

Electrochemical properties of ZrO₂-coated LiNi_{0.8}Co_{0.2}O₂ cathode materials

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Abstract

The effect of a ZrO₂ coating on the structure and electrochemical properties of the cathode material LiNi_{0.8}Co_{0.2}O₂ was investigated using EPMA, TEM, XRD, and electrochemical impedance spectroscopy (EIS). In particular, we focused on the distribution of the ZrO₂ on the particle surface to study the relationship between electrochemical properties of the coated cathode and the distribution of the coating materials in the particle. Based on the results from composition analysis and electrochemical tests, it was found that the coating layer consisted of nano-sized ZrO₂ particles attached nonuniformly to the particle surface and the ZrO₂ layer significantly improved the electrochemical properties of the cathode by suppressing the impedance growth at the interface between the electrodes and the electrolyte.

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1. Introduction

Among various cathode materials for lithium batteries, LiCoO₂ has been mainly used for commercial applications due to its superior electrochemical stability. The LiCoO₂ cathode, however, has suffered from high cost, toxicity, and low capacity [1]. As an alternative, LiNiO₂ has been developed for cost reduction to circumvent the environmental issues by replacing Co with Ni. The LiNiO₂ cathode, on the other hand, has shown premature capacity fading on cycling and has exhibited thermal instability in its charged state due to decomposition at elevated temperatures [2]. In order to overcome these problems, two different modification methods were developed. The first method was metal doping into the cathode and the LiNi_{1-x}Co_xO₂ (0.2 < x < 0.3) compound, as an example, was developed based on the fact that LiCoO₂ and LiNiO₂ have the same layered structure [3–5]. Other metals such as Al [6–8], Ti [9], Zn [10], Ga [11], and Sr [12] 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 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. Various inactive metal oxides (MgO [13–15], TiO₂ [16–18], ZnO [19], Li₂O–2B₂O₃ [20], Al₂O₃ [21], ZrO₂ [22–25]) and metal phosphates [26,27] have been used for the surface coating. This treatment was believed to reduce the reaction of electrodes with the electrolyte in the charged state since direct contact between the electrode and electrolyte was restricted by the inactive coating layer. However, a detailed mechanism of the beneficial coating effect is still fragmentary.

In this study, we investigated the effect of a zirconium oxide coating on the electrochemical performance of LiNi_{0.8}Co_{0.2}O₂. The cathode was synthesized by an acid dissolution method followed by a coating process using a sol–gel method. We employed various analytical techniques such as EPMA, TEM, XRD, and electrochemical impedance spectroscopy (EIS) to understand the mechanism of the improvement in the electrochemical properties of the ZrO₂-coated cathode.

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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 the role 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 flowing oxygen. A slight excess amount of lithium (1.1) was used to compensate the loss during calcining at high temperatures. For the 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 by sonication. The mixture was then dried at 50°C and heat-treated at 120°C for 6 h and at 700°C for 6 h in flowing oxygen. The coated cathode contained approximately 1 wt.% of zirconium oxide.

The crystal structures of bare and coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders were examined using X-ray diffraction. X-ray diffraction experiments were performed with a RINT/DMAX-2500 (RIGAKU/JAPAN). The surface of coated particles was also examined using a HRTEM (Technai G²⁰/FEI). The distribution of the material coated 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 the particles coated with ZrO_2 using an Electron Probe X-ray Microanalyzer (JEOL/JXA-8900R) to investigate the distribution of the ZrO_2 in the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particles. Electrochemical impedance spectroscopy experiments were performed in the charged state of 4.3 V for each cycle using an impedance analyzer (IM6e Zahner Electrik) over the frequency range from 10^5 Hz to 10^{-2} Hz with the amplitude of 5 mV.

Composite electrodes were prepared by mixing 87 wt.% of the fine $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particles, 8 wt.% acetylene black (conductor), and 5 wt.% polyvinylidene difluoride (PVdF, binder). The mixture was spread on an Al foil and dried at 80°C for 24 h.

The charge and discharge characteristics of the cathodes were examined using CR2032 type coin cells. The cell was consisted

of a cathode, a lithium metal anode, and a separator. The electrolyte solution was 1 M $\text{LiPF}_6/\text{EC} + \text{EMC} + \text{DMC}$. The volume ratio of ethylene carbonate (EC), ethylmethyl carbonate (EMC), and dimethyl carbonate (DMC) was 1:1:1. Cells were cycled in the range of 3.0–4.3 V and the charge and discharge experiment was carried out at $1/5C$ rate for the first cycle and at $1/2C$ rate for the following 49 cycles.

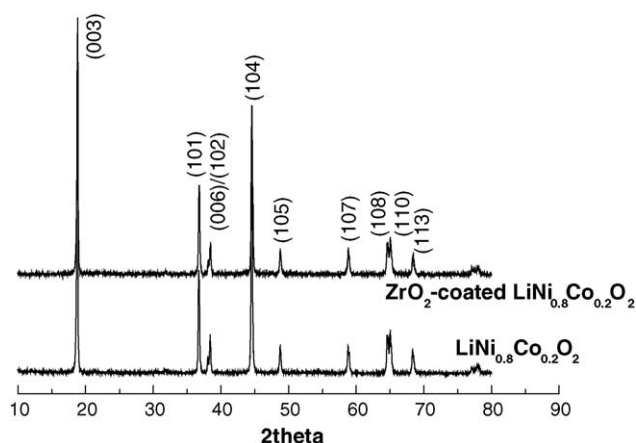
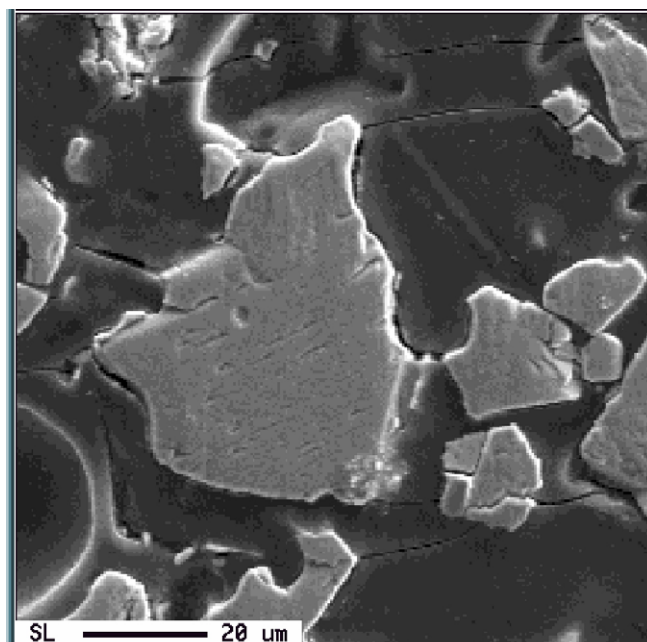
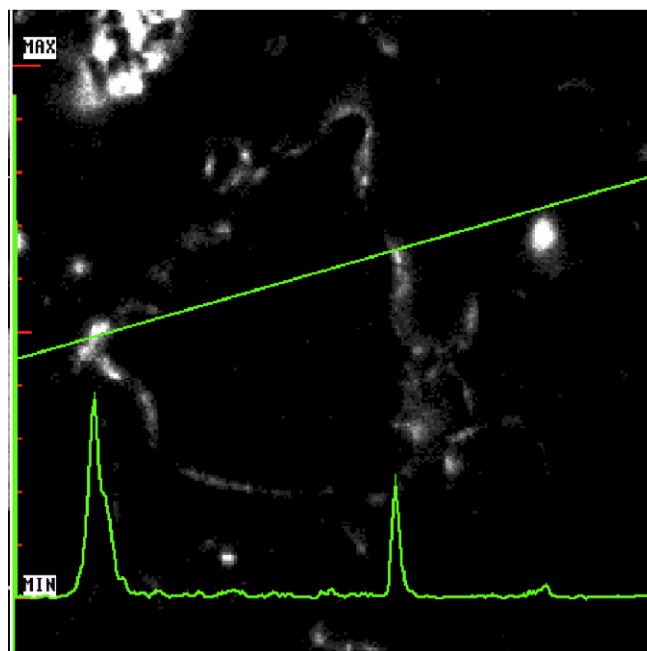


Fig. 1. XRD patterns of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and ZrO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders.



(a)



(b)

Fig. 2. EPMA analysis; SEM image (a), elemental (Zr) mapping, and line profile (b) of the ZrO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powder synthesized at 900°C for 24 h and coated at 700°C for 6 h in O_2 atmosphere.

3. Results and discussion

3.1. Crystal structure and surface morphology

The crystal structures of bare and ZrO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particles were investigated by XRD. The resulting XRD patterns are shown in Fig. 1. They exhibit a pattern corresponding to the layered $\alpha\text{-NaFeO}_2$ type structure (space group, $R\text{-}3m$). There was no difference between coated and uncoated particles except that the $I(003)/I(104)$ peak intensity ratio of coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was decreased from 1.39 to 1.27. The decrease of the $I(003)/I(104)$ peak ratio represented a decrease of the lithium content in the unit-cell due to the additional heat treatment during the coating process [28]. For coated particles, no impurity peaks due to ZrO_2 coating appeared in the diffraction pattern. This suggested that the amount of coating material was too small to detect ZrO_2 on the surface of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$.

Electron Probe X-ray Microanalysis was performed to examine the distribution of ZrO_2 in the particle. Fig. 2a shows an SEM image of the cross sections of the coated particles. The secondary electron image in Fig. 2a, however, did not provide any noticeable evidence about the uniform distribution of ZrO_2 on the particle surface. On the other hand, elemental mapping and the

line profile of Zr indicated the existence of Zr atoms on the particle surface. The EPMA results in Fig. 2b suggested that the ZrO_2 did not diffuse into the particle and the coating layer was consisted of discontinuous lumps attached to the particle surface. Fig. 3a shows a TEM image of a coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle. It also shows that the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle was nonuniformly covered with nano-sized ZrO_2 particles. Energy dispersive X-ray spectroscopy (EDX) was used to examine the composition of the nanoparticles on the surface of the bare particles. Fig. 3b and c showed EDX spectra from the points A and B in Fig. 3a. The spectrum from the particle attached on the surface indicated that the nano-sized particles were ZrO_2 , which was coincided with the EPMA analysis.

3.2. Electrochemical properties

Cycle tests were performed at 3.0–4.3 V under the same charge–discharge conditions. The cycling performance of the bare $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and ZrO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ are shown in Fig. 4. The initial capacity of the bare $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was 181.1 mAhg^{-1} while the coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ showed an initial capacity slightly less than 170 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

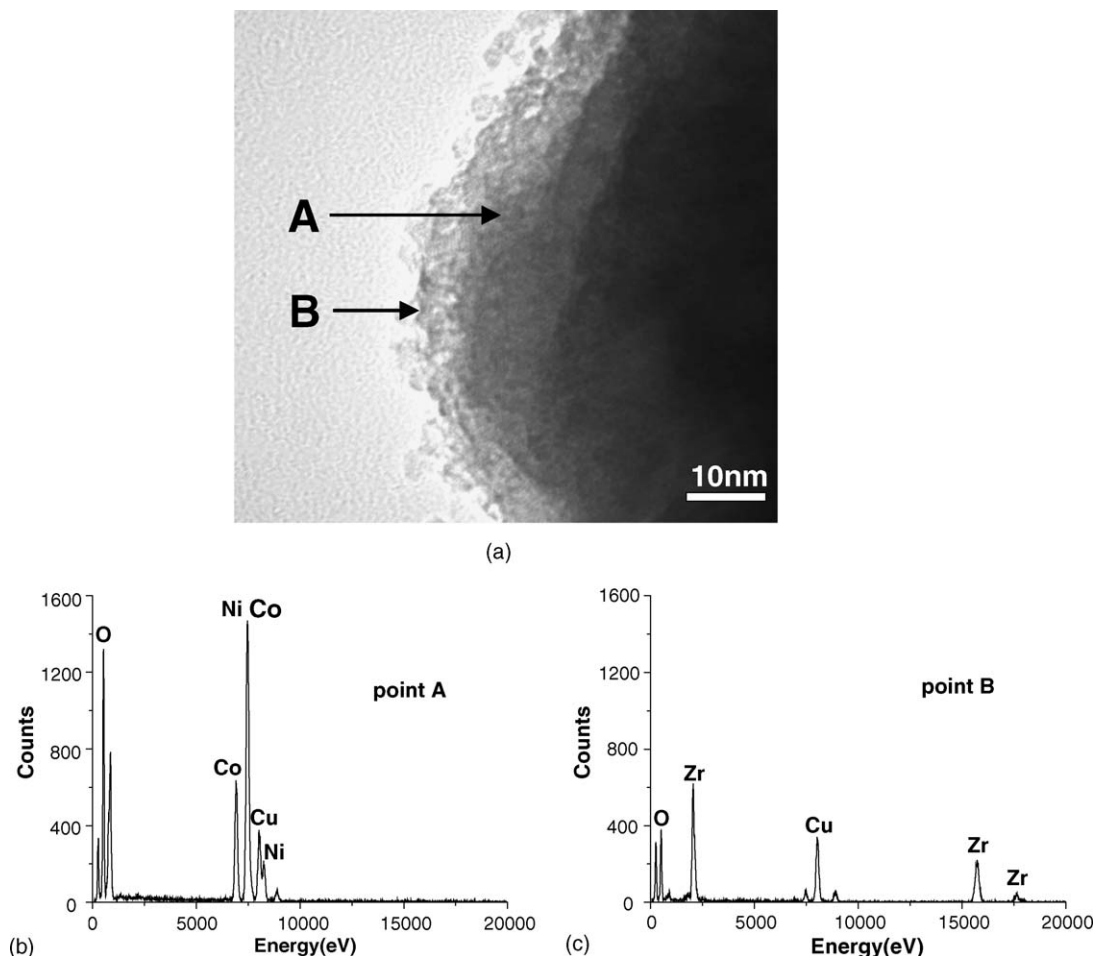


Fig. 3. TEM image of a ZrO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle (a) and EDX spectra obtained at the points A (b) and B (c) in the micrograph.

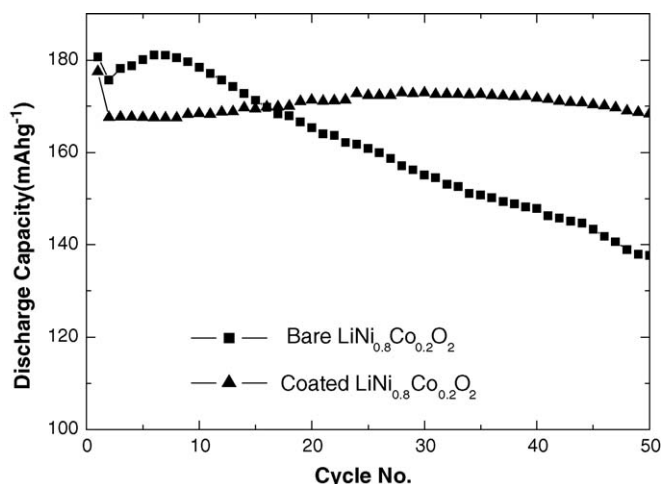


Fig. 4. Discharge capacities of bare LiNi_{0.8}Co_{0.2}O₂ and ZrO₂-coated LiNi_{0.8}Co_{0.2}O₂ as a function of the cycle number. The cycle tests were carried out initially by charging and discharging at the 1/5C rate for the first cycle and at the 1/2C rate for subsequent 49 cycles. Charge and discharge cut-off voltages were set between 3.0 V and 4.3 V.

shown in Fig. 4, LiNi_{0.8}Co_{0.2}O₂ showed a 24.6% capacity loss in 50 cycles, whereas only a 2.6% of capacity loss was observed in the case of coated LiNi_{0.8}Co_{0.2}O₂, suggesting that considerable improvement of the electrochemical properties of LiNi_{0.8}Co_{0.2}O₂ by ZrO₂ coating was possible.

According to the previous studies [22,23], it was reported that the ZrO₂ coating on the cathode particles effectively suppressed the phase transitions during Li intercalation/deintercalation and it greatly improved the capacity retention. In order to examine the suppression of phase transition during the charge–discharge experiment, cyclic voltammetry was used to investigate the effect of the ZrO₂ coating. This was because the shape of the CV curve represented the electrochemical properties of the electrode and it disclosed the phase transitions during the charge–discharge tests, which strongly affected the capacity fading during cycle tests [29]. In general, when a cathode experiences a phase transition, a peak occurs in the CV curve due to coexistence of two phases. However, Fig. 5 showed similar specific cyclic voltammograms from the bare and ZrO₂-coated LiNi_{0.8}Co_{0.2}O₂ indicating that the improvement of capacity retention was not due to suppression of the phase transition. Another coating effect, which was reported in the literature, was the prevention of electrode reactions with electrolyte since the oxide-coated layer isolated them [17,20,24]. In general, the reaction at the interface induces impedance increase and it causes the capacity fading of the cathode [16,19,25,30].

Fig. 6 shows that differential capacity versus cell potential curves at the 2nd, 30th, and 50th cycles for bare and coated LiNi_{0.8}Co_{0.2}O₂. The peaks in the curve corresponded to the phase transitions, which were similar to the cyclic voltammograms. In the case of bare LiNi_{0.8}Co_{0.2}O₂ (Fig. 6a), the charge peaks shifted to higher potentials and the discharge peaks shifted to lower potentials as the number of cycles increased. The splitting between the charge and discharge peaks in the case of the coated LiNi_{0.8}Co_{0.2}O₂ (Fig. 6b), however, was much smaller

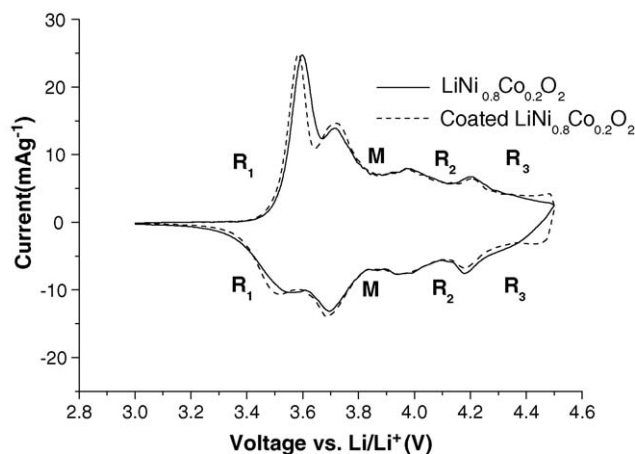
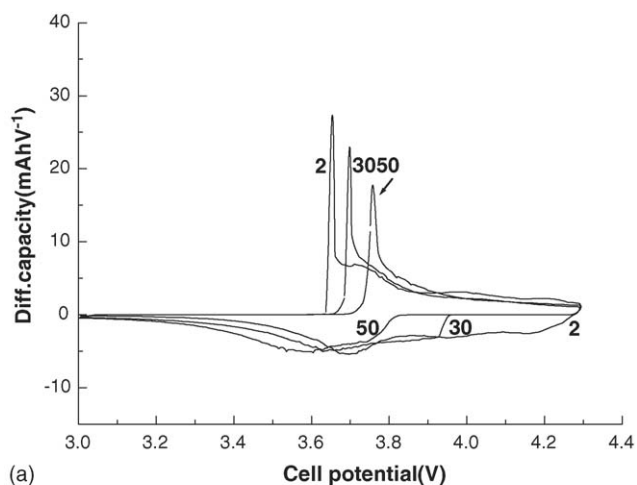
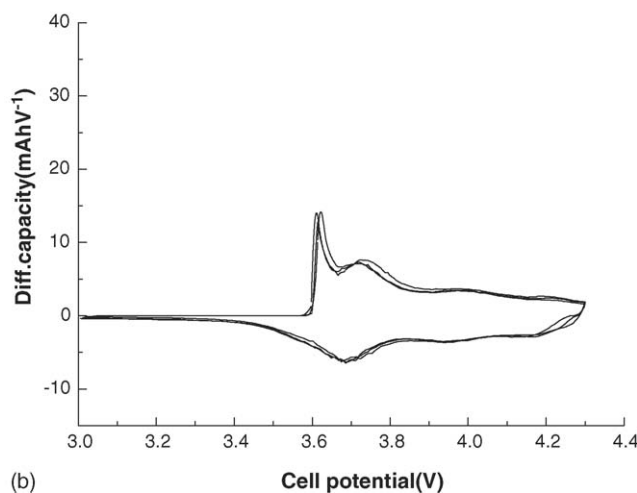


Fig. 5. Cyclic voltammograms of bare LiNi_{0.8}Co_{0.2}O₂ and ZrO₂-coated LiNi_{0.8}Co_{0.2}O₂. The voltage scan rate was 0.01 mV s⁻¹. R and M denote the rhombohedral and monoclinic phase, respectively.



(a)



(b)

Fig. 6. Differential capacity (dQ/dV) vs. cell potential diagrams of bare LiNi_{0.8}Co_{0.2}O₂ (a) and ZrO₂-coated LiNi_{0.8}Co_{0.2}O₂ (b). Charge and discharge cut-off voltages were set between 3.0 V and 4.3 V.

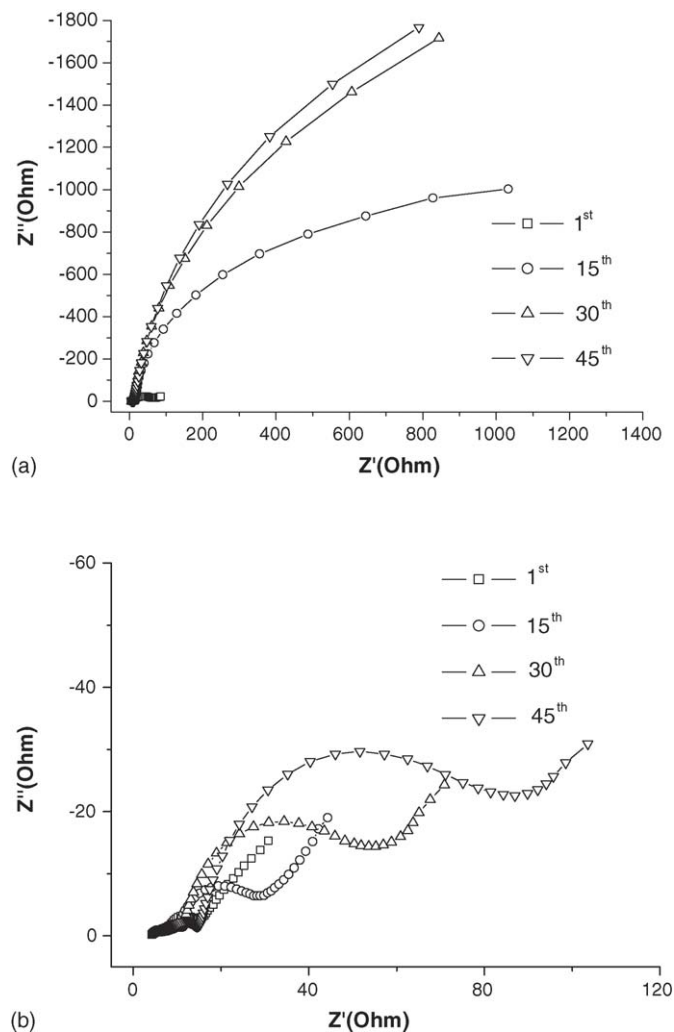


Fig. 7. Nyquist plots of coin cells with bare $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (a) and ZrO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode (b) charged to 4.3 V after various cycles.

than that of the bare cathode (Fig. 6a). 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 and Dahn [25,30].

Electrochemical impedance spectroscopy experiments were performed to investigate the impedance growth of the cell during charge–discharge cycling. Fig. 7 shows the Nyquist plots measured using the uncoated and ZrO_2 -coated cathode at the terminated voltage of 4.3 V after 1st, 15th, 30th, and 45th cycles. In general, each impedance spectrum consists of three parts: a semicircle in the high frequency range which reflects the resistance to Li^+ ion migration through the surface films and film capacitance; another semicircle in the medium-to-low frequency range due to charge-transfer resistance and interfacial capacitance between the electrodes and the electrolyte; and a sloping line at low frequency range which reflects Li^+ ion diffusion in the solid electrodes [31,32]. All three parts appear clearly in each plot of Fig. 7b. In the case of the bare cathode, however, uncompleted second semicircles were observed as cycling proceeded. According to Chen et al. [33], the cell impedance was mainly determined by the cathode-side impedance, especially by the

charge-transfer resistance. Thus, we focused on comparison of the second semicircle which represents the charge-transfer resistance. In Fig. 7a, the cell impedance of the uncoated cathode drastically increased during cycling, while the cell impedance of the coated cathode did not increase much. From these results, 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 impedance growth.

4. Conclusions

The effects of a ZrO_2 coating on the electrochemical properties of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ were investigated, focusing on the distribution of the coating material on the surface of the cathode and its role in modifying the electrochemical properties of the cathode. The results are summarized as follows:

- (i) The crystal structure of the synthesized $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was not affected by the ZrO_2 coating and the ZrO_2 phase was not observed from the XRD analysis due to its detection limit.
- (ii) 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.
- (iii) From the electrochemical tests, it was found that the ZrO_2 coating on the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ improved its cycling stability considerably due to the suppression of impedance growth during charge–discharge cycling and not by the suppression of the phase transition.

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