling

Table 3
EDAX analysis of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -coated LiMn_2O_4 powder

	Atomic%
O	39.87
Mn	57.28
Ni	2.24
Co	0.61

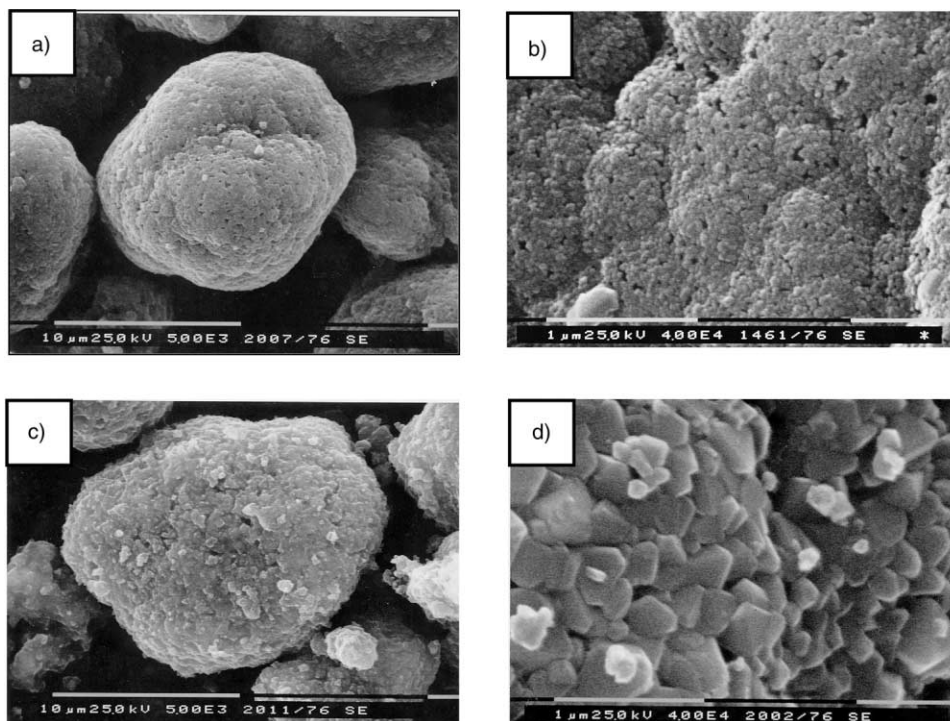


Fig. 5. Changes of surface morphology of (a and b) as-received LiMn_2O_4 and (c and d) LiCoO_2 -coated LiMn_2O_4 after storing at 65°C for 80 h.

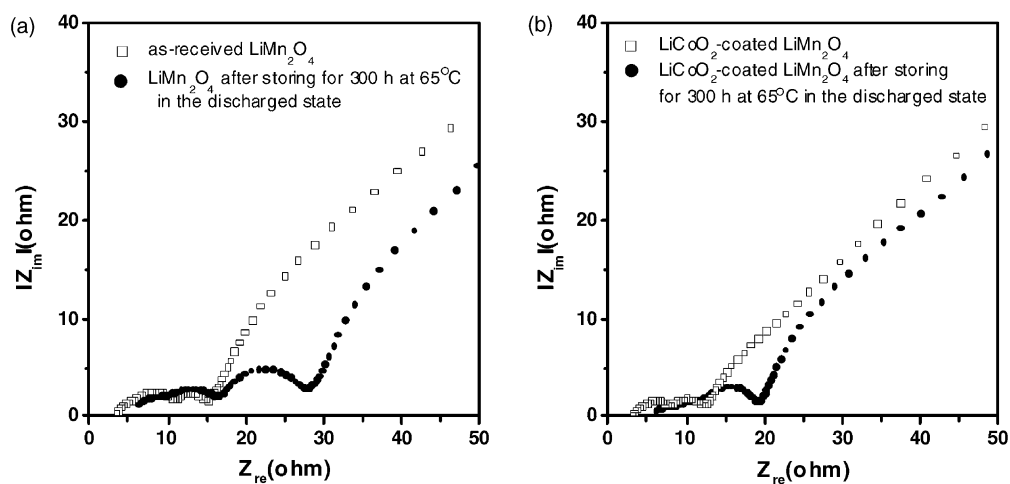


Fig. 6. EIS spectra for the cells with active electrodes of (a) as-received LiMn_2O_4 and (b) LiCoO_2 -coated LiMn_2O_4 after five cycles at room temperature and storage at 65°C for 300 h, respectively.

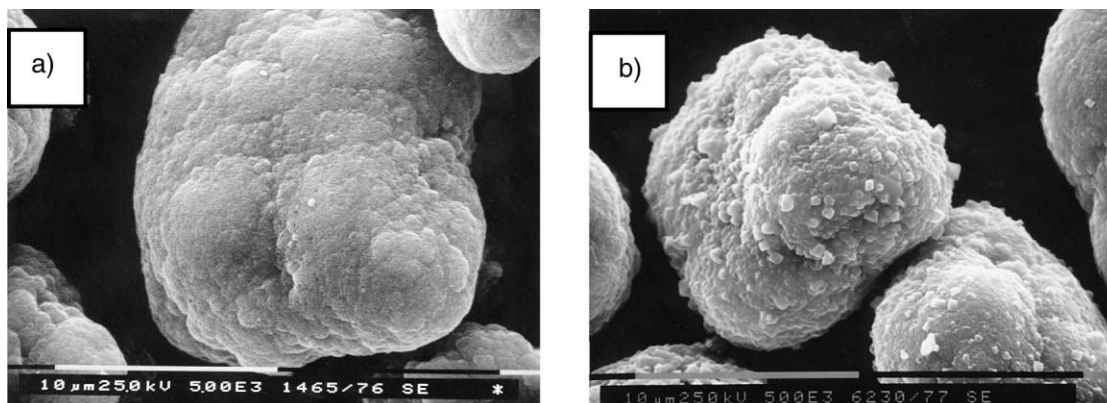


Fig. 7. Surface morphologies of (a) as-received LiMn_2O_4 and (b) $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -coated LiMn_2O_4 .

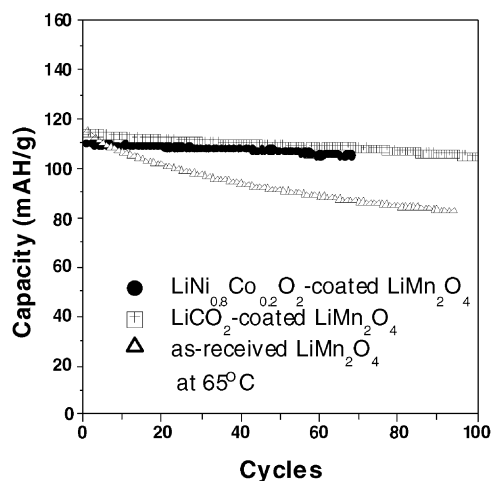


Fig. 8. Cycling behavior of as-received LiMn_2O_4 and $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ -coated LiMn_2O_4 ($X = 0.2$ and 1) at 65°C .

at 65°C . While the capacity of pure LiMn_2O_4 decreased drastically with cycling at 65°C , LiCoO_2 -coated LiMn_2O_4 shows only 0.08% per cycle loss in capacity. In the case of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -coated LiMn_2O_4 , its cycle stability at high temperature is also as excellent as that of LiCoO_2 -coated LiMn_2O_4 although a little initial capacity loss is observed. Therefore, it is proposed that $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -coating is also very effective in improving the elevated temperature properties.

4. Conclusions

The surface of LiMn_2O_4 was encapsulated with fine $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($X = 0.2$ and 1) particles as a coating material for improving the storage property and the cyclic property at high temperature. LiCoO_2 -coated LiMn_2O_4 maintains the initial capacity after storing in the discharged state at 65°C for 300 h, while pure LiMn_2O_4 shows 19% loss of the initial capacity. The cycle stability of LiMn_2O_4

at high temperature was also improved by $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($X = 0.2$ and 1) coating. The reason for the improved elevated temperature properties is that the surface coating reduces the dissolution of Mn, which results from the suppression of the electrolyte decomposition. Consequently, it is proposed that the surface coating with $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($X = 0.2$ and 1) is very effective in obtaining the excellent elevated temperature properties of LiMn_2O_4 .

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