

Effect of Calcination Temperature of Size Controlled Microstructure of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ Cathode for Rechargeable Lithium Battery

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Size controlled, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode powders were prepared by co-precipitation method followed by heat treatment at temperatures between 750 and 850 °C. The synthesized samples are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical performance. The synthesized $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ after calcined at 750 °C has a good electrochemical performance with an initial discharge capacity of 190 mAh g⁻¹ and good capacity retention of 100% after 30 cycles at 0.1C (17 mA g⁻¹). The capacity retention of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ after calcined at 750 °C is better than that at 800 and 850 °C without capacity loss at various high C rates. This is ascribed to the minimized cation disorder, a higher conductivity, and higher lithium ion diffusion coefficient (D_{Li}) observed in this material. In the differential scanning calorimetry DSC profile of the charged sample, the generation of heat by exothermic reaction was decreased by calcined at high temperature, and this decrease is especially at 850 °C. This behavior implies that the high temperature calcinations of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ prevent phase transitions with the release of oxygen.

Key Words : Cathode material, $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$, Calcination temperature, Lithium ion battery, Lithium ion battery Co-precipitation

Introduction

Li-ion batteries, with high energy density and power capability, have become an important power source for portable electronic device, such as cellular phones, computers and, more recently, hybrid electric vehicle (HEV) and, electric vehicle (EV).¹ Most commercialized Li-ion batteries use LiCoO_2 as a cathode material due to its ease of production, stable electrochemical cycling, and acceptable specific capacity.^{2,3} The relatively high cost of cobalt and the lure of large capacity have, however, lead to the study of other possible alternatives. In this aspect, LiNiO_2 has been proposed as an alternative cathode material for LiCoO_2 due to its structural similarity, higher capacity and low cost. However, there are some difficulties in using LiNiO_2 as cathode material due to the following facts: (i) difficulty involved in the synthesis of stoichiometry LiNiO_2 , (ii) safety problems associated with the instability of delithiated form of LiNiO_2 (oxygen evolution occurs at elevated temperatures) and (iii) poor cyclic performance due to its structural instability upon electrochemical studies.⁴ Some groups investigated the effect of other metal ion substitution on $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (M=Mn, Co, Mg, Fe, Al or combination of two metal ions) in order to improve the electrochemical properties.⁶⁻⁹

Among metal ions doping, Co substitution showed a promising candidate for lithium ion batteries. This is due to the significant improvement in the thermal stability of delithiated phase of LiNiO_2 , thereby reducing the safety problems associated with it.¹⁰ A small amount of doping of cost effective metal ion like Al^{3+} has profound effect on the

structure and electrochemical behavior of $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$. Based on the investigation of Ohzuku *et al.*,¹¹ it is understood that the Al^{3+} doping retains Ni in 3+ state and enhances the stabilization of layered structure. In addition, the doping of Al^{3+} for Ni prevents the cell from over charging and hence improves the cell safety.

$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ is one of the most promising materials for automobile-use due to the high capacity and electrochemical property.^{12,13} In spite of the improved electrochemical performance of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, the major barriers that hinder commercial-scale application are its insufficient cycle life and safety concerns above 55 °C.¹⁴ Another problem of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ with high Ni content is the rapid reaction to moisture and ambient CO_2 , resulting in the formation of LiOH and Li_2CO_3 on the cathode particle surface.^{15,16} Li extraction from the lattice gives rise to cation ion mixing, in turn leading to severe capacity fading and reduced reversible capacity. Thus far, few studies have investigated the effect of calcined temperature on the variation of the structural and electrochemical properties of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$.

In this work, the co-precipitation method is used for preparing $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode materials. The structure and electrochemical properties of the powder were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and charge-discharge tests. From these analyses, we investigated the relation between the structural stability and electrochemical property of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode materials as a function of calcination temperature in the range of 700-850 °C.

Experimental

In the present study, we adapted the co-precipitation method to the synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ from nickel(II) sulfate hexa-hydrate $[\text{NiSO}_4 \cdot 6\text{H}_2\text{O}]$, cobalt(II) hepta-hydrate $[\text{CoSO}_4 \cdot 7\text{H}_2\text{O}]$, aluminum mono-hydrate $[\text{Al}(\text{OH})_3 \cdot \text{H}_2\text{O}]$ and lithium carbonate $[\text{Li}_2\text{CO}_3]$. A spherical $\text{Ni}_{0.85}\text{Co}_{0.15}(\text{OH})_2$ precursor was prepared through a co-precipitation process in a continuously stirred tank. At first, a stoichiometric amount of metal solution at a concentration of 2 mol L^{-1} was pumped into a continuously stirred tank reactor (CSTR, 4 L) under a N_2 atmosphere. At the same time, 2 mol L^{-1} of a NaOH solution (aq.) and the desired amount of a NH_4OH solution (aq.) as a chelating agent were also separately pumped into the reactor. The pH of the whole reaction process was kept at 11.0. The obtained $\text{Ni}_{0.85}\text{Co}_{0.15}(\text{OH})_2$ precursor was thoroughly mixed with an appropriate amount of Li_2CO_3 and $\text{Al}(\text{OH})_3 \cdot \text{H}_2\text{O}$ calcined at 750, 800 and 850 °C for 15 h in O_2 atmosphere.

XRD patterns for the cathodes were obtained using a Siemens D-5000 diffractometer in the 2θ range from 10 to 70° with Cu $\text{K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The morphology of the obtained powder was observed with scanning electron microscopy (SEM).

To prepare the positive electrode, 80% $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder, 10% super-P carbon black (Aldrich), and 10% PVdF (Kureha KF100) binder were added in a crucible. After two hours of grinding, the viscous slurry was coated on aluminum foil using a doctor blade to make a film with a uniform thickness. The film was then dried at 60 °C for 6 h and 120 °C for 6 h in a vacuum oven. The thickness of the cathode film was approximately 40 μm . The CR2016 type coin cell was assembled in a glove box using the above cathode film, lithium, a porous polyethylene film, and a 1 M LiPF_6 solution in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 vol/vol). The lithium metal foil was used as both the counter and reference electrode. After assembling the coin cells, it was charged and discharged galvanostatically between 2.0 and 4.4 versus Li/Li^+ , at a constant current density (170 mA g^{-1} was assumed to be 1C rate). The CV

curves were obtained at 0.05 mV s^{-1} and between 2.0–4.3 V. All the electrochemical measurements were carried out at 25 °C. Electrochemical impedance spectroscopy (EIS) was carried out at room temperature after assembling the coin cell using frequencies from 0.01 Hz to 0.1 MHz and an alternating-current amplitude of 10 mV by using coin cell (to electrode). Nyquist plots (Z' vs $-Z''$) were collected and analyzed using Zplot and Zview software. Differential scanning calorimeter (DSC) samples for the cathode were prepared by the following treatment before test. The cells containing the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrode were charged to 4.4 V at a current density of 17 mA g^{-1} , and it was held at that potential until the current density reached 1.7 mA g^{-1} . Then, these cells were disassembled in a dry room to remove the charged positive electrode. The positive electrode (4.5 mg) and little fresh electrolyte (3 μL) were sealed in a high pressure DSC pan at a rate of 50 mL min^{-1} under flowing air and nitrogen. Presumably this is associated with reason for addition of the electrolyte between the cathode and the electrolyte in order to observe the exothermic reaction. The heating rate and temperature range of the DSC tests were 5 °C/min and 25–350 °C, respectively.

Results

Powder Characterization.

Microscopic Examination $\text{Ni}_{0.85}\text{Co}_{0.15}(\text{OH})_2$ Precursor:

Figure 1 shows the microscopic images and SEM images of the $\text{Ni}_{0.85}\text{Co}_{0.15}(\text{OH})_2$ precursor. Co-precipitation of $\text{Ni}_{0.85}\text{Co}_{0.15}(\text{OH})_2$ was carried out continuously in a CSTR reactor and the morphology change of the products was monitored regularly by an optical microscope. At the beginning of the reaction, mainly fine particles were formed and then combine with each other to form irregular-shaped and micron-sized agglomerates. The particles grew gradually into a uniform spherical morphology without further agglomeration. After 32 h of precipitation, a steady state was reached, in which the particle size ranges from 5 to 8 μm . Finally, the particles obtained after 40 h of precipitation had a spherical shape. It was obvious that $\text{Ni}_{0.85}\text{Co}_{0.15}(\text{OH})_2$ powders had

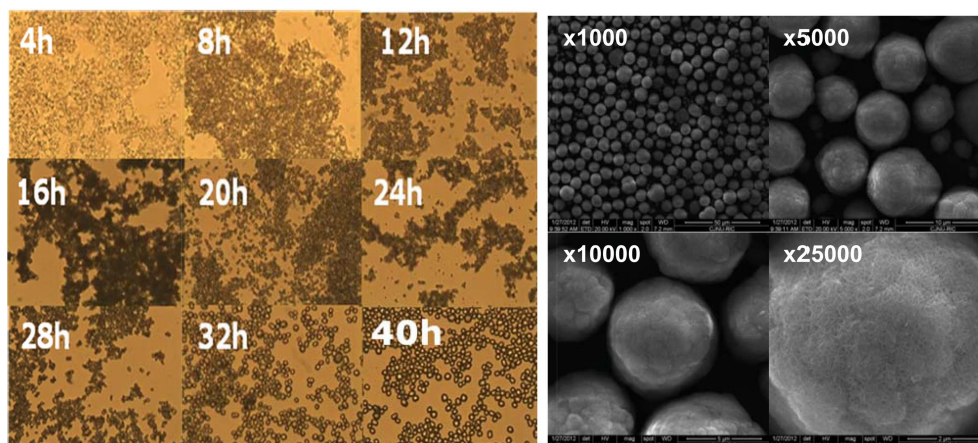


Figure 1. Optical microscope images and electron micrographs of the $\text{Ni}_{0.85}\text{Co}_{0.15}(\text{OH})_2$ precursor as a function of time.

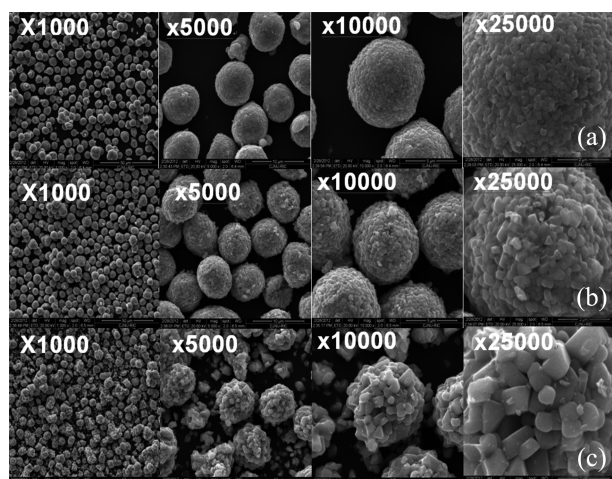


Figure 2. SEM images of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders prepared at (a) 750, (b) 800, and (c) 850 °C for 10 h.

spherical morphology in the secondary particles and the estimated particle size was about 5–8 μm in diameter, while the primary particles were round shaped and densely agglomerated in secondary forms.

Morphology of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ Particles: Figure 2 shows SEM images of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ as a function of calcination temperature. The powders which large 5–8 μm sized sphere secondary particle, comprise primary small particles that were composed of smooth-edged 0.2–0.5 μm sized polyhedral primary particles. The secondary particle size unchanged, but the primary particle size increased gradually from 0.2 μm at 750 °C to 0.3 μm at 800 °C while significant particle size growth to 0.5 μm and more edged at 850 °C. The primary particle size of the lithiated powders increased and edged with increasing calcination temperature, in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, which indicated decreasing surface area.

Structural Characterization of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ Particles: The XRD patterns of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ materials in terms of calcination temperature are shown in Figure 1. The lattice parameters shown in Table 1 were calculated using XRD analysis software (TOPAS 4.1). All peaks corresponded to a layered $\alpha\text{-NaFeO}_2$ structure of space group $R\bar{3}m$. The $I_{(003)}/I_{(104)}$ ratio has been used as an indicator of cation mixing,¹⁷ that is, values lower than 1.3 indicate a high degree of cation mixing, due to occupancy by other ions in the lithium interslab region¹⁸ and the reversible capacity of the cathode material tends to decrease when the ratio is less than 1.2.^{19–21} In this work, the calcined at 750 °C sample shows the highest ratio $I(003)/I(104)$ of 1.65, indicating that this sample has the lowest amount of cation mixing, meaning a very small concentration of Ni^{2+} ions in the Li (3b) interlayer sites. However, as the calcination temperature increases to 850 °C, the ratio of $I(003)/I(104)$ decreases dramatically, indicating that this sample has a high cation mixing. According to Reimers *et al.*,²² the R -factor, defined as the ratio of the sum of the intensities of the hexagonal characteristic doublet peaks (0 0 6) and (0 1 2) to that of (1 0

Table 1. The lattice parameter, R -factor and peak ratio (003) to (104) in the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders as a function of calcination temperature

T (°C)	Lattice parameter		c/a	(003)/(104)	R-factor
	a (Å)	c (Å)			
(a) 750	2.8666 (± 0.0001)	14.1828 (± 0.0006)	4.947	1.65	0.44
(b) 800	2.8659 (± 0.0001)	14.1840 (± 0.0008)	4.949	1.62	0.44
(c) 850	2.8671 (± 0.0001)	14.1790 (± 0.0009)	9.945	1.52	0.43

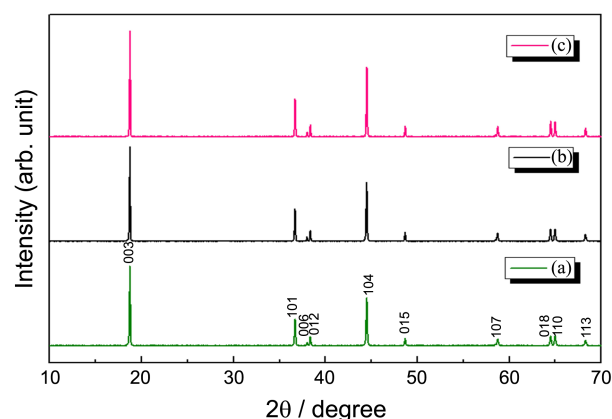


Figure 3. XRD patterns of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders prepared at (a) 750, (b) 800, and (c) 850 °C for 10 h.

1) peak can be utilized to estimate hexagonal ordering [$I(0\ 0\ 6) + I(0\ 1\ 2)/I(1\ 0\ 1)$], and the lower the R -factor, the better the hexagonal ordering. In this study, the R -factors were 0.44, 0.44 and 0.43 for the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ sintered at 750, 800 and 850 °C, respectively. The values were low and similar regardless of the heating temperature, which indicated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ materials calcined in this work had a strong hexagonal structural ordering.²³

Electrochemical Behavior.

Cyclic Voltammetry (CV): Figure 4 shows the CV results at various temperatures for 10 h. The half-cells made of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode with a lithium anode were slowly cycled between 3.0 and 4.3 V at a scan rate of 0.05 mVs^{-1} . There was a distinct difference in the peak width and the peak positions among the graphs. It is widely believed that the peaks in CV of the cathode material are closely related with the phase transitions occurring with the lithium intercalation; monoclinic (M) to rhombohedral (R2) phase around 4.0 V, and again to another rhombohedral (R3) phase near 4.2 V.²⁴ The second and third oxidation peaks in the CV diminished in intensity with increasing heat temperature, which was attributed to lowest cation mixing of the 750 °C prepared sample easing the phase transition. The major reduction peak locating at 3.7 V of the 750 °C calcined sample was slightly higher than that of sample calcined at 800 and 850 °C in the CV results. Possibly, this behavior implies that calcination at 750 °C, which has the lowest cation mixing,

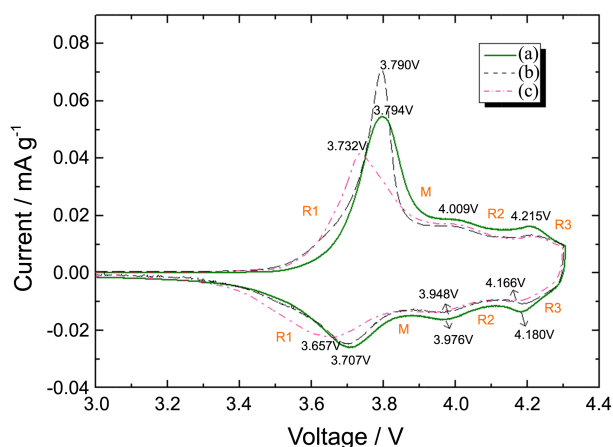


Figure 4. Cyclic voltammetry (CV) cycled between 3.0 and 4.3 V at a scan rate of 0.05 mV/s of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders prepared at (a) 750, (b) 800, and (c) 850 °C for 10 h.

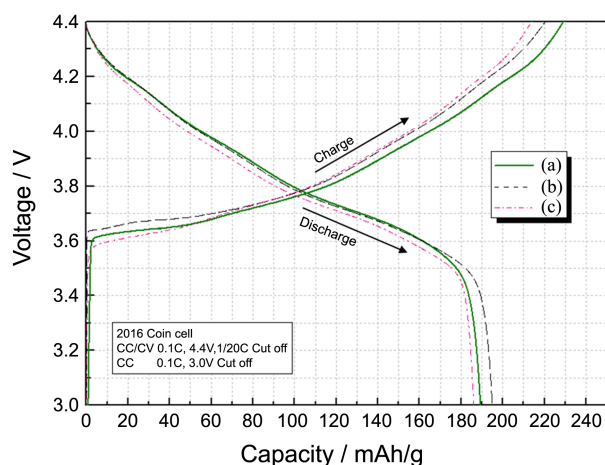


Figure 5. Initial charge/discharge curves for the cells at a current density of 17 mA g^{-1} prepared at (a) 750, (b) 800, and (c) 850 °C for 10 h.

prevented the structural change of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ or reaction with electrolyte on cycling.

Initial Charge-discharge: Figure 5 shows the initial charge/discharge curves for the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cells at a current density of 170 mA g^{-1} . The initial discharge capacity for the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ heat treated at 750 °C was 189 mAh g^{-1} , and the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cells heat treated at 800 and 850 °C gave a discharge capacity of 194 and 186 mAh g^{-1} , respectively. The discharge capacity of the sample sintered at 850 °C is lower than others. One of the possible reasons for this phenomenon is due to the evaporation of Li. So, the elemental analyses of the as-prepared samples were performed using AES-ICP analysis. As indicated in Table 2, components Li, Ni, Co and Al were detected for all samples. The amounts of Ni, Co and Al were little difference for all samples. It was the difference in the relative content, while the amount of Li was apparently different. The deduced formulas for all the samples were also listed in term of the measured results of atom ratio of AES-ICP.

Another characteristic that was found that was a distinct

Table 2. Chemical composition of calcined samples determined by AES-ICP

Calcination temperature (°C)	Molar ratio			
	Li	Ni	Co	Al
1. 750	1.052	0.8156	0.1456	0.0486
2. 800	1.038	0.8105	0.1460	0.0434
3. 850	0.979	0.8063	0.1423	0.0409

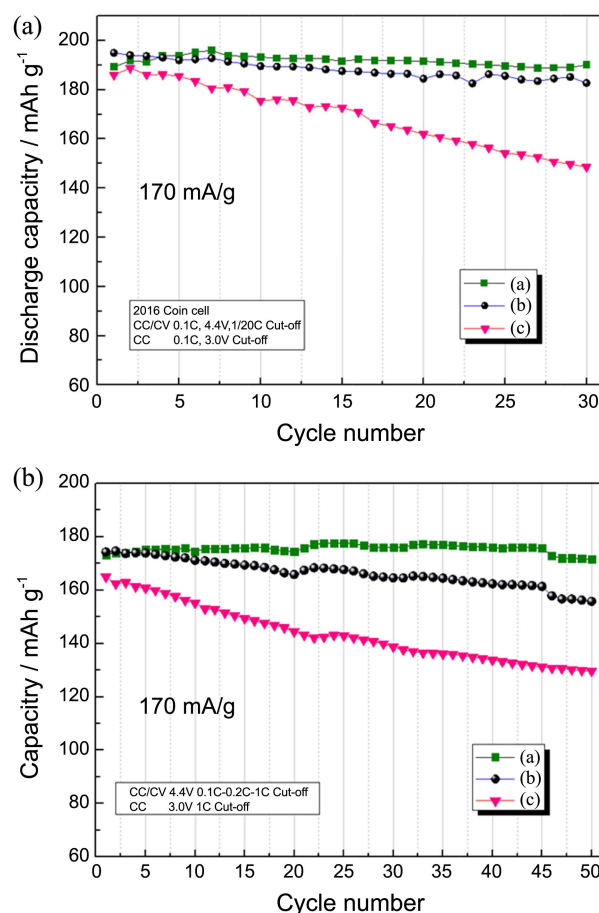


Figure 6. Cyclic performance of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cells between 3.0 and 4.4 V with a current density at (a) 0.1C (17 mA g^{-1}), and (b) 1C (170 mA g^{-1}).

plateau in the charge/discharge curves. The plateau correspond to structural changes in the charge/discharge process, a phase transitions between a monoclinic phase and a hexagonal phase and a transitions between a hexagonal phase and another hexagonal phase, which is characteristic of Ni-rich materials.²⁵

Cycle Performance: Figure 6 shows the cycling performance of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrode according to heat-treatment temperatures at 0.1 (a) and 1 C (b). The $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ materials calcined at 750, 800 and 850 °C at 0.1 C (a) delivered initial discharge capacities of 189, 194 and 186 mAh g^{-1} , respectively. The capacity retentions of each cathode material after 30 cycles were 100%, 93% and 73%, respectively. On the other hand, the $\text{LiNi}_{0.8}\text{Co}_{0.15}$

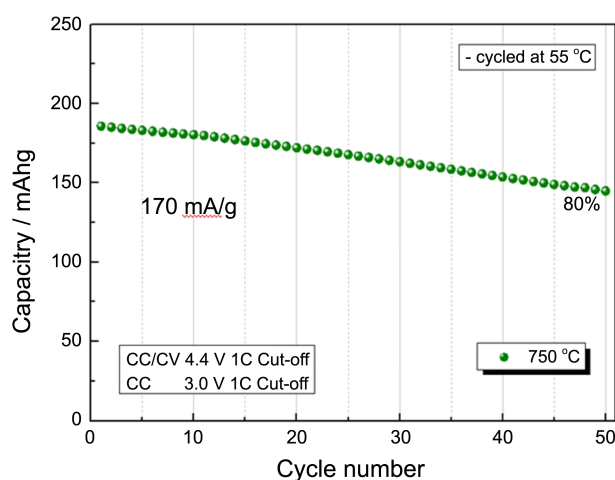


Figure 7. Cyclic performance of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ prepared at 750 °C cells at a current density of 170 mA g^{-1} (1C) between 3.0 and 4.4 V at 55 °C.

$\text{Al}_{0.05}\text{O}_2$ materials calcined at 750, 800 and 850 °C at 1 C (b) delivered an initial discharge capacity of 173, 174 and 164 mAh g^{-1} , respectively, with a capacity retention of each cathode material after 50 cycles of 98%, 89% and 78%, respectively. The $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ material calcined at 750 °C exhibited relatively high initial capacity of 189 and 173 mAh g^{-1} at 0.1 (a) and 1 C (b), showing highest capacity retention of 100 and 98%, respectively. These results can be attributed to the enhanced structural stability and minimized cation mixing reflected by the highest $I_{(003)}/I_{(104)}$ value shown in Table 1.

Figure 7 shows the Cyclic performance curves of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ prepared at 750 °C cells at a current density of 170 mA g^{-1} (1C) between 3.0 and 4.4 V at 55 °C. The electrode showed a gradual decrease in capacity, leading to a capacity retention of 80% after 50 cycles. The capacity retention of the cathode powders at the high temperature of 55 °C are lower than those obtained at room temperature. We believe that the decay of the capacity retention is due to not only surface structural degradation but also electrolyte decomposition at 55 °C.

Differential Capacity Versus Cell Voltage: The differential capacity versus cell voltage diagram describes the ‘capacity density’, dQ/dV , at a specific voltage during galvanostatic charge/discharge process. In other words, it simply contributes to the total measured capacity. The difference between two diagrams is that CV describes the quasi-equilibrium state of a cathode material with respect to the varying voltage, whereas the differential capacity versus voltage diagram provides a more realistic explanation for the actual state of the cathode material under the galvanostatic cycling. Because the two diagrams share a similarity in their meaning, they show a similar pattern for the same materials. Therefore, the differential capacity versus voltage diagram can be a useful analyzing tool for the galvanostatically cycled cathode material instead of CV.

The differential diagrams for the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cells are shown at Figure 8. The integrated intensity of the first

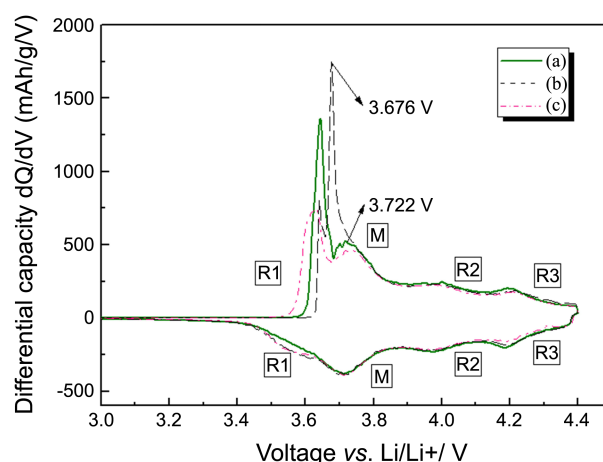


Figure 8. Differential capacity vs. voltage diagrams cycled between 3.0 and 4.4 V at a current density of 17 mA g^{-1} prepared at (a) 750, (b) 800, and (c) 850 °C for 10 h.

oxidation peak calcined at 800 °C was lower than that of the samples heat-treated at 750 and 850 °C. On the other hand, the integrated intensity of the second oxidation peak was centered at 3.676 V that value is slight lower than that of CV measure (3.79 V). In addition, the integrated intensity of the oxidation peak calcined at 850 °C showed a smooth phase transition, which was attributed to large cation disorder that prevented uniform structural change by cycling. This result leads us to believe that retarded and non-uniform phase transition calcined at 800 and 850 °C may be a plausible reason to explain the poor cycle performance.

Electrochemical Impedance Spectroscopic (EIS) Studies:

Figure 9 shows the impedance spectra of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ calcined at 750, 800 and 850 °C before cycling at a rate of 0.1C at the 4.4 V charged states. Each of the impedance spectra includes three parts. The semicircle at the high frequencies reflects the resistance for Li^+ migration through the surface film (R_{SEI}) and film capacitance (C_{SEI}). The semicircle at medium to lower frequencies presents the charge-transfer resistance (R_{CT}) and interfacial capacitance between the electrolyte and electrodes (C_{CT}). The sloping line at low frequencies reflects Li^+ diffusion in the solid-state

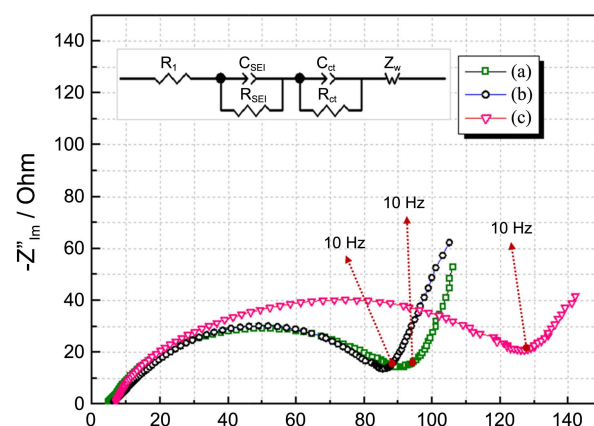


Figure 9. Nyquist plots of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cells prepared at (a) 750, (b) 800, and (c) 850 °C for 10 h.

Table 3. Resistance values in the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cells as a function of calcination temperature

	$R_{\text{SEI}} (\Omega)$	$R_{\text{ct}} (\Omega)$
(a) 750 °C	10.38	87.5
(b) 800 °C	24.16	89.26
(c) 850 °C	46.47	128.7

electrode (Z_w).

Simplified equivalent circuits models (the inset of Figure 9) are constructed to analyze the impedance spectra. In the models, R_1 is the bulk resistance, which reflects the combined resistance of the electrolyte, separator, and electrodes in the cell. According to the studies by Chen *et al.*²⁶ on the EIS of lithium ion cells, cell impedance is mainly attributed to cathode impedance, especially charge-transfer resistance.

As shown in Table 3, the R_{SEI} and R_{CT} values of the sample calcined at 750 °C were much smaller than those of the samples calcined at 800 and 850 °C. Increased surface film and charge-transfer resistances are indicative of the formation of a larger fraction of the non-conducting interfacial films as a result of side reactions with electrolytes.

The low frequency region of the straight line is attributed to the diffusion of the lithium ions into the bulk of the electrode material, the so-called Warburg diffusion.

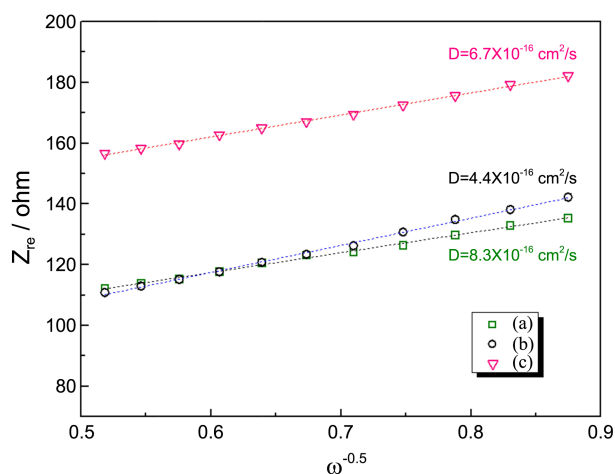
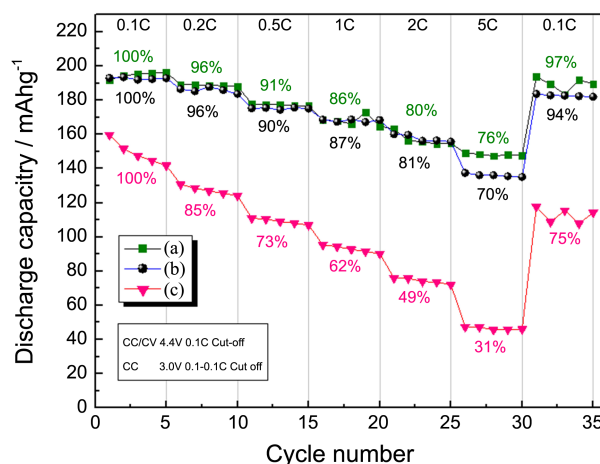
In fact, EIS may be considered as one of the most sensitive tools for the study of differences in the electrode behaviour due to surface modification. The plot of the Z_{re} vs. the reciprocal square root of the lower angular frequencies is illustrated in Figure 10. The straight lines are attributed to the diffusion of the lithium ions into the bulk of the electrode materials, the so-called Warburg diffusion. This relation is governed by Eq. (1). It is observed that the Warburg impedance coefficient (σ) is $65.527 \Omega \text{ cm}^2 \text{ s}^{-0.5}$ for sample (a), and this is the lowest value in comparison with those of the other samples. Also, the diffusion coefficient values of the lithium ions in the bulk electrode materials are calculated using Eq. (2). The equation for the calculation of D_{Li} values by EIS can be expressed as:^{27,28}

$$Z_{\text{re}} = R_{\text{ct}} + R_s + \sigma \omega^{-0.5} \quad (1)$$

$$D_{\text{Li}} = \frac{(RT)^2}{2(An^2F^2C_{\text{Li}}\sigma)^2} \quad (2)$$

Where T is the absolute temperature, R the gas constant, n the number of electrons per molecule during oxidation, A the surface area (1 cm^2), F the Faraday's constant, C_{Li} the concentration of lithium ion, ω the angular frequency, and σ the Warburg factor which has relationship with Z_{re} . The $Z_{\text{re}} - \omega^{-1/2}$ plots are presented in Figure 10. A linear characteristic could be seen for both curves. According to Eqs. (1) and (2), D_{Li} values of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ materials calcined at 750, 800 and 850 °C were calculated to be approximately $8.3 (\pm 0.9) \times 10^{-16}$, $4.4 (\pm 0.9) \times 10^{-16}$ and $6.7 (\pm 0.7) \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$, respectively. The obtained diffusion coefficient ($8.3 (\pm 0.9) \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$) for cell (a) explains the higher mobility for Li^+ ion diffusion in this cell rather than the other cells. Therefore, the charge-transfer reaction is stronger in the electrode (750 °C) than in the other electrodes. The cycling characteristics are also affected by particles properties such as particle morphology and electronic/ionic conductivity.

Rate Capability Studies (C-rate): Rate capability is one of the most important electrochemical characteristics of lithium secondary battery required for EVs and renewable energy storage application. Figure 11 shows the discharge capacities of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cells calcined at various temperature as a function of C rate (1C corresponds to 170 mAhg^{-1}) between 3.0 and 4.4 V. The cells were charged galvanostatically with a current density of 0.1C (17 mAhg^{-1}) before each discharge and were then discharged at a C-rate ranging from 0.1C to 5C. As observed in Figure 11, two materials calcined at 750 and 800 °C showed similar electrochemical performance at low C rate. However, with increasing C rate, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ calcined at 750 °C delivered a higher discharge capacity than that of sample calcined at 800 °C. For instance, the discharge capacity of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ calcined at 750 °C at a 5C rate was 149 mAhg^{-1} , compared to only 137 mAhg^{-1} when calcined at

**Figure 10.** $Z_{\text{re}} - \omega^{-1/2}$ plots of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cells prepared at (a) 750, (b) 800, and (c) 850 °C for 10 h.**Figure 11.** Rate capability test of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cells prepared at (a) 750, (b) 800, and (c) 850 °C for 10 h.

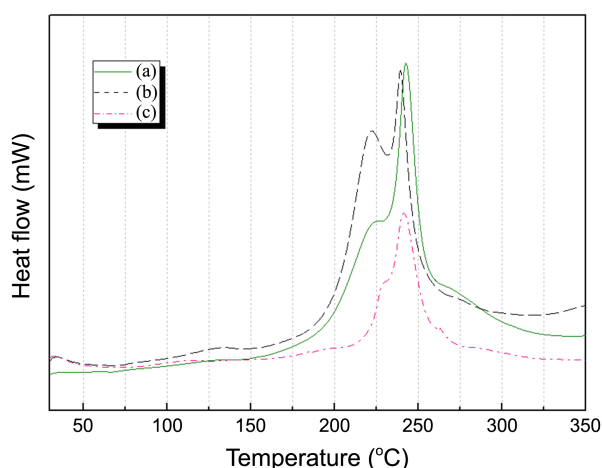


Figure 12. Differential scanning calorimetry (DSC) profile of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cells at charged at 4.4 V as a function of calcination temperature.

800 °C. $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ calcined at 850 °C showed extremely low discharge capacity regardless of C rate. This result encourages us to believe that the structure and surface of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ calcined at 750 °C does not block Li^+ intercalation but rather functions as an expediter for Li^+ transport to the host structure as a result of the reduced interfacial resistance between the cathode and the electrolyte.

DSC Analysis: The thermal stability of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrode as a function of heat treatment was investigated using DSC analysis. The thermal stability of cathode materials, especially in a charged state, is an important factor for the practical application of a lithium battery system. Figure 12 shows the DSC scan of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrode calcined at 750, 800 and 850 °C at a charged state to 4.4 V. The peaks below 130 °C may be related to the decomposition of organic compounds residing on the particle surface.^{29,30} The peak below 130 °C increased in intensity with increasing heat temperature, which is in good agreement with the EIS analysis of thicker solid electrolyte interphase (SEI) film. The sample calcined at 750 °C started thermal reaction with the electrolyte at around 170 °C and generated heat continuously to over 300 °C. The DSC profile of the sample calcined at 850 °C displayed superior thermal stability to that of the samples calcined at 750 and 800 °C. The onset temperature was shifted to a higher temperature of 240 °C, and heat generation was decreased to 202 J/g showing that the SEI film effectively retarded the reaction between the electrode and the electrolyte in a charged state and enhanced the thermal stability of the electrode. The reduced surface area of the sample calcined at 850 °C was one of the reasons preventing the reaction with the electrolyte. However, the sample calcined at 850 °C showed very poor electrochemical property in the previous work. Another reason for this phenomenon might be the reduction oxygen evolution by disorderness increase of crystal structure including cation mixing. The elucidation of this phenomenon requires further research works in the future.

Conclusions

In this study, layered $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode materials were synthesized via the co-precipitation method. The morphology of the prepared powders consisted of spherical agglomerates with a particle diameter varying from 5–8 μm . The diffraction of $I_{(003)}/I_{(104)}$ lines was 1.65, 1.62 and 1.52 for samples prepared at 750, 800 and 850 °C, which was evidence for cation mixing of Li and Ni in the host structure with increasing heat-treatment temperature. The $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ material calcined at 750 exhibited a relatively high initial capacity of 189 and 173 mAhg^{-1} at 0.1 and 1 °C, and showed the highest capacity retention of 100 and 98%, respectively, which was attributed to the enhanced structural stability and minimized cation mixing reflected by the highest $I_{(003)}/I_{(104)}$ value. In the EIS results, the R_{SEI} and R_{CT} values of the sample calcined at 750 °C were much smaller than those of the samples calcined at 800 and 850 °C. This result suggests that an increased surface film and charge-transfer resistances are indicative of the formation a larger fraction of non-conducting interfacial films as a result of side reactions with the electrolytes. The DSC profile of the sample calcined at 850 °C displayed superior thermal stability to that of the sample calcined at 750 and 800 °C, because the SEI film effectively retarded the reaction between the electrode and the electrolyte in a charged state and enhanced the thermal stability of the electrode. However, the sample calcined at 850 °C did not show good electrochemical property.

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