

Short communication

Relationship between physical properties and electrochemical performances for $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ positive active materials

Kenji Shizuka*, Shouji Takano, Kenji Okahara

Mitsubishi Chemical Group Science and Technology Research Center, Inc., 8-3-1 Chuo, Ami, Inashiki, Ibaraki 300-0332, Japan

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Abstract

We investigated the relationship between physical properties and electrochemical performances for $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ positive active materials. The improvement of rate capability by excess Li was related to the increased electrical conductivity that was accompanied by Ni^{3+} increase. Electrochemical impedance measurements indicated that the charge-transfer resistance decreases with increased excess Li content (electrical conductivity) for $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$. The value of charge-transfer resistance was compared with the simulated value by the equivalent circuits' model considering the volume resistivity of positive active material.

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Keywords: $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$; Lithium-ion battery; Excess lithium; Conductivity; Impedance; Simulation

1. Introduction

Layered $\text{Li}(\text{Ni},\text{Mn},\text{Co})\text{O}_2$ compounds have been investigated intensively as a positive active material of lithium-ion secondary batteries and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ has commercialized. Cobalt-less composition is desired because of low price. $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ compounds are attractive in their characters, such as high theoretical capacity and thermal stability. However, the problem of these compounds is that less cobalt content induces lower rate capability. It is known that the lithium excess materials show higher rate capability than lithium stoichiometric ones. We have found that the rate performance is related with the volume resistivity of pristine powder of materials. The reduction of electrical resistivity was related to the Ni^{3+} increase that compensated for the loss of valence by excess Li [1,2]. In this paper, electrochemical analysis of $\text{Li}_{1+y}\text{Ni}_{5/12}\text{Co}_{1/6}\text{Mn}_{5/12}\text{O}_2$ cathode materials with different excess lithium content y was performed to elucidate how the change of the volume resistivity (electrical conductivity) contributes to the cell performance.

2. Experimental

The $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ materials were prepared by the heat treatment of their precursors which were dried mixtures of

Ni, Mn, and Co oxides or hydroxides and LiOH. For the obtained samples, powder properties such as volume resistivity, specific surface area (BET), particle distribution, and electrochemical properties (cell performance, ac impedance measurement), etc. were examined.

The specific surface area was measured by the single-point BET method. The particle distribution was measured by the laser diffraction method. The morphology was observed by the SEM. The volume resistivity of pristine powders was measured by a four-probe method under the pressure of 40 MPa. The charge–discharge experiments were carried out by laminated-type cells with aforementioned cathode and a graphite anode and a 1 M $\text{LiPF}_6\text{-EC/EMC/DMC}$ electrolyte. Impedance spectroscopic analysis was carried out using symmetric coin-type cells including a pair of the identical cathodes, which were obtained by disassembling the coin cells with a lithium metal anode for the specific state of charge. Size of the electrode used for the coin cell was a diameter of $\text{Ø}12$ mm and thickness of 35 μm .

3. Results and discussion

3.1. The role of Ni valence for $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$

It has been previously suggested that the oxidation states of Ni, Co and Mn are 2+, 3+ and 4+, respectively, in the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ series [3–7]. In our previous work, we have characterized several $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ which are Co-less

* Corresponding author. Tel.: +81 29 887 5284; fax: +81 29 887 3308.
E-mail address: shizuka.kenji@mp.m-kagaku.co.jp (K. Shizuka).

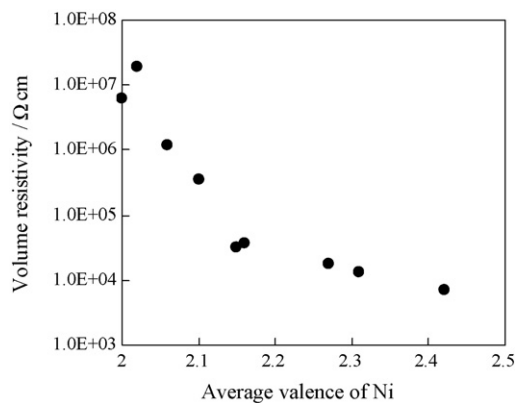


Fig. 1. Relationship between average valence of Ni and volume resistivity for $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$.

and/or Li-rich composition [1,2]. These results indicated that part of Ni was oxidized from Ni^{2+} to Ni^{3+} due to the oxidation of Ni as excess Li content increased in $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$.

It should be considered that excess Li substitute the transition metals in metal-layer, and in order to keep the electroneutrality, the substitution of a Li^+ for a transition metal ion changes two Ni^{2+} to two Ni^{3+} . Ni valence m can be calculated from x and y value in $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ as follows:

$$m = 2 + \frac{y}{x}$$

Fig. 1 shows the relationship between the average valence of Ni and the volume resistivity for $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$. The average valence of Ni was calculated from x and y value of elemental analysis. This result indicated that the volume resistivity of pristine powder has good correlation with Ni valence.

3.2. Powder properties of $\text{Li}_{1+y}\text{Ni}_{5/12}\text{Co}_{1/6}\text{Mn}_{5/12}\text{O}_2$

Since the electrochemical property depends greatly on the powder properties of positive active materials such as the volume resistivity, specific surface area, particle distribution and morphology, they are important properties considered in characterizing these materials. So, these powder properties were evaluated for the prepared $\text{Li}_{1+y}\text{Ni}_{5/12}\text{Co}_{1/6}\text{Mn}_{5/12}\text{O}_2$ ($y=0.04, 0.13$) samples containing a different amount of lithium. Table 1 shows that the various powder properties for $\text{Li}_{1+y}\text{Ni}_{5/12}\text{Co}_{1/6}\text{Mn}_{5/12}\text{O}_2$ ($y=0.04, 0.13$). It was found from the result that these samples are almost the same with the exception of the volume resistivity. Therefore, we considered that the effect due to the difference of specific surface area, particle distribution and morphology were negligible.

Table 1
Powder properties for $\text{Li}_{1+y}\text{Ni}_{5/12}\text{Co}_{1/6}\text{Mn}_{5/12}\text{O}_2$ ($y=0.04, 0.13$)

y	Volume resistivity ($\Omega \text{ cm}$)	d_{50} (μm)	SSA ($\text{m}^2 \text{ g}^{-1}$)
0.04	3.2E+05	6.1	1.1
0.13	1.4E+04	5.9	1.0

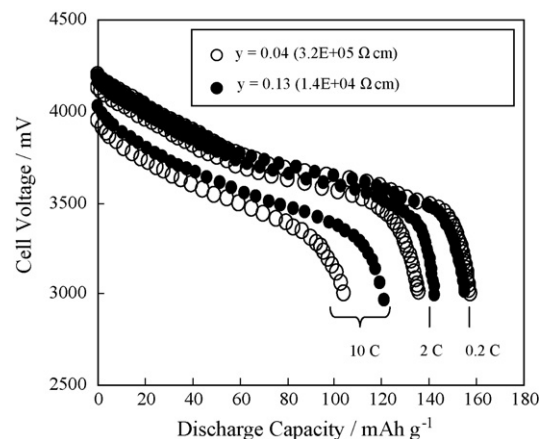


Fig. 2. Comparison of rate capability for $\text{Li}_{1+y}\text{Ni}_{5/12}\text{Co}_{1/6}\text{Mn}_{5/12}\text{O}_2$ ($y=0.04, 0.13$) cell at 25°C .

3.3. Cell performance of $\text{Li}_{1+y}\text{Ni}_{5/12}\text{Co}_{1/6}\text{Mn}_{5/12}\text{O}_2$

Fig. 2 shows the discharging capacity at various C-rates for $\text{Li}_{1+y}\text{Ni}_{5/12}\text{Co}_{1/6}\text{Mn}_{5/12}\text{O}_2$ ($y=0.04, 0.13$) samples containing a different amount of lithium. The lithium excess sample ($y=0.13$) having low volume resistivity in pristine state showed good rate capability. In order to analyze the impedance of cathode only, the symmetrical cell was used. The view of the impedance measurement of cathode by the symmetrical cell is shown in Fig. 3.

Fig. 4 shows the Nyquist plots of $\text{Li}_{1+y}\text{Ni}_{5/12}\text{Co}_{1/6}\text{Mn}_{5/12}\text{O}_2$ ($y=0.04$ (a), 0.13 (b)) symmetrical cell at various states of charge. Each spectrum had only one arc corresponding to the charge-transfer resistance R_{ct} of the cathode material and the arc size decreased with the increase of SOC from 0% to 60%, however, it slightly increased at SOC 100%. The lithium excess $\text{Li}_{1.13}\text{Ni}_{5/12}\text{Co}_{1/6}\text{Mn}_{5/12}\text{O}_2$ had also only one arc and its size was smaller than that of $\text{Li}_{1.04}\text{Ni}_{5/12}\text{Co}_{1/6}\text{Mn}_{5/12}\text{O}_2$ at each SOC.

Fig. 5 indicates the charge-transfer resistance of the samples containing different amount of lithium. The R_{ct} of lithium excess sample was smaller than that of stoichiometric one and the effect of reducing resistance was large especially in the low SOC. As the cathode material in discharge state is close to the pristine state, it is suggested that the R_{ct} at discharge state is influenced by the volume resistivity at the pristine state. The simulation in impedance spectroscopy by equivalent circuits considering electrical resistance is able to explain the behaviors of charge-transfer resistances of the samples having different volume resistivities.

Fig. 6 shows the proposed equivalent circuits' model considering the resistance of cathode particle. R_{ct} shown in Fig. 5 should be composed by parallel–serial connection of cathode particles with parameters $R_p n$, $C_{dl} n$ and $R_{ct} n$. $R_p n$ is the resistance of each cathode particle (or between particles) which

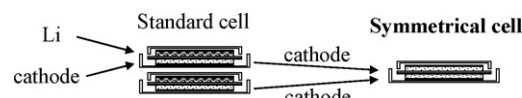


Fig. 3. View of the impedance measurement of cathode by the symmetrical cell.

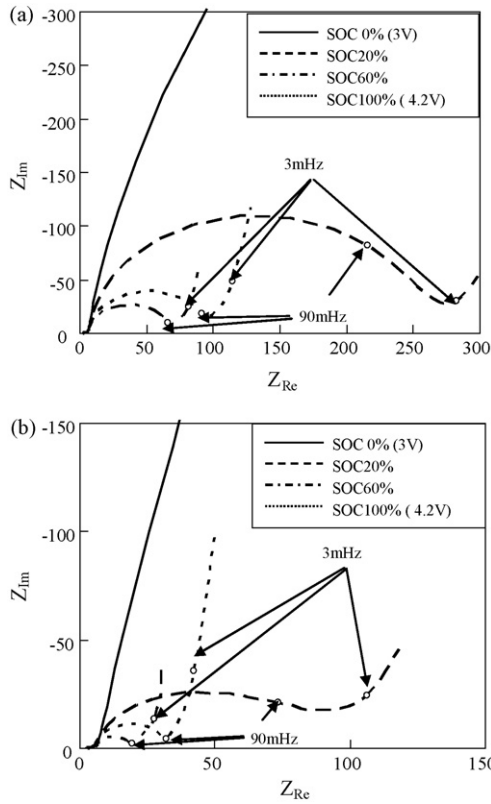


Fig. 4. Family of Nyquist plots of $\text{Li}_{1+y}\text{Ni}_{5/12}\text{Co}_{1/6}\text{Mn}_{5/12}\text{O}_2$ ($y=0.04$, 0.13) cell at different SOC.

can be calculated from the volume resistivity of positive active material powder. $C_{dl}n$ is double layer capacitance and $R_{ct}n$ is charge-transfer resistance of each cathode particle, respectively.

Fig. 7 shows the simulated result based on this parallel–serial circuit model for six pieces of cathode particle in two cases of $R_{p}n = 1\text{E}+08 \Omega$ and $1\text{E}+09 \Omega$ assuming that $C_{dl}n$ and $R_{ct}n$ values of each particle are the same. In this study, $C_{dl}n$ and $R_{ct}n$ were set as $1\text{E}-10 \text{F}$ and $9\text{E}+08 \Omega$, respectively. It was shown that $R_{p}n$ increased by 10 times as R_{ct} increased by 2 times. This result indicated that the resistance of the cathode particle could be contributed to the R_{ct} by the parallel–serial circuit model.

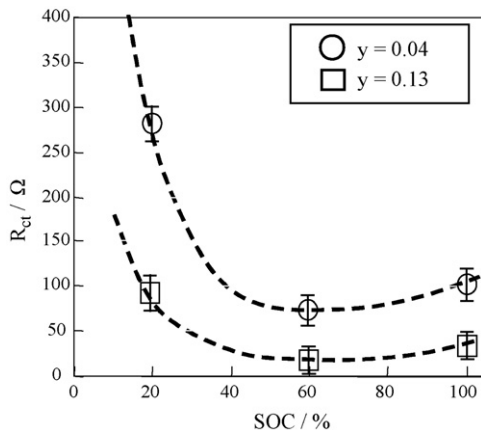


Fig. 5. Comparison of charge-transfer resistance for $\text{Li}_{1+y}\text{Ni}_{5/12}\text{Co}_{1/6}\text{Mn}_{5/12}\text{O}_2$ ($y=0.04$, 0.13) cell at different SOC.

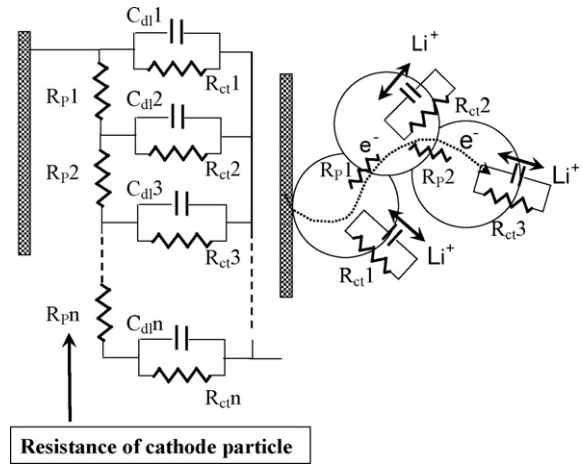


Fig. 6. Proposed equivalent circuits model considering the resistance of cathode particle.

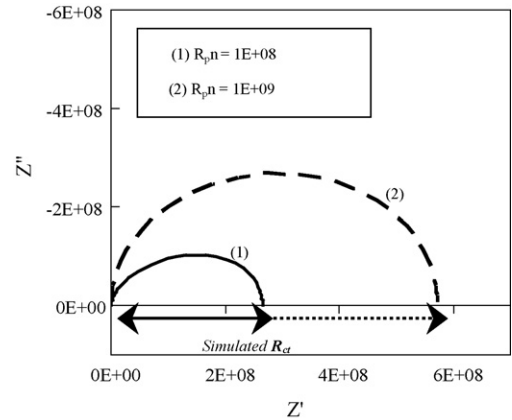


Fig. 7. Simulated result based on the parallel–serial circuit model with six pieces of particle ($C_{dl}n = 1\text{E}-10 \text{F}$, $R_{ct}n = 9\text{E}+08 \Omega$, $n = 1-6$).

In addition, Fig. 8 shows the relationship between $R_{p}n$ and simulated R_{ct} so that the experimental result can be compared with the simulated one. Table 2 shows the comparison between experimental R_{ct} and simulated one. For the calculation, experimental R_{ct} with coin-type symmetrical cell at SOC 20% in Fig. 5 was converted into a value of cylindrical size of $\phi 6 \mu\text{m}$ base $\times 36 \mu\text{m}$ thickness (equivalent to size of six particles) and

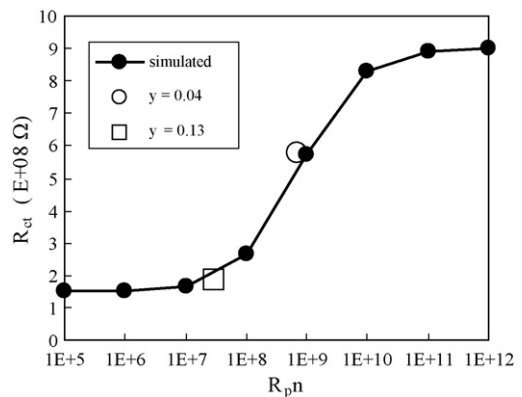


Fig. 8. Relationship between $R_{p}n$ and R_{ct} .

Table 2
Comparison between experimental value and simulated value for R_{ct}

y	Experimental R_{ct} (Ω) ^a	Converted R_{ct} (Ω) ^b	R_{pn} (Ω) ^c	Simulated R_{ct} (Ω) ^d
0.04	280	5.8E+08	6.8E+08	5.1E+08
0.13	90	1.9E+08	3.0E+07	1.9E+08

^a Measured value at SOC 20% in Fig. 5 for the electrode of $\varnothing 12$ mm \times 70 μ m (35 μ m \times 2) thickness.

^b Converted value from experimental R_{ct} for six particle model ($\varnothing 6$ μ m \times 36 μ m thickness).

^c Calculated value from volume resistivity in Table 1 for the particle of $\varnothing 6$ μ m \times 6 μ m thickness.

^d Simulated value by proposed equivalent circuit model in Fig. 6 for six particle model ($\varnothing 6$ μ m \times 36 μ m thickness).

R_{pn} was calculated as resistance of cylindrical size of $\varnothing 6$ μ m base and 6 μ m thickness (equivalent to size of one particle) from with the volume resistivity in Table 1. As shown in Fig. 8 and Table 2, the simulated R_{ct} was in good agreement with the experimental R_{ct} .

4. Conclusion

In this study, the relationship between physical properties and electrochemical performances for $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ positive active materials was investigated. The improvement of rate capability by excess Li was related to the increase of electrical conductivity that was accompanied by Ni^{3+} increase. Electrochemical impedance measurements with the symmetrical cell indicated that the charge-transfer resistance R_{ct} decreased with increased excess Li content y for $\text{Li}_{1+y}\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$.

To understand the relationship between electrical conductivity of positive active material and charge-transfer resistance R_{ct} ,

the equivalent circuits' model considering the volume resistivity was proposed and examined. As a result the simulated R_{ct} by this model was in good agreement with the experimental R_{ct} . Therefore, it is concluded that the volume resistivity contributes strongly to the value of R_{ct} .

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