



Electrochemical Properties of High Nickel Content $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1})\text{O}_2$ with an Alumina Thin-Coating Layer as a Cathode Material for Lithium Ion Batteries

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The cathode material, high Nickel content $\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}$ (NCM), was synthesized by co-precipitation with NH_4OH used as a complexing agent. The prepared materials are made in the formation of spherical particles of $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1})\text{O}_2$ of several micrometers in diameter. Al_2O_3 was coated by an impregnation method and its content was gradually increased to 1, 2 and 5 wt%. As a result, 1 wt% coated Al_2O_3 compared to pristine NCM exhibited 82% and 80% retention rates at 5 C and 1 wt% Al_2O_3 coated NCM recovery at 0.2 C after 5 C showed 100%. In addition, capacity retention of 1 wt% NCM + Al gently decreased in 100 cycle life characteristics, and capacity retention of 95% or more was confirmed.

Keywords: Lithium Ion Secondary Battery, Cathode Surface Coating, Alumina Coating Materials, Electrochemical Performance, Cathode Material.

1. INTRODUCTION

Clean energy power sources—The power of wind, hydro and tidal—can be considered as alternative energy sources to conventional fossil fuels. However, most of these resources cannot be controlled, and to store and regulate energy is difficult because of intermittent characteristics. Maintenance costs are also high, so they cannot be considered a complete solution [1–3].

Li-ion rechargeable battery system has been the most attractive area in the past 20 years in the field of electrochemistry. Lithium-ion batteries (LIBs) are used in high-demand environments where there is an urgent need for more efficient use of energy from the supply of finite resources that are likely to be depleted [4–7]. High energy density and a relatively simple reaction mechanism are considered as some of the beneficial characteristics of LIBs. Today, they are used in large-scale applications, including electric vehicles (EVs) as well as most portable electronic products. They are a core resource of mobile energy and a means of environmental-friendly

transportation and energy storage (plug-in hybrid electric vehicles (PHEVs), hybrid electric vehicles (HEVs), and energy storage systems (ESSs). It is required to increase the densification of energy and power through material engineering in the battery system to increase battery performance. In addition, it is needed to intensively study the development of lithium-ion battery materials to solve the problem of cycle life and safety [8–10].

Since the theoretical capacity (~ 280 mAh/g) of the layered lithium transition metal oxide shows the highest capacity when compared with the spinel-type (~ 150 mAh/g) and olivine type (~ 170 mAh/g), it is widely used as a very important cathode material [11]. The capacity per unit volume is considered to be more important than the weight because the cathode and anode are packed in cells of a certain size [8]. Among the transition metals in the layered structure, NCM-based cathode active materials have been actively studied because of the excellent electrochemical performance of LiCoO_2 (LCO), economical cost of LiNiO_2 (LNO) and stability of LiMn_2O_4 (LMO) [11].

Despite these advantages, Ni^{2+} (0.69 Å) ions, which are similar in size to Li^+ (0.76 Å) ions in the high-temperature

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synthesis process, occupy the lithium layer in the layered structure as the Ni content increases. This phenomenon, called cation mixing, is caused by the formation of a rock-salt of Ni–O, which causes local electrochemical reactions to disappear and interferes with the movement of lithium ions. The electrochemical performance of the battery is therefore adversely affected. Since the rate of increase of cation mixing generally increases as the content of Ni increases, studies are underway to control the synthesis conditions of the NCM composition in order to alleviate this problem [12–18].

Herein, $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1})\text{O}_2$, which is a layered system, was synthesized and Al_2O_3 was layered on the surface of NCM to extend and improve the quality of performance lifetime and its properties have been observed by the change of electrochemical characteristics [19].

2. EXPERIMENTAL DETAILS

2.1. Co-Precipitation Synthesis

Figures 1(A)–(C) shows that the synthetic process of creating cathode materials and adding Al_2O_3 coating and gradient of concentration in the cathode material. Co-precipitation synthesis was carried out as a method for synthesizing $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1})\text{O}_2$. Co-precipitation synthesis is a synthetic method that relieves local electrode deterioration, a phenomenon that occurs due to the different oxidation and reduction potentials of the transition metal ions. Co-precipitation relieves the instability of charging and discharging, which occurs with irregular particle shape. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, a nickel precursor, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, a manganese precursor, and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, a cobalt precursor, were used as precursors for the co-precipitation synthesis. NaOH was used as a precipitating agent, and NH_4OH was used as a complexing agent.

First, a complexing agent was added to distilled water to adjust the pH to greater than 10 to synthesize the precursor. A proportion of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ is then added to the solution, along with the complexing agent and precipitant and then stirred. Since the uniformity and degree of precipitation of the particles are different depending on how stirring is performed during forming the particles in the coprecipitation process, it is important to stir the particles under a constant condition at the time of stirring. The reaction mixture thus obtained was sufficiently dried in an oven at 105 °C and pulverized using induction. LiOH was selected as a raw material for lithium, and acetone was added thereto at a ratio of Li/M of 1.03:1. After thorough mixing, the base mixture was pyrolyzed at 600 °C for 10 hours using an electric furnace to prepare the $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1})\text{O}_2$ electrode material.

2.2. Coating Method— Al_2O_3

The ratios of Al_2O_3 to $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1})\text{O}_2$ are 1, 2 and 5 wt%. $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1})\text{O}_2$ was dissolved in ethanol (50 mL) and homogeneously mixed for a sufficient time

using a stirrer at a room temperature. Thereafter, the mixture was placed in a crucible and an Al_2O_3 -coated $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1})\text{O}_2$ material was prepared through an electric furnace.

2.3. Surface and Chemical Analysis

The particle size and surface morphology of the $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1})\text{O}_2$ samples were observed by scanning electron microscopy (SEM, JEOL JSM-6490LV, 20 kV) and TEM (Transmission Electron Microscopy, Tecnai G² 200 kv FEI) [20]. BET (Brunauer-Emmett-Teller, Quantachrome QUADRAZORB-SI) surface analysis was performed to calculate the surface area of the NCM spheres by measuring adsorption/desorption of Nitrogen gas molecules. The crystalline phase of these prepared samples was identified with a powder diffractometer (SHIMADZU Lab X XRD-6000) with a graphite-monochromator with Cu K α radiation operating at 40 kV and 40 mA. ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry, Thermo Scientific iCAP 7000) was used to confirm the molecule structure and chemical composition of the cathode active material [21].

2.4. Sample Preparation and ICP-OES Analysis

In order to analyze the NCM ratio of the samples, they are digested in mixing an acidic solution of HNO_3 and HCl (1:3) at 180 °C on the hot plate. After changing the clear solution, the concentration of samples is determined by ICP-OES.

2.5. Electrochemical Performance

A CR2032 coin cell was fabricated to determine the electrochemical characteristics of the electrode material. The cathode parts were prepared by blending these materials— $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1})\text{O}_2$, Super-P, and polyvinylidene fluoride (PVdF, Kureha KF-1100) as a binder in a weight ratio of 80:10:10. These mixed materials are dissolved in NMP (*N*-methyl-2-pyrrolidone, Sigma Aldrich, 99.5%) solution. The electrode slurry obtained through this process was spread on an Al-foil collector in the form of a thin film applied for a doctor blade method. After that, the NMP solution was evaporated and dried sufficiently to obtain an intact film shape, and a pressing process was performed. In addition, the round electrode having a diameter of 16 mm was made using a perforator, and then adequately dried to remove water. The casted electrode was processed in a glove box contained in high purity Argon gas to prevent the oxidation of lithium metal and reactivity with water while making the coin cell. Ethylene carbonate/diethyl carbonate (EC/DEC 1:1 v/v) was employed as a solvent, in which 1M LiPF_6 salt was dissolved. The galvanostatic charge-discharge capacity, rate capability, and cyclic performance were performed at current densities of 0.2 C between 3.0 and 4.3 V versus Li/Li^+ with a multichannel battery performance equipment (TOSCAT-3100, Toyo Co.).

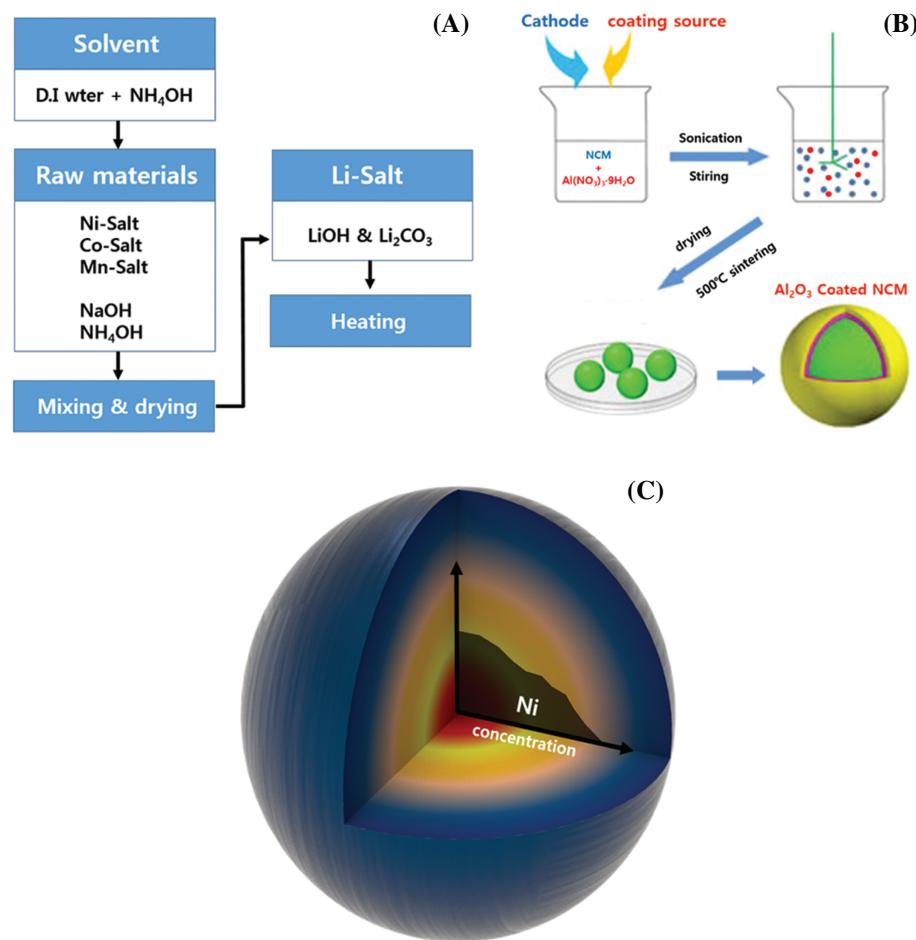


Figure 1. (A) Synthesis process of cathode materials in lithium batteries (B) schematic diagram of Al_2O_3 coating process. The colors shown in the diagram are not meant to be significant. However, the reason for distinguishing colors in the final NCM is Ni, Co, Mn, and Al_2O_3 due to the concentration gradient, respectively. (C) The gradient of concentration in NCM active materials.

3. RESULTS AND DISCUSSION

In Figures 2(A)~(D), SEM images represented the surface morphology and shape of the cathode active material particles according to the ratio of Pristine NCM and coated Al_2O_3 . As a result of analyzing the shape of particles, it was confirmed that particles of $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1})\text{O}_2$ cathode active material prepared through co-precipitation synthesis have a spherical shape of a few micrometers in diameter and are uniformly distributed. In addition, as shown in Table I, the surface of the spherical particles was confirmed by EDS, and it was confirmed that the ratios of Ni, Co, and Mn were uniformly distributed. It is important to distribute spherical particles uniformly because a heterogeneous composition may cause cyclic stability problems due to the occurrence of deterioration phenomena in specific particles. As a result of the EDS measurement of $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1})\text{O}_2$ coated with Al_2O_3 , the Al_2O_3 coating ratio was also confirmed in Table I. TEM images show that Al_2O_3 -coated $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1})\text{O}_2$ cathode active material surface was observed, as shown in Figure 3. It was confirmed that several micron-sized spherical particles

were dispersed well without aggregation in a low magnification TEM image. As a result of the coating through heat treatment, it was confirmed that Al_2O_3 was coated with a thin layer on the outside of spherical particles.

BET measurement was performed to confirm the change of the specific surface area of $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1})\text{O}_2$ cathode active material according to the coating ratio of Al_2O_3 in Table II. The BET was calculated from the amount of nitrogen adsorbed/desorbed using nitrogen as the adsorbent gas. The specific surface area of pristine NCM was found to be $0.188 \text{ m}^2/\text{g}$, $0.213 \text{ m}^2/\text{g}$ and $0.789 \text{ m}^2/\text{g}$, respectively, when the specific surface area was $1.107 \text{ m}^2/\text{g}$ and Al_2O_3 was coated 1 wt%, 2 wt% and 5 wt%. As a result, Al_2O_3 was coated on pristine NCM, and the specific surface area was reduced compared to pristine NCM. When 1 wt% of Al_2O_3 was coated, Al_2O_3 was included in all NCM surface coatings and the smallest specific surface area was $0.188 \text{ m}^2/\text{g}$. As the amount of Al_2O_3 was increased to 2 wt% and 5 wt%, it was found that the residual Al_2O_3 did not participate in the reaction. BET specific surface area was measured in the same manner for the

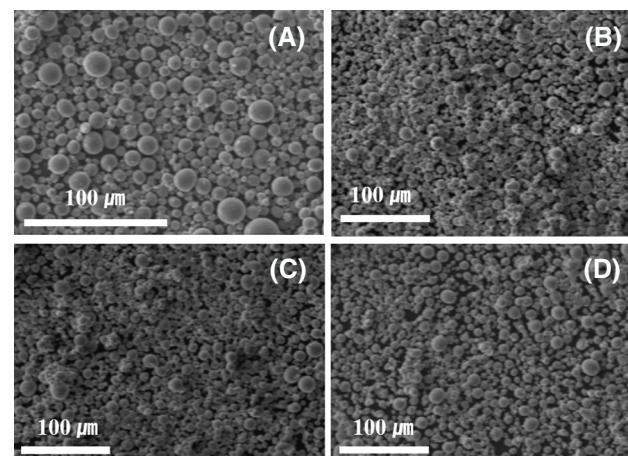


Figure 2. SEM images of Li(Ni_{0.7}Co_{0.2}Mn_{0.1})O₂ without/with coated Al₂O₃. (A) Pristine NCM (B) 1 wt% Al₂O₃ coated NCM (C) 2 wt% Al₂O₃ coated NCM and (D) 5 wt% Al₂O₃ coated NCM.

cathode material, and the specific surface area was found to be high.

X-ray diffraction (XRD) analysis was performed to confirm the structure properties of synthesized pristine Li(Ni_{0.7}Co_{0.2}Mn_{0.1})O₂ and Al₂O₃ coated Li(Ni_{0.7}Co_{0.2}Mn_{0.1})O₂. The results are shown in Figure 4. The main peaks are shown at 18°, 36°, 44° and 48° within 10° to 70° of the theta range, and this result was indexed by ICDD CARD # 66-0856. In particular, no impurity phase was found in the NCM synthesized by increasing the amount of Al₂O₃ coating by 1, 2 and 5 wt%, and it was confirmed that the coated Al₂O₃ was not affected by the structural effect.

ICP-OES analysis was conducted to confirm the chemical composition of the synthesized cathode active material in Table III(a). Prior to the measurement, the sample was subjected to acid decomposition at 180 °C, with a filling factor of 5% and pressure at 5 bar (EPA 3051), by using a microwave in the pretreatment and preparing the sample with deionized water in a 50 mL volumetric flask. This was followed by qualitative and quantitative analysis of ICP-OES. As a result of ICP-OES analysis, it has been observed that the synthesis was similar to the stoichiometric ratio of NCM 7:2:1, which was initially designed,

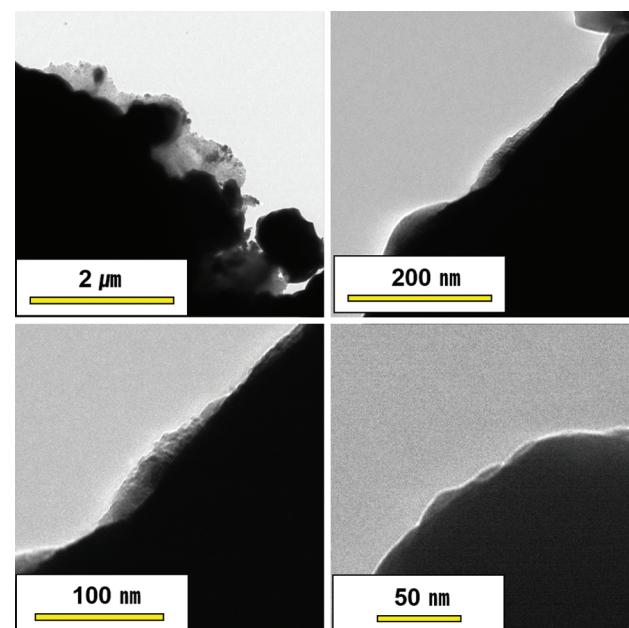


Figure 3. TEM images of 1 wt% Al₂O₃-coated Li(Ni_{0.7}Co_{0.2}Mn_{0.1})O₂ cathode active material surface.

as shown in Table III(b). A slight difference in the ratio can be confirmed by the range of error in the ICP-OES measurement. The Method Detection Limit of the equipment used for the analysis is 2 mg/kg, with any content below that labeled as not detected (Not Detected, N.D.). It is very important to manage the concentration of impurities because impurities cause electrochemical effects such as deterioration of the capacity and cycle stability in the battery system. It was confirmed that the impurity content was below the reference value when compared with the standards required for the commercialized cathode active material, and it was considered that the impurities measured at the time might be attributable to the influence of the reagent or test environment used in the synthesis.

The charging and discharging characteristics of Li(Ni_{0.7}Co_{0.2}Mn_{0.1})O₂ coated with the Al₂O₃ were confirmed by examining what kind of electrochemical property changes the coating layer caused, as shown in Figure 5(A). The voltage range was limited to between 3.0~4.3 V. The current density was measured at 0.2 C. The discharge capacities of Pristine NCM, NCM + 1 wt% Al, NCM + 2 wt% Al and NCM + 5 wt% Al at 0.2 C were 192, 190, 192 and 185 mAh/g, respectively. There was no significant difference in the discharge capacity of one cycle except when Al₂O₃ was coated at 5 wt%. In general, an increment in the surface modulus leads to a

Table I. SEM-EDS results of element contents (%) at the multi-points.

Elements	Spectrum			
	569	570	571	572
C	7.51	3.58	7.00	3.73
O	44.27	12.33	43.43	15.44
Cr	0.27	0.44	0.91	0.47
Mn	1.83	2.91	1.87	3.10
Fe	1.11	2.12	1.15	1.74
Co	5.70	9.88	5.80	9.53
Ni	39.32	68.75	39.84	65.98
Total	100	100	100	100

Table II. BET results of pristine NCM and alumina coated NCMs.

	Pristine NCM	NCM + Al 1 wt%	NCM + Al 2 wt%	NCM + Al 5 wt%
Surface area (m ² /g)	1.107	0.188	0.213	0.789

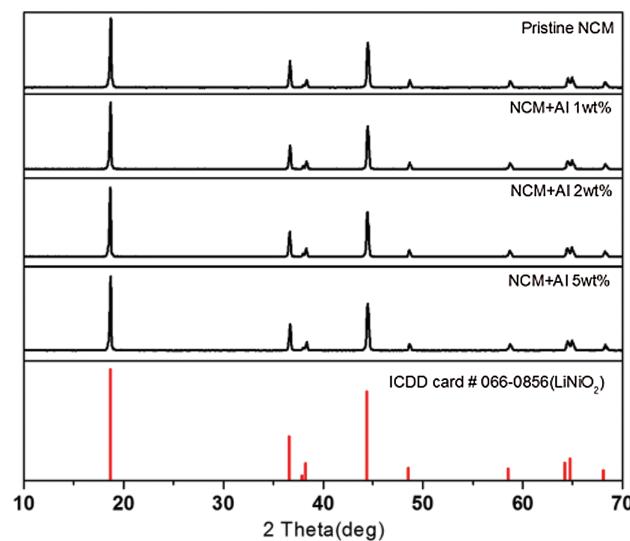


Figure 4. XRD results of pristine NCM and alumina coated NCMs.

reduction in the amount of active material showing a direct charge/discharge capacity, so that a small amount of the capacity reduction is attributable to this property.

As a result of evaluating the reliability and stability of the battery, the rate characteristics were evaluated in order to confirm the output characteristics as the charge/discharge speed was changed in Figure 5(B). The measurement conditions were as follows. The current density on the charge was fixed at 0.2 C, and the current density on discharge was changed to 0.2, 0.5, 1, 2, and 5 C. The C-rate was increased in Pristine NCM, NCM + Al 1 wt%, NCM + Al 2 wt% and NCM + Al 5 wt% samples. Notable results were that the Pristine NCM and 1 wt%

of NCM + Al showed capacity retention rates of 80% and 82%, respectively, compared to the initial 0.2 C discharge capacity. In addition, at the recovery stage returning to 0.2 C after 5 C, the recovery rate of NCM + 1% Al showed a 100% capacity recovery rate. The electrochemical improvement results obtained by coating Al₂O₃ are known to be closely related to the toughness of the surface-modified oxide material. In general, the coating material is not entirely covered with the entire surface of the cathode active material, but only a local portion is coated. Such a coating material is known to change the surface energy under or around the coating film in order to prevent elution of the transition metal. Particularly, NCM, which is a layered cathode material in which lithium is deintercalated, can easily collapse from the surface during overcharging, thereby causing an exothermic reaction, deteriorating the safety of the battery. That is, by stabilizing the structure through the coating and surface modification of Al₂O₃, which is a stable material, it exhibits an effect of suppressing phase transition by increasing the activation energy for the structural collapse and phase transition reaction occurring from the surface [22].

In Figure 5(C), the life cycle characteristics of 100 cycles were evaluated to confirm the stability improvement of the cycle for Al₂O₃ coating, which is known as a stable material. The voltage range was between 3.0 and 4.3 V. The current density was tested at 0.2 C as in the charge/discharge evaluation. The initial discharge capacity of Pristine NCM was 180 mAh/g, which was higher than the samples coated with Al₂O₃. However, the discharge capacity steadily decreased due to the progress of the cycle. After 100 cycles, the initial discharge capacity was 162 mAh/g. Its capacity of the sample coated with 1 wt% of Al₂O₃ was 175 mAh/g, which was lower than that of pristine NCM. However, the capacity decrease was diminished when the cycle proceeded, especially after 30 cycles. Al₂O₃ coated with 2 and 5 wt% of the sample also had lower initial capacity than pristine NCM, but the initial capacity decrease until 50 cycles was gentle, and after 100 cycles, the capacity retention rate of 2 and 5 wt% was 93 and 89%, respectively. The stability of the Al₂O₃ coated samples was improved by evaluating the lifetime characteristics of the electrochemical properties. The reason for the improvement of lifetime characteristics of the cathode active material through the coating is that Al₂O₃ diminishes the contact area between the cathode active material and the electrolyte to prevent the formation of surface films to disturb the diffusion of Li⁺ ions such as ROLi and ROCO₂Li on the surface of the cathode active material [19, 23, 24]. In this study, it was shown that a sample coated with 1 wt% of Al₂O₃ exhibited excellent electrochemical properties. When the content is more than 1 wt%, the remaining uncoated coating material acts as an impurity or exists in an excessive amount, which interferes with a basic charge/discharge reaction or acts as a factor to

Table III. ICP results of impurities (a) and main elements of Al coated NCMs (b).

	(a)				
	Pristine NCM	NCM + Al 1 wt%	NCM + Al 2 wt%	NCM + Al 5 wt%	Commercial Spec.
Ca	91	57	41	55	<50
Cd	N.D.	N.D.	N.D.	N.D.	<2
Cr	N.D.	N.D.	N.D.	N.D.	<2
Cu	N.D.	N.D.	N.D.	N.D.	<2
Fe	16	5	5	6	<5
Mg	19	14	11	16	<50
Na	N.D.	374	421	526	<250
Si	28	N.D.	N.D.	N.D.	<50
Zn	N.D.	N.D.	N.D.	N.D.	<2

	(b)				
Element	Pristine NCM	NCM + Al 1 wt%	NCM + Al 2 wt%	NCM + Al 5 wt%	
Al	–	0.0215	0.0661	0.2671	
Ni	29.0	25.6	22.8	32.9	
Co	3.0	1.8	1.8	2.6	
Mn	1.5	1.7	1.5	1.7	

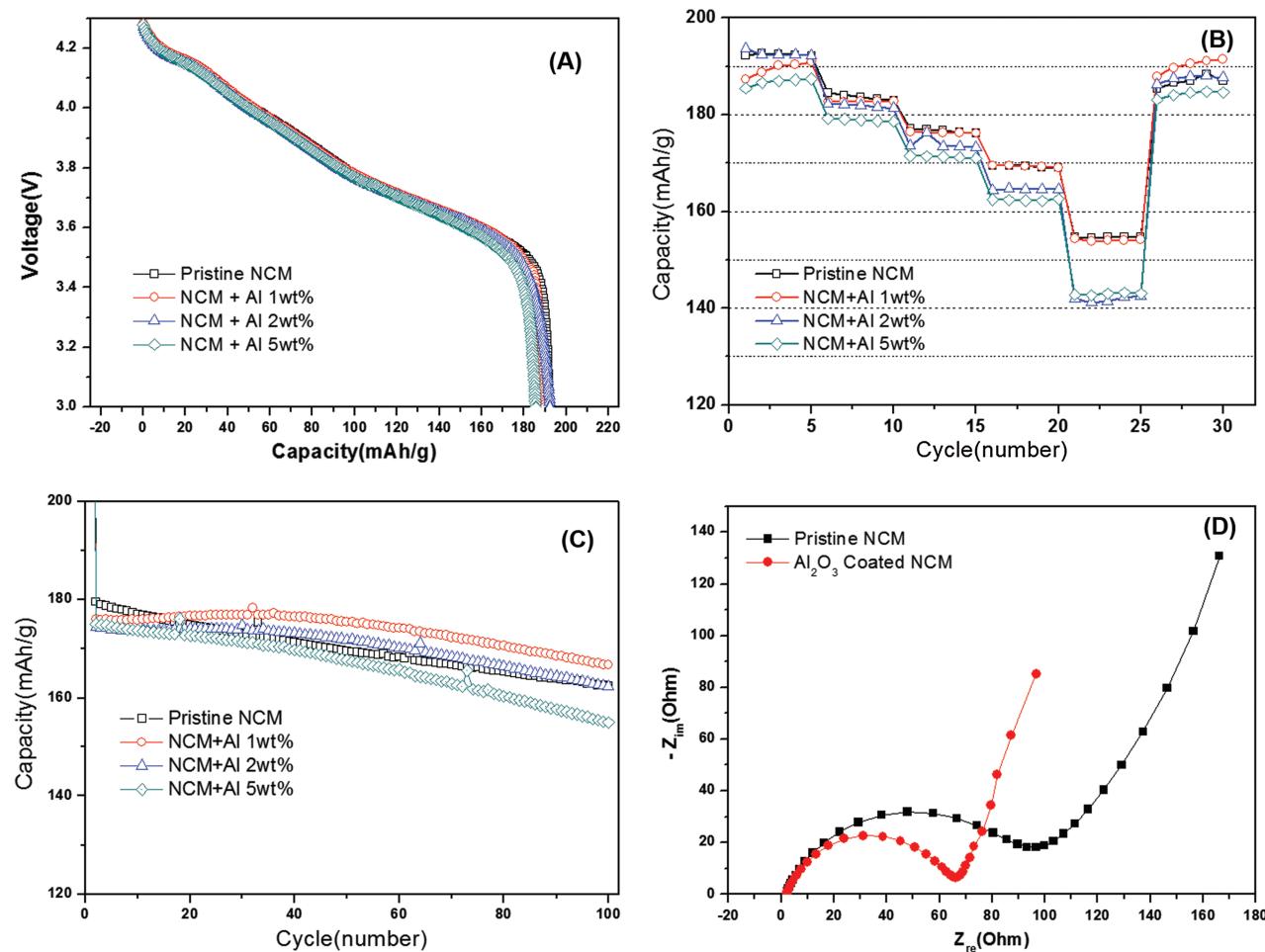


Figure 5. Electrochemical properties of pristine NCM, NCM + 1 wt% Al, 2 wt% Al and 5 wt% Al. (A) Galvanostatic discharge profiles (B) rate capability performance (C) cycling and (D) electrochemical impedance analysis data.

increase resistance, resulting in low electrochemical performance.

Electrochemical Impedance Spectroscopy (EIS) can determine the electrochemical characteristics and inside the structure with the highest accuracy. The electrochemical impedance spectroscopy of both samples was performed in the frequency range from 0.1 to 100 kHz to check the difference of electrochemical performance of these two samples. Figure 5(D) shows typical Nyquist plots of Li(Ni_{0.7}Co_{0.2}Mn_{0.1})O₂ and Al₂O₃-coated Li(Ni_{0.7}Co_{0.2}Mn_{0.1})O₂ composite electrodes. These graphs refer to a semicircle in the high-frequency region and a straight line in the low-frequency region. As a result of EIS measurement, the resistance of NCM coated with Al₂O₃ compared to pristine Li(Ni_{0.7}Co_{0.2}Mn_{0.1})O₂ was decreased from 95 Ω to 67 Ω. In Figure 5(D), the slope in the impedance of Al₂O₃-coated Li(Ni_{0.7}Co_{0.2}Mn_{0.1})O₂ composite is larger than that of Li(Ni_{0.7}Co_{0.2}Mn_{0.1})O₂, indicating that Al₂O₃-Coated NCM material can affect to improve the electrochemical activity of Li(Ni_{0.7}Co_{0.2}Mn_{0.1})O₂. In conclusion, the enhanced electrochemical performance is caused by the decrease of charge transfer resistance and

faster lithium-ion diffusion originated from Al₂O₃ coating in EIS measurement.

4. CONCLUSION

LiNi_{1-x}MxO₂ ($0 \leq x \leq 0.5$, M = Co, Mn, etc.) layered structure lithium-ion battery cathode materials were synthesized. Their basic physical properties, chemical analysis, and electrochemical properties were confirmed. Particularly, the change of electrochemical properties due to the coating and surface modification of Al₂O₃, which is a stable material, was investigated. The cathode material, Li(Ni_{0.7}Co_{0.2}Mn_{0.1})O₂, was synthesized in spherically shaped particles of several microns in size and uniformly distributed using NH₄OH. Al₂O₃ was coated on the surface of the material to solve the problem of transition metal elution and cation mixing, which is a problem of the Ni-rich NCM cathode material, and the amount of alumina was gradually increased from 1, 2 and 5 wt%, respectively. XRD analysis of the NCM synthesized above confirmed the same structure as LiNiO₂, and no structural change was observed even when coated with Al₂O₃. In addition, TEM

analysis showed that Al_2O_3 was coated with a layer on the NCM anode material surface. In addition, SEM-EDS and ICP component analysis showed that Al_2O_3 coating content was proportional to the change in coating content.

As the evaluation of electrochemical characteristics, basic charge/discharge capacity rate characteristics and long-term cycle evaluation were carried out, Pristine NCM, NCM + Al 1 wt%, NCM + Al 2 wt% and NCM + Al 5 wt% were charged and discharged under the condition of 0.2 C, and a capacity of 190 mAh/g except for 5 wt% of Al_2O_3 was observed. The increase of the surface modification is thought to be due to the decrease in the amount of active material showing the direct charge/discharge capacity and the remaining amount of Al_2O_3 acting as an impurity, which is not coated so that a small amount of capacity is reduced. As a result of the evaluation of rate characteristics, the material with 1 wt% of Al_2O_3 coated on pristine NCM exhibited a high capacity retention rate of 80% and 82% at 5C and a recovery rate of 0.2% at 5C, with 1% of NCM + Al showing 100%. Also, as a result of the evaluation of the lifetime characteristics, it was confirmed that the capacity reduction was gradual because as the cycle of NCM + Al 1 wt% progressed, the capacity retention ratio was 95% or more during 100 cycles.

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