

Improving the Capacity Retention of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ by ZrO_2 Coating

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Abstract : The effect of ZrO_2 -coating on the electrochemical properties of the cathode material $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was investigated using EPMA, TEM, and EIS. In particular, we focused on the distribution of the ZrO_2 on the particle surface to study the relation between electrochemical properties of the coated cathode and the distribution of the coating materials in the particle. Based on the results from the composition analysis and electrochemical tests, it was found that the coating layer consisted of nano-sized ZrO_2 particles attached non-uniformly on the particle surface and the ZrO_2 layer significantly improved the electrochemical properties of the cathode by suppressing the impedance growth at the interface between the electrodes and the electrolyte.

Keywords: $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, Zirconium oxide, Coating, Lithium ion batteries.

1. Introduction

Recently, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ has been considered as a promising alternative for conventional LiCoO_2 cathodes for rechargeable Li-batteries since the Ni substitution to LiCoO_2 not only increases specific capacity, but also reduces toxicity of the Li-batteries. The safety level and electrochemical performance of this material, however, have not been sufficient enough to be used as a commercial cathode.^{1,2)}

In order to overcome these problems, two different modification methods were developed by several research groups. The first method was the metal doping into the cathode and $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($0.2 < x < 0.3$) compounds, as an example, was developed based on the fact that LiCoO_2 and LiNiO_2 have the same layered structure.³⁻⁵⁾ Other metals such as Al,⁶⁻⁸⁾ Ti,⁹⁾ Zn,¹⁰⁾ Ga,¹¹⁾ and Sr¹²⁾ also have been used for partial substitution of Ni or Co to enhance the electrochemical performance of the cathode. It is known that the beneficial effects of the metal doping are, in general, attributed to the suppression of phase transitions or lattice changes during charge-discharge cycling. The other modification method was the coating of electrochemically inactive materials on the cathode. Recently, various inactive metal oxides (MgO ,¹³⁻¹⁵⁾ TiO_2 ,¹⁶⁻¹⁸⁾ ZnO ,¹⁹⁾ $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$,²⁰⁾ Al_2O_3 ,²¹⁾ ZrO_2 ²²⁻²⁵⁾) and metal phosphates^{26,27)} have been used for surface coating of the cathode. This treatment was believed to reduce the reaction of the electrodes with the electrolyte at charged state since direct contact between the electrode and the electrolyte was restricted by the inactive coating layer. However, the detailed mechanism of the beneficial coating effect is still fragmentary.

In this study, we investigated the effect of zirconium oxide coating on the electrochemical performance of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. The cathode was synthesized by acid dissolution method^{32,33)} followed by a coating process using a sol-gel method. We employed various analytical techniques such as EPMA, TEM, and EIS to understand the mechanism of the improvement of electrochemical properties of the ZrO_2 coated cathode.

2. Experimental

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was prepared by an acid dissolution method. In this method, insoluble starting materials such as metal carbonates or metal hydroxides were dissolved by a strong organic acid, which also played as a chelating agent. The gel was formed at 140°C by mixing Li_2CO_3 , $\text{Ni}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, and acrylic acid in distilled water and fired at 500°C for 6 h in air, followed by firing at 730°C for 24 h in the flowing oxygen atmosphere. A slight excess amount of lithium (1.1) was used to compensate the loss during the calcining at high temperatures. For ZrO_2 coating on $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, zirconium acetate hydroxide $(\text{CH}_3\text{COO})_x\text{Zr}(\text{OH})_y$ ($X+Y=4$) was dissolved in distilled water and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was thoroughly mixed with the coating solution through sonication. The mixture was then dried at 50°C and heat-treated at 120°C for 6 hours and at 700°C for 6 hours in flowing oxygen. The coated cathode appeared to contain approximately 1 wt.% of zirconium oxide.

The surface of coated particles was also examined using a HRTEM (Technai G²⁰/FEI). The distribution of coating material on the surface or inside of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle was analyzed by examining the cross section of a particle coated

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with ZrO_2 with Electron Probe X-ray Micro Analyzer (JEOL/JXA-8900R) to investigate the distribution of ZrO_2 in the $LiNi_{0.8}Co_{0.2}O_2$ particles. EIS (electrochemical impedance spectroscopy) experiments were performed at the charged state of 4.4 V for each cycle using an impedance analyzer (IM6e Zahner Electrik) over the frequency range from 10^5 Hz to 10^{-2} Hz with an amplitude of 5 mV.

Composite electrodes were prepared by mixing 87 wt.% of the fine $LiNi_{0.8}Co_{0.2}O_2$ particles, 8 wt.% acetylene black (conductor), and 5 wt.% PVdF (polyvinylidene difluoride, binder). The mixture was spread on an Al foil and dried at $80^\circ C$ for 24 hours.

The charge and discharge characteristics of the cathodes were examined assembling CR2032 type coin cells. The cell was consisted of a cathode, a lithium metal anode, and a separator. The electrolyte solution was 1 M $LiPF_6/EC+EMC+DMC$. The volume ratio of EC (ethylene carbonate), EMC (ethylmethyl carbonate), and DMC (dimethyl carbonate) was 1:1:1. Cells were cycled in the range of 3.0 to 4.4 V and the charge and discharge experiment was carried out at $1/5$ C rate for the first cycle and at $1/2$ C rate for the following 49 cycles.

3. Results and Discussion

Electron Probe X-ray Micro Analysis was performed to examine the distribution of ZrO_2 around the active material particle. Fig. 1 shows an elemental mapping and a line profile of Zr indicating the existence of Zr atoms on the particle surface. The EPMA results in Fig. 1 suggested that the ZrO_2 did not diffuse into the particle probably due to the large size of Zr compared with Ni and Co, and the coating layer consisted of discontinuous lumps attached on the particle surface. Fig. 2 shows a TEM image of a coated $LiNi_{0.8}Co_{0.2}O_2$ particle. It also showed that the $LiNi_{0.8}Co_{0.2}O_2$ particle was non-uniformly

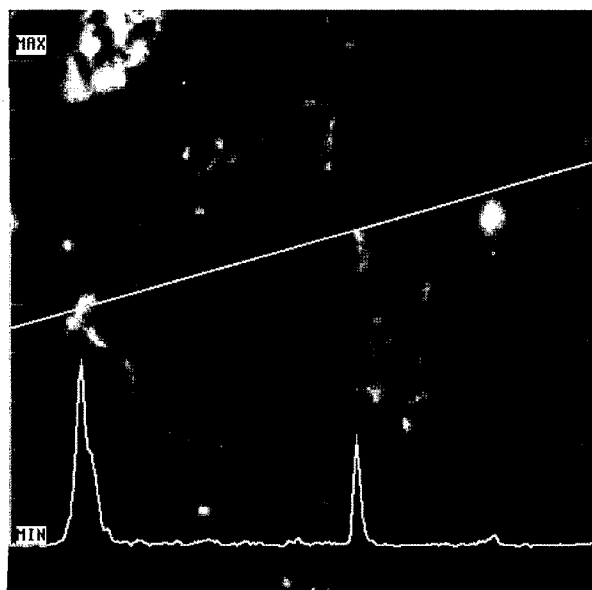


Fig. 1. EPMA analysis; elemental (Zr) mapping, and line profile of the ZrO_2 -coated $LiNi_{0.8}Co_{0.2}O_2$ powder synthesized $900^\circ C$ for 24 h and coated $700^\circ C$ for 6 h in O_2 atmosphere.

covered was nano-sized ZrO_2 particles.

Cycle tests were performed at 3.0~4.4 V under the same charge-discharge conditions. The cycling performance of the bare $LiNi_{0.8}Co_{0.2}O_2$ and ZrO_2 -coated $LiNi_{0.8}Co_{0.2}O_2$ were shown in Fig. 3. The initial capacity of bare $LiNi_{0.8}Co_{0.2}O_2$ was 198.1 $mAhg^{-1}$ while the coated $LiNi_{0.8}Co_{0.2}O_2$ showed a slightly decreased initial capacity of 196.9 $mAhg^{-1}$. On the other hand, the capacity retention of the cathode material was significantly improved by coating a small amount of ZrO_2 . As shown in Fig. 4b, $LiNi_{0.8}Co_{0.2}O_2$ showed 30.9% capacity loss in 50 cycles, whereas only 11% of capacity loss was observed in the case of coated $LiNi_{0.8}Co_{0.2}O_2$, implying that considerable improvement of the electrochemical properties of $LiNi_{0.8}Co_{0.2}O_2$ by ZrO_2 coating was possible.

It was reported in the literature that the improvement in the capacity retention was closely related with the prevention

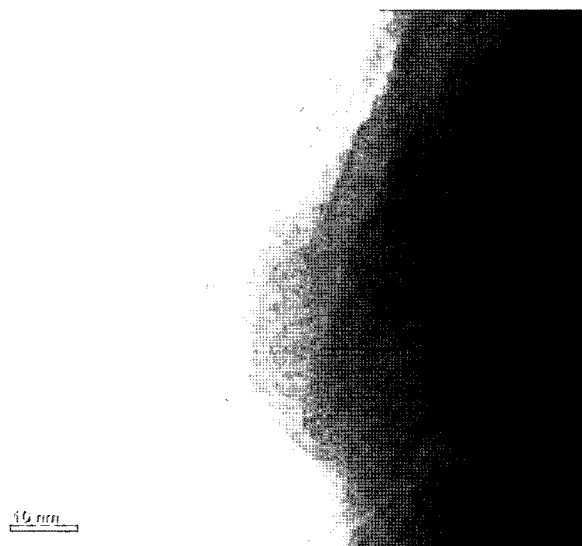


Fig. 2. TEM image of a ZrO_2 -coated $LiNi_{0.8}Co_{0.2}O_2$ particle.

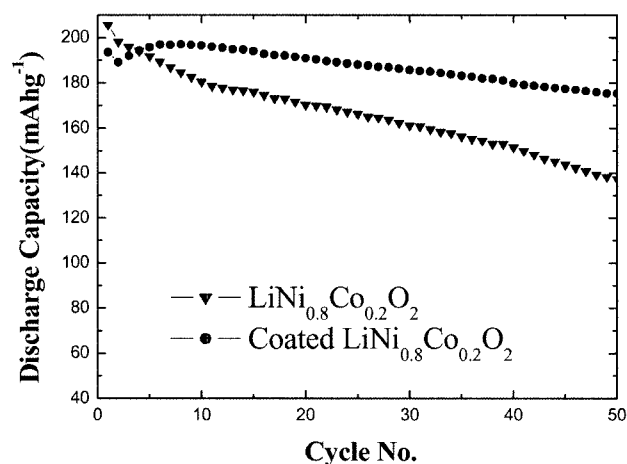


Fig. 3. Plots of discharge capacities of bare $LiNi_{0.8}Co_{0.2}O_2$ and ZrO_2 -coated $LiNi_{0.8}Co_{0.2}O_2$ as a function of the cycle number. The cycle tests were carried out initially by charging and discharging at the $1/5$ C rate for first cycle and at the $1/2$ C rate for subsequent 49 cycles. Charge and discharge cut-off voltages were set between 3.0 and 4.4 V.

of the electrode reactions with the electrolyte at the delithiated states since the oxide coating layer isolated them.^{17,20,24)}

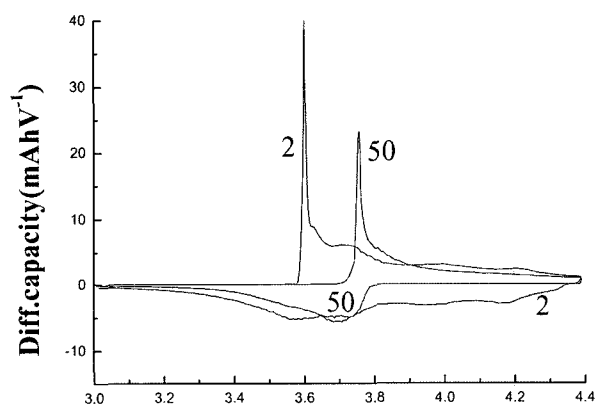
In general, the reaction at the interface lead to impedance growth and it causes the capacity fading of the cathode.^{16,19,25,28)}

Fig. 4 shows that differential capacity versus cell potential curves at 2 and 50 cycles for bare and coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. The peaks in the curve corresponded to the phase transitions, which were similar to the cyclic voltammograms. In the case of bare $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (4a), charge peaks shifted to higher potentials and discharge peaks shifted to lower potentials as the number of cycle increased. Splitting between charge and discharge peaks in the case of coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (4b) was much smaller than that from the bare cathode (4a). This indicated that the impedance growth was much slower for the cell produced with coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. A similar result in the case of LiCoO_2 was reported by Chen *et al.*^{25,28)}

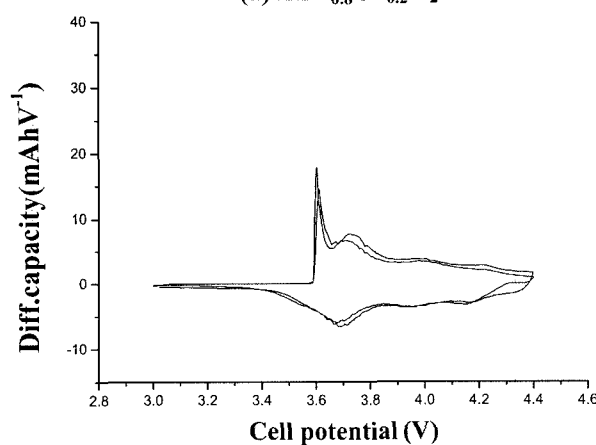
Electrochemical impedance spectroscopy (EIS) experiments were performed to investigate the impedance growth of the cell produced with bare and coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ during charge-discharge cycling. Fig. 5 represents the Nyquist plots measured using the uncoated and ZrO_2 -coated cathode at the terminated voltage of 4.4 V after 1, 10, 20, and 30 cycles. In

general, each impedance spectrum consists of three parts: a semicircle at the high frequency range reflects the resistance for Li^+ ion migration through the surface films and film capacitance; another semicircle at medium-to-low frequency range reflects a charge-transfer resistance and an interfacial capacitance between the electrodes and the electrolyte; and a slop line at low frequency range reflects Li^+ ion diffusion in the solid state electrodes.^{29,30)} All of three parts exist clearly in each plot of Fig. 5b. In the case of the bare cathode, however, the uncompleted second semicircles were observed as the cycling proceeded. According to Chen *et al.*,³¹⁾ the cell impedance was mainly determined by the cathode-side impedance, especially the charge-transfer resistance. Thus, we have focused on comparison of the second semicircle which represents charge-transfer resistance. In the Fig. 5a, the cell impedance of uncoated cathode dramatically increased during cycling, while the cell impedance of coated cathode did not increase much.

From these results, it was inferred that the smaller capacity loss of the coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ than the bare $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ appeared due to the inactive ZrO_2 coating layer on the cathode surface, which considerably suppressed the impedance growth.

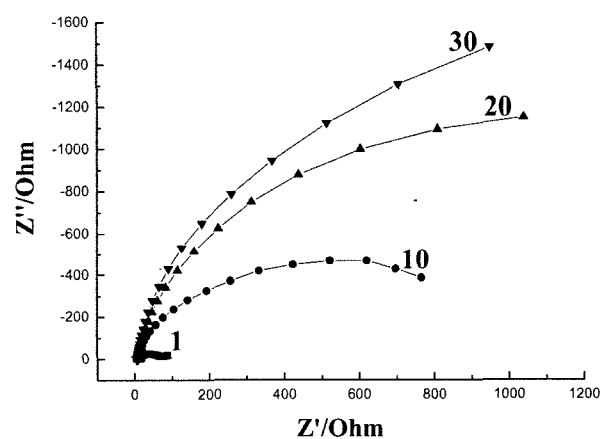


(a) $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$

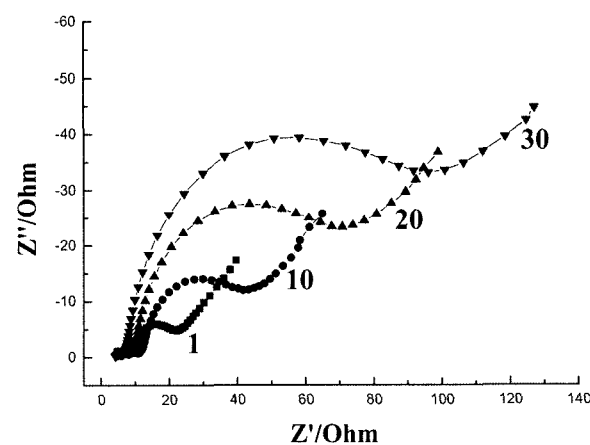


(b) ZrO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$

Figure 4. Differential capacity (dQ/dV) vs cell potential diagrams of bare $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (a) and ZrO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (b). Charge and discharge cut-off voltages were set between 3.0 and 4.4 V.



(a) $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$



(b) ZrO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$

Figure 5. Nyquist plots of coin cells with bare (a), ZrO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode (b) charged to 4.4 V after various cycles.

4. Conclusions

The effects of ZrO₂ coating on the electrochemical properties of the LiNi_{0.8}Co_{0.2}O₂ were investigated and the distribution of the coating material on the surface of the cathode was also examined. From the surface analyses, it was found that the coated layer on the cathode particles was non-uniform and the coating material did not diffuse into the cathode particles. From the electrochemical tests, it was found that the ZrO₂ coating on the LiNi_{0.8}Co_{0.2}O₂ improved its cycling stability considerably due to the suppression of the impedance growth during the charge-discharge cycling.

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