

Electrochemical characteristics of metal oxide-coated lithium manganese oxide (spinel type) Part II. In the range of 3.0–4.4 V

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Abstract

Metal oxide-coated spinel was investigated with respect to electrochemical characteristics. Metal oxide coating on commercial spinel powder ($\text{LiMn}_{2-x}\text{M}_x\text{O}_4$, $\text{M} = \text{Zr, Ni, Ti, Japan}$) was carried out using the sol–gel method. $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel exhibited stable cycle performance in the range from 3.0 to 4.4 V, and it had lower charge transfer resistance and higher double layer capacitance than bare spinel in later cycles. In the SEM image of the powder after the cell test, bare spinel showed abnormal surfaces formed by decomposition of the electrolyte, while $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel displayed a normal surface covered with a surface film. Therefore, it is expected that an $\text{Al}_2\text{O}_3/\text{CuO}_x$ layer coated on the spinel powder can function as a protective film, which suppresses the reaction between electrolyte and active material.

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1. Introduction

Layered LiCoO_2 , LiNiO_2 , and spinel LiMn_2O_4 are widely studied as 4 V cathode materials. Among these systems, spinel lithium manganese oxide is the most attractive cathode for lithium secondary batteries in terms of low cost, easy preparation, and environmental friendliness [1–3]. However, LiMn_2O_4 exhibits poor cycle performance at room temperature.

The reason for capacity fading is attributed to several factors: (a) spinel dissolution; (b) structural instability in the charged state; (c) electrolyte decomposition; and (d) Jahn–Teller effect.

To minimize capacity fading, the substitution of a small amount of dopant ions at the Mn sites has been proposed as a successful way of improving the cycling stability of LiMn_2O_4 [4–10]. Much work has been directed toward the surface modification of cathode material to suppress phase transition or to change the surface properties. In previous reports, researchers such as Amatucci et al. [11] have pro-

posed a surface treatment by using organic and inorganic compounds to decrease the reactivity of the interface between electrode and electrolyte. Recently metal oxide-coated cathodes [12–16] have been shown to exhibit relatively good capacity retention without decrease in the original capacity.

We report the preparation of metal oxide-coated spinel using sol solution (including chloride compounds) which may dissolve the spinel element a little during the coating process. Therefore, it is quite possible that spinel treated with acidic sol solution may comprise a new surface during the coating/heating process. The main interest of this work is to investigate the effect of surface modification of spinel on a wide potential range (3.0–4.4 V).

2. Experimental

A sol precursor for an Al_2O_3 coating on spinel powder was prepared by mixing ethyl alcohol and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Junsei, Japan). Next, $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ (Nikki, Japan, $\text{M} = \text{Zr}$) was immersed in the sol precursor. To reduce the dissolution of manganese attributable to the low pH of the sol precursor, the immersion time was adjusted a few seconds. After

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drying at 80 °C, the powder obtained was heated at 500 °C for 3 h. After being washed with water, it was filtered and then dried at 80 °C.

$\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated powder was prepared as follows. Aluminum sol (including $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$)-coated powder was heated to 150 °C under air, then cooled at room temperature. After additional cupric sol (including $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) coating, it was heated and filtered again in the same way.

The percentage of each element in the metal oxide-coated powder was measured by using the AA method. The morphology of powder obtained was observed using a field emission scanning electron microscope (FE-SEM). XRD measurements were done by means of a diffractometer using Cu K α radiation. Active materials were mixed with acetylene black and polyvinylidene fluoride (PVdF) using acetone. The slurry was spread on the aluminum foil current collector, followed by pressing and drying. The electrolyte was a mixture of ethylene carbonate (EC), dimethylcarbonate (DMC), and ethylmethylcarbonate (EMC) containing 1 M LiPF_6 salt. Electrochemical behavior was determined in a $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ ($\text{M} = \text{Zr}$)/MCMB (as anode) cell sealed in a metallized plastic bag. Impedance spectroscopy was used to determine the dominant factor for electrochemical properties on repeated cycling. Charge–discharge tests were performed

Table 1
Element percentage of metal oxide-coated spinel

Sample name	Weight fraction (%)	
	Al	Cu
Bare spinel	–	–
Al_2O_3 -coated spinel	0.30	–
$\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel	0.28	0.72

galvanostatically at a C/2 rate (3.0–4.2 V or 3.0–4.4 V) in a multi-channel battery tester.

3. Results and discussion

The morphology of the powder obtained was viewed by SEM (Fig. 1). Fig. 1(a) indicates that the bare powder was composed of small particles of about 500–600 nm. The surface of powder (angular feature) is smooth. As shown in Fig. 1(b),(c), Al_2O_3 -coated and $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel were covered with nano-sized aluminum oxide and aluminum oxide/copper oxide, respectively.

Elemental percentages of the samples analyzed by AAS are given in Table 1.

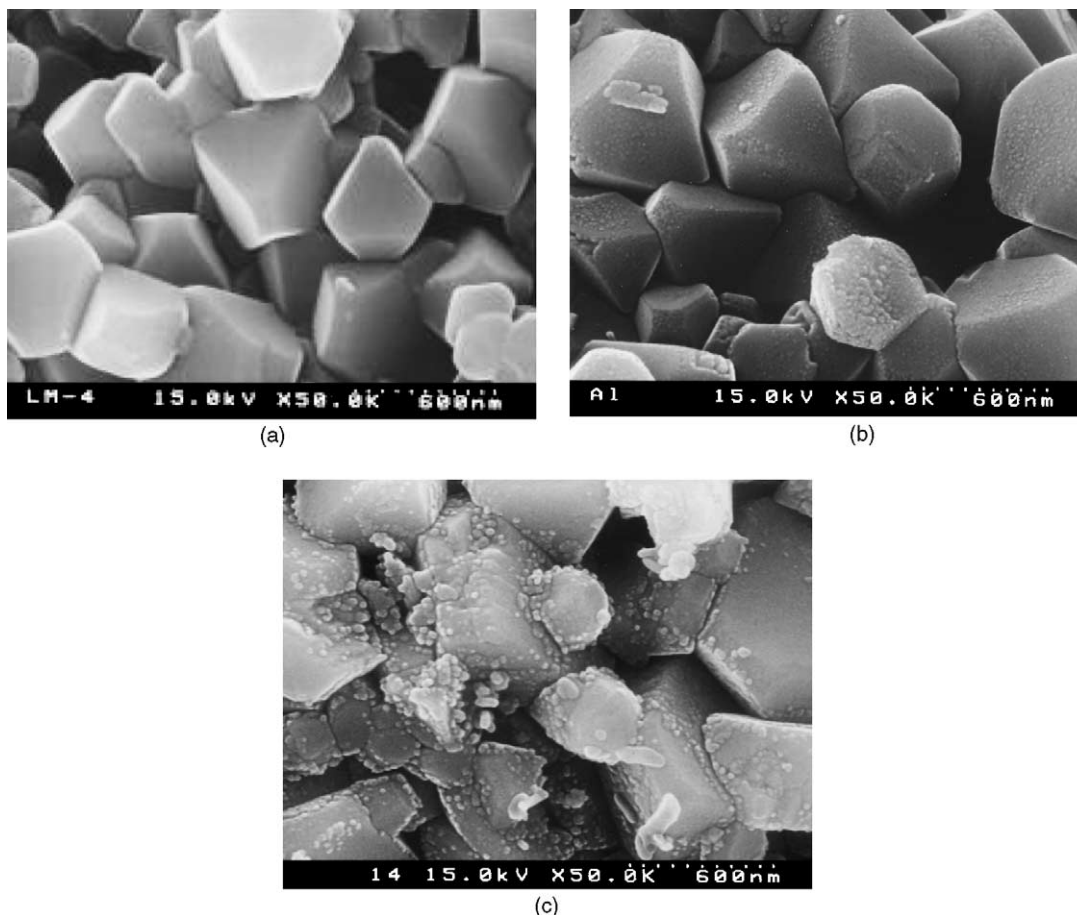


Fig. 1. SEM micrograph of bare spinel and metal oxide-coated spinel: (a) bare spinel; (b) Al_2O_3 -coated spinel; (c) $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel.

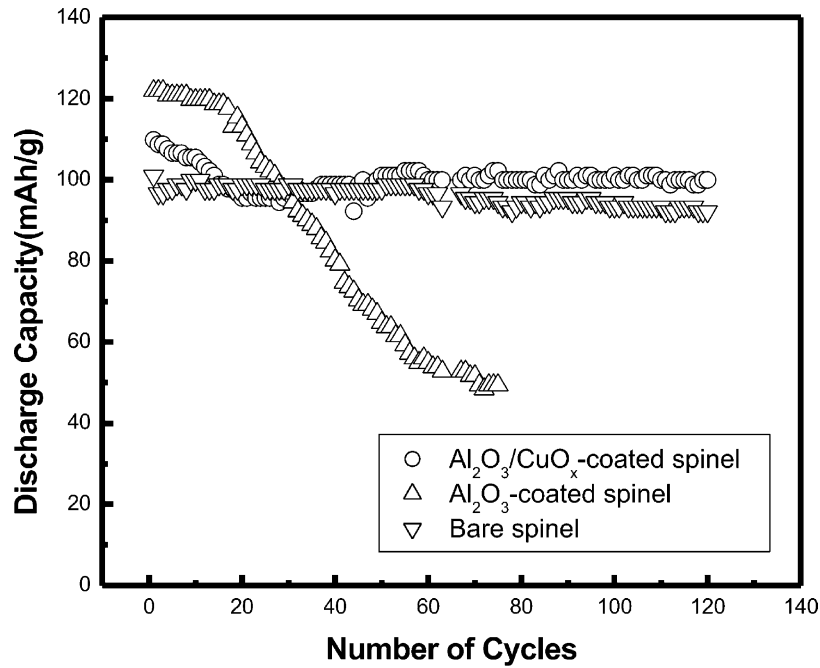


Fig. 2. Cycle behavior of bare spinel and metal oxide-coated spinel vs. MCMB cell. (C-rate: C/2; cut-off range: 3.0–4.2 V).

The discharge capacity of the spinel/MCMB cell as a function of the number of cycles is shown in Fig. 2. At the C/2 charge–discharge rate, initial discharge capacity of Al_2O_3 -coated and $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel is slightly higher than that of bare spinel. The reason for the increase of the initial capacity may be the change of structure, which has a direct relation on the formation of a solid solution in the spinel. With increasing number of cycles, the dis-

charge capacity of Al_2O_3 -coated spinel decreases suddenly. This is due to a structural defect formed by the penetration of acid species (from the sol precursor) into the surface of the spinel in the coating process. In spite of the fact that degradation of capacity occurring after 50 cycles is similar to that of Al_2O_3 -coated spinel, additional coating of copper oxide enabled the $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel to have stable cycle performance. This result is interpreted

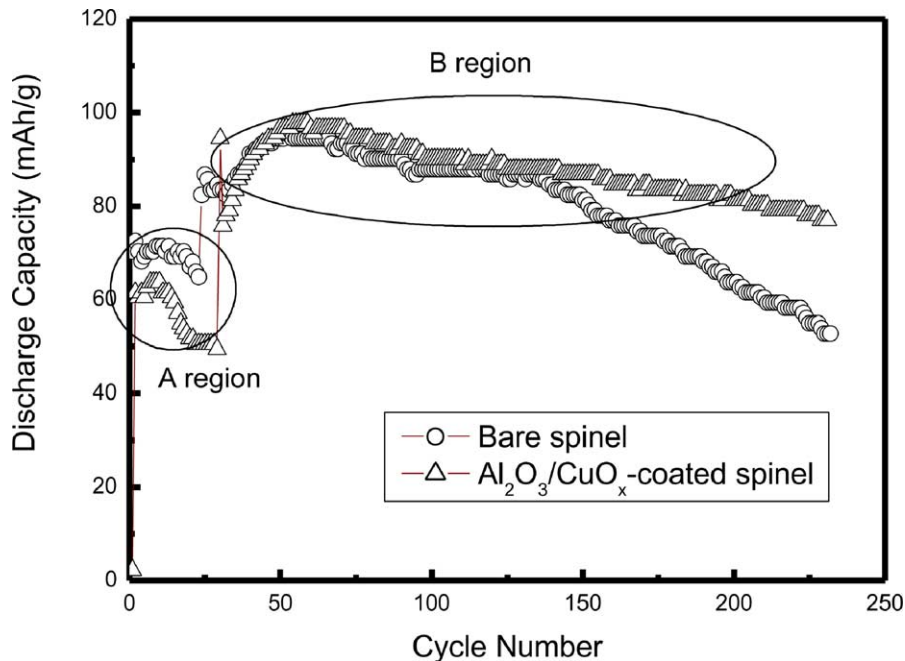


Fig. 3. Cycle behavior of bare spinel and $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel vs. MCMB cell. (C-rate: C/2; cut-off range: 3.0–4.4 V).

as being due to coverage of the defect by additional coating.

Fig. 3 shows cycling behavior of spinel/MCMB cell with two charge methods. In the A region, the cell was tested at constant current with an upper voltage cut-off of 4.4 V. In the B region, the cell was tested under combined conditions of galvanostatic and potentiostatic (4.4 V) charge. Low initial capacity and degradation of capacity are present in the A region. The results indicate that the spinel used has low rate capability and that the cycle behavior of bare spinel is bet-

ter than that of $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel. The difference between bare spinel and $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel appears in terms of electronic conductivity. In the B region, the capacity of the spinels was recovered by change of charge condition and then the capacity declines upon cycling.

It is generally known that poor performance of cells charged to high cut-off voltage (over 4.4 V) is due to electrolyte decomposition caused by the interfacial reaction of the electrolyte/active material. From cycle behavior reflected by Fig. 3 (B region), it is expected that the $\text{Al}_2\text{O}_3/\text{CuO}_x$

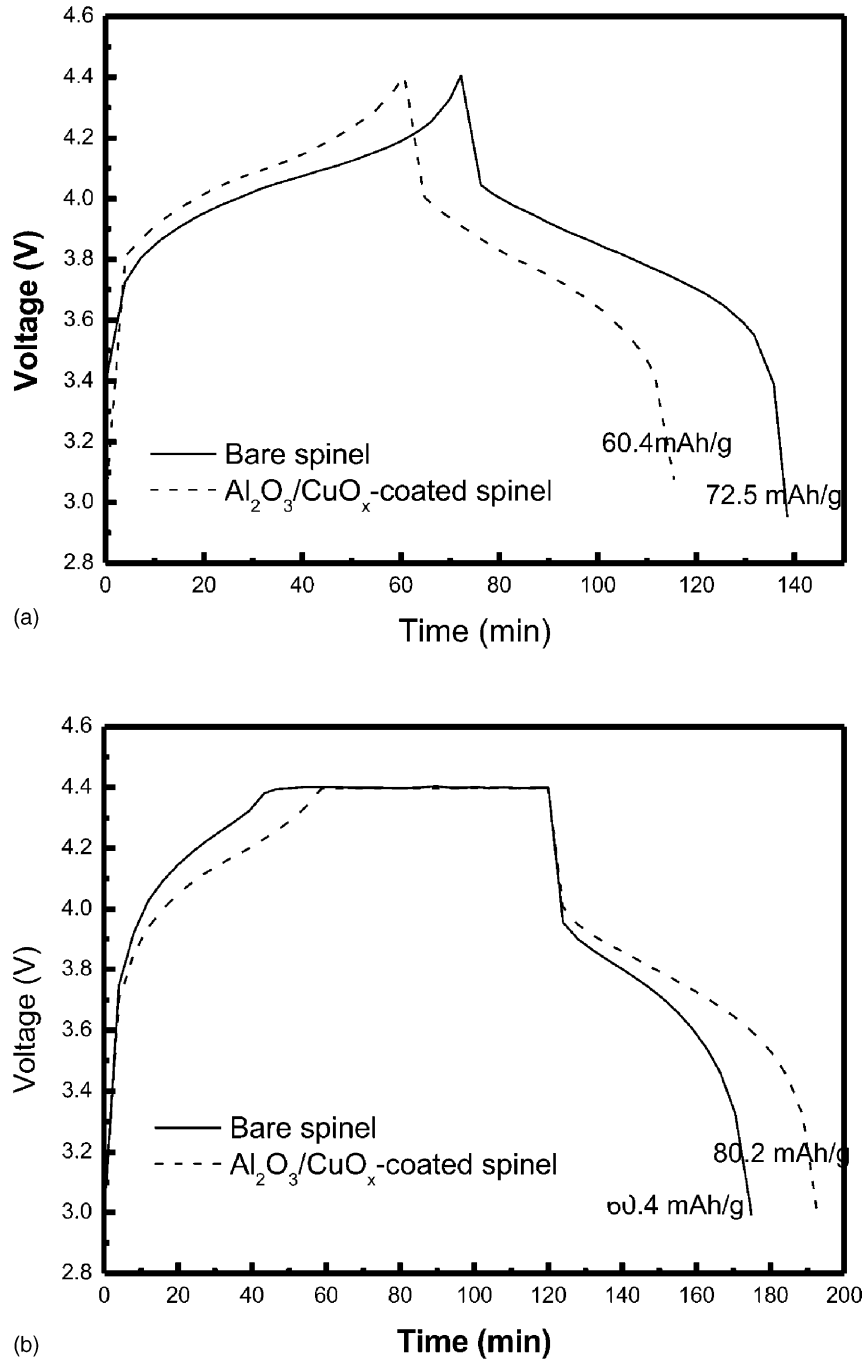


Fig. 4. Charge–discharge profile of bare spinel and $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel vs. MCMB cell: (a) at 2 cycles (A region); (b) at 200 cycles (B region).

coating on the spinel can function as a protective film, which may suppress the reaction between electrolyte and active material.

Fig. 4(a) shows the charge–discharge profile of bare and $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel at two cycles (A region). As demonstrated in Fig. 3 (A region), there is a difference of charge–discharge profile due to electronic conductivity. At 200 cycles (Fig. 4(b)), it can be seen that from charge profile, cell resistance of bare spinel is higher than that of $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel.

In order to evaluate the electrochemical resistance of bare spinel and $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel, ac impedance spec-

troscopy was carried out (Fig. 5) after 220 cycles. There are two semi-circles that indicate surface film resistance (R_{film}) and charge transfer resistance (R_{ct}), respectively.

By employing an equivalent circuit (Fig. 6) of the spinel/MCMB cell to simulate impedance data, we plotted values of R_{ct} and double layer capacitance (C_{dl}) from constant phase elements (CPE) as a function of voltage (Fig. 7). There is difference of R_{ct} and C_{dl} between the two samples as a function of lithium content (voltage). $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel has lower resistance and higher capacitance than bare spinel. This was thought to be due to the $\text{Al}_2\text{O}_3/\text{CuO}_x$ layer, which acts as some kind of protective film suppressing

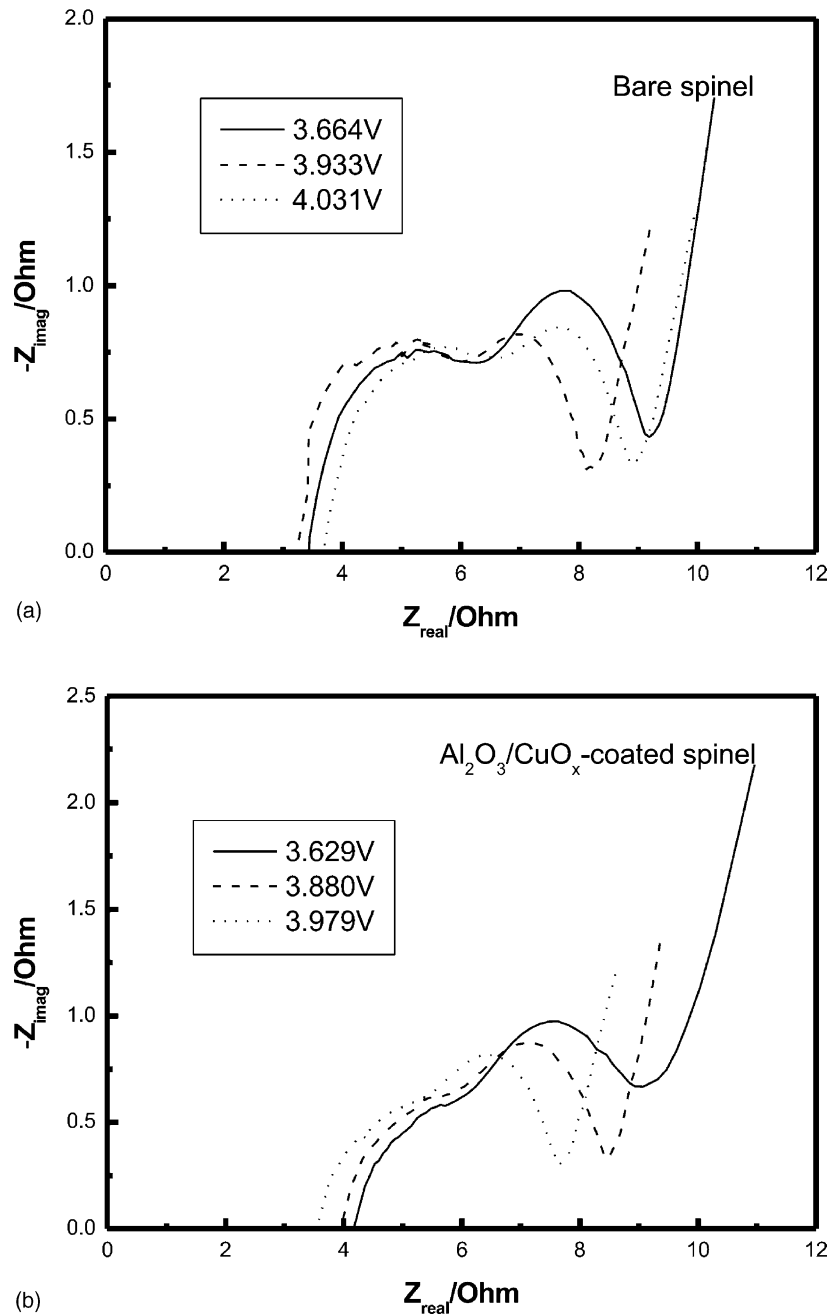


Fig. 5. AC impedance nyquist plot of bare spinel and $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel vs. MCMB cell after 220 cycles.

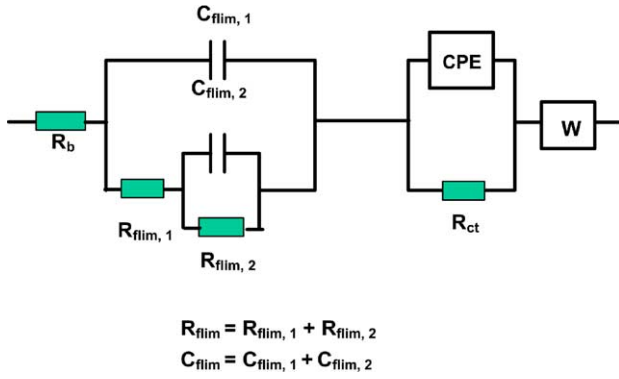


Fig. 6. Proposed equivalent circuit for spinel/MCMB cell.

the interfacial reaction (electrolyte decomposition), despite disadvantages such as a decrease of electronic conductivity with coating.

The changes of morphology after the cell test are given in Fig. 8. Abnormal surfaces formed on the bare spinel after the cell test may be a byproduct of the decomposition of electrolyte.

XRD patterns for two spinel samples after the cell test are present in Fig. 9. The [400] peak shifting to a higher angle and broadening are present in this figure. However, it is noted that neither new phases nor notable splitting is observed in comparison with the fresh bare sample. Accordingly, we assume that the degradation of capacity comes

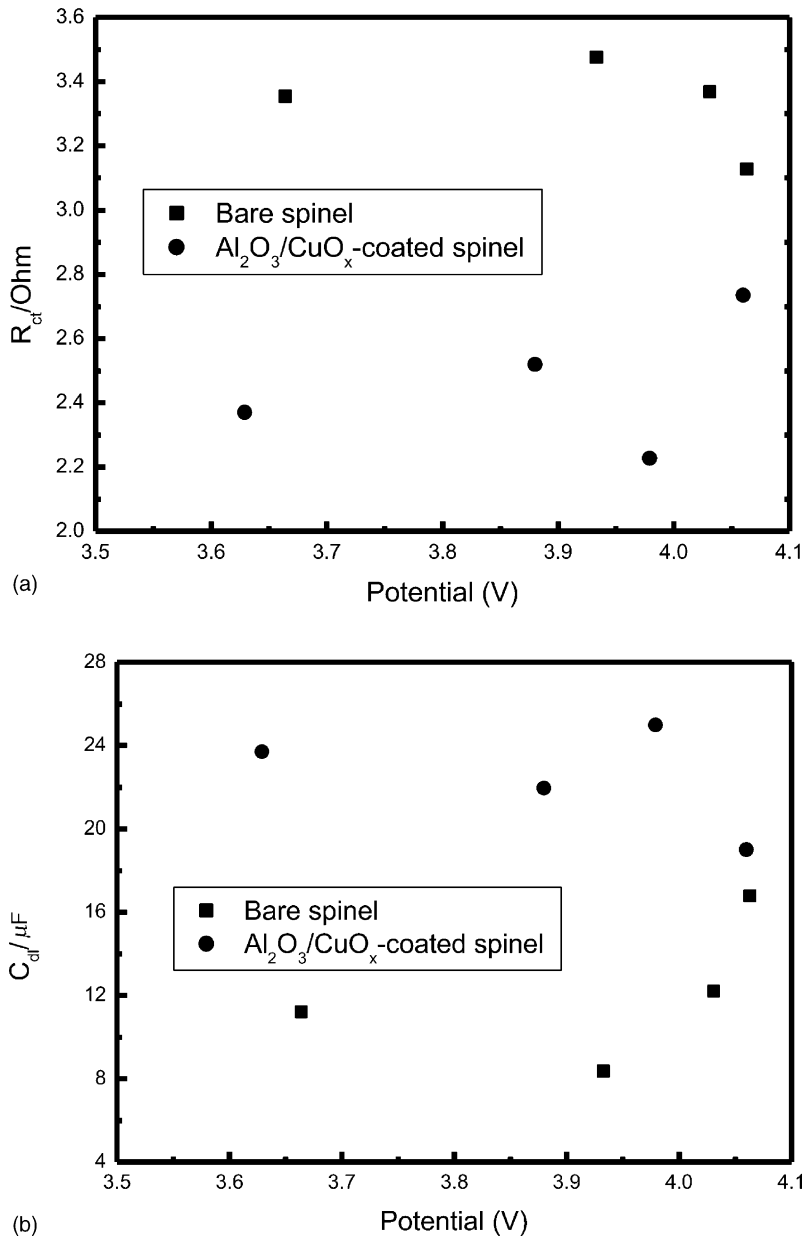


Fig. 7. Charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) of bare spinel and Al_2O_3/CuO_x -coated spinel vs. MCMB cell after 220 cycles.

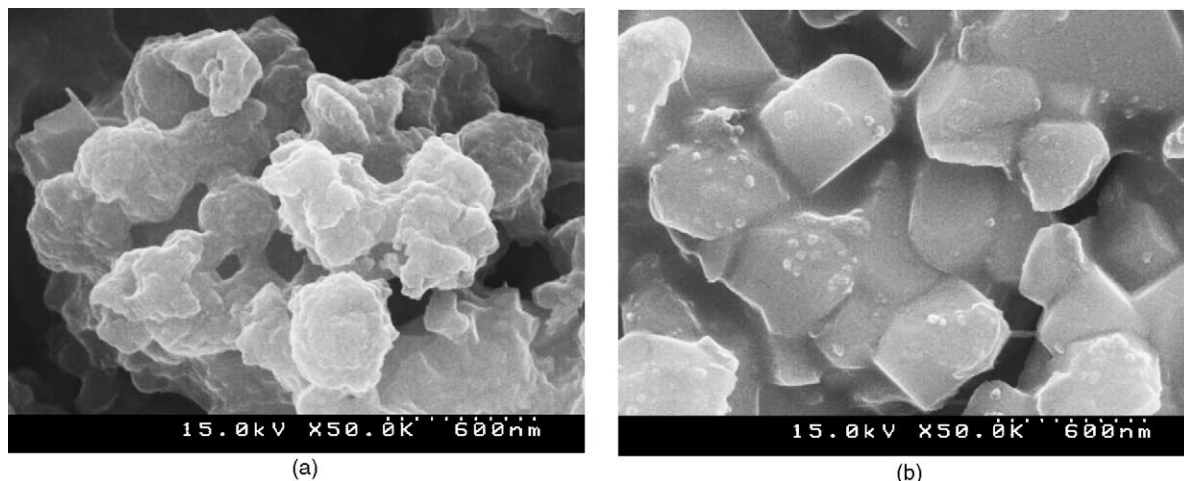


Fig. 8. SEM micrograph of bare spinel and Al₂O₃/CuO_x-coated spinel after cell test: (a) bare spinel; (b) Al₂O₃/CuO_x-coated spinel.

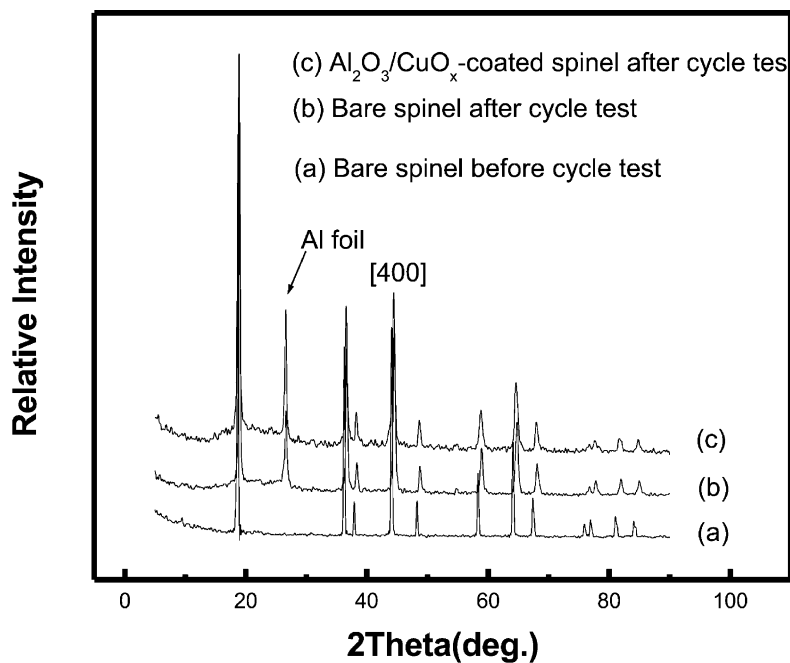


Fig. 9. XRD patterns for fresh bare spinel and two spinel samples after cell test.

from the increase of electrochemical resistance attributable to electrolyte decomposition.

4. Conclusions

An additional coating of copper oxide enabled Al₂O₃/CuO_x-coated spinel to have stable cycle performance. Al₂O₃/CuO_x-coated spinel had lower charge transfer resistance and a higher double layer capacitance than bare spinel. It is expected that the Al₂O₃/CuO_x coating on the spinel can function as a protective film, which may suppress the reaction between electrolyte and active material.

Acknowledgements

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