

# La 개질을 통한 Ni-rich $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ 양극재의 고도로 안정화된 미세 구조 및 우수한 전기화학적 성능

## Highly stabilized microstructure and excellent electrochemical performances of Ni-rich $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ cathode via La modification

이승환<sup>a</sup>

Seung-Hwan Lee<sup>a</sup>

<sup>a</sup> Department of Materials Science and Engineering, Kangwon National University, Associate Professor, 1, Kangwondaehak-gil, Chuncheon-si, Gangwon-do, 24341, Republic of Korea

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### Abstract

Although the mileage of electric vehicles can be increased based on the excellent energy density of the  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ , it is known that the reason for limiting its use is the low lifespan and poor surface stability due to the structural deformation of the  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ . To improve the structural stability of  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ , electrochemical performance is improved by La coating on the surface. La-modified  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  shows an initial capacity of 210.6 mAh/g, a capacity retention rate of 89.9 % after 50 cycles, and a retention rate of 52.5% at 6.0 C. These are superior performances than the pristine sample, because the structural stability of the  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  cathode is improved by the La coating.

*Keywords:* Energy density, lifespan, surface stability, La-modified  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ , structural stability

### 1. Introduction

Nowadays, energy storage devices (ESDs) are widely used in renewable energy, electric vehicles (EVs), hybrid electric vehicles (HEVs), uninterruptible power supplies (UPS) and data centers. Lithium-ion batteries (LIBs) are one of the representative ESDs due to their high energy density. However, LIBs have disadvantages of poor long-cycle performance and power density<sup>[1-3]</sup>.

Among the methods to overcome these drawbacks, there is a lot of research on cathode, which is the most important component that determines the performance of LIBs. Specifically, doping, surface coating, simultaneous doping and coating, core-shell, single crystallization and so on are being reported to improve the long-term stability and rate capability<sup>[4]</sup>.

The  $\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$  (NCM) material, the ternary mixed phase of  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$  and  $\text{LiMnO}_2$  materials, is considered the most promising candidate among the various cathode materials. It was reported that  $\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$  (NCM) has the advantages of  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$  and  $\text{LiMnO}_2$ <sup>[1, 2]</sup>. Among the various compositions, Ni-rich NCM (Ni  $\geq$  80 %) has attracted attention because of its high energy density. However, in the case of Ni-rich NCM (Ni  $\geq$  80 %) cathode, it has a low lifespan characteristic due to structural deterioration<sup>[3]</sup>. Thus, various studies (doping, coating, single crystal, morphology control) are being conducted to enhance the structural and electrochemical integrity<sup>[5]</sup>.

Among them, surface modification by various coating materials with high conductivity and excellent chemical stability is one of the most effective method. Therefore, in this paper, we improved the

\* Corresponding author. Tel.: +82-33-250-6265  
fax: +82-33-259-5545

E-mail address: [shlee@kangwon.ac.kr](mailto:shlee@kangwon.ac.kr) (Seung-Hwan Lee).

electrochemical performance of  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  using La and compared it with the pristine sample.

## 2. Result and Discussion

### 2.1 XRD patterns

The XRD peaks of La modified and pristine  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  powders are shown in Fig. 1. The XRD patterns of both samples deliver typical  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  sample<sup>[6]</sup>. Also, it can be confirmed that there is no secondary phase. Moreover, (006)/(102) peaks and (018)/(110) peaks are well separated, which can be inferred that the layered structure of La modified and pristine  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  is well formed. Therefore, we can infer that the both samples are well synthesized. We calculate the (003) and (104) peak intensity ratios  $I(003)/I(104)$  to confirm the cation mixing representing the mixing of Li and Ni ions. The La modified sample has a  $I(003)/I(104)$  value of 1.76, which is much higher than that of the pristine sample (1.55). It indicates that cation disordering of the La modified  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  is effectively inhibited through surface modification<sup>[7]</sup>.

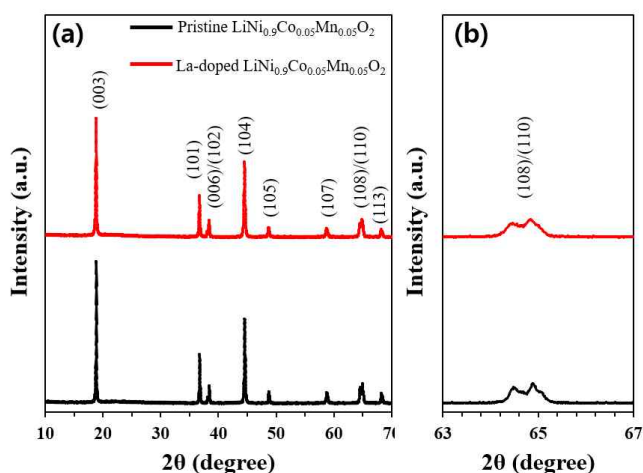


Fig. 1 XRD patterns of (a) La modified and pristine  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  and (b) magnified view of (108)/(110) peak

### 2.2 Particle morphologies

Fig. 2 shows the FE-SEM images of both samples (Fig. (a), (c) : pristine  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ , Fig. (b), (d) : La modified  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  to confirm the change of the particle morphology. The secondary particles are made up of numerous primary particles.

Both samples shows little difference in size or shape of primary/secondary particles. The secondary particles of both samples are spherical in shape and about 15.0  $\mu\text{m}$  in size (Fig. (a) and (b), and the size of the primary particle is about 100 - 200 nm (Fig. (c) and (d)). The excellence of the greatly porous structure and high electrolyte/electrode interface area can lead to excellent electrochemical performances, especially cycle and rate stability. Moreover, Fig. 2(e) confirms that La has successfully exist on the surface of  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ <sup>[8]</sup>.

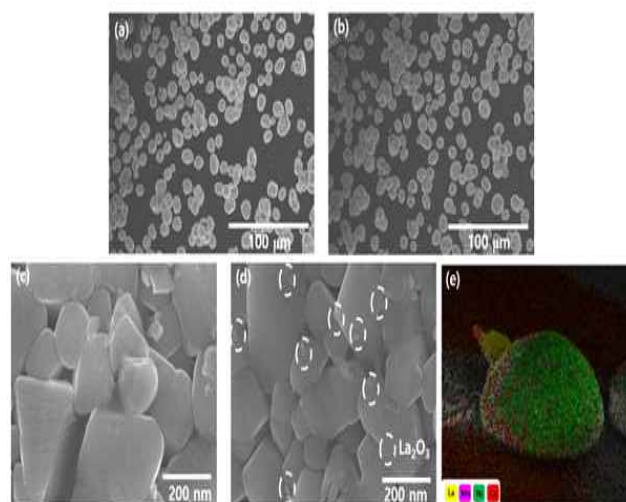


Fig. 2 FE-SEM images of (a, c) pristine and (b, d) La modified  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ , and (e) EDX pattern of La modified  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$

### 2.3 Electrochemical performances

For commercialization of La modified  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  cathode, the loading level of the La modified and pristine samples with high areal loadings ( $14.2 \text{ mg}/\text{cm}^2$ ) are fabricated. Fig. 3 shows the initial charge/discharge capacities of both sample at 0.1 C in the voltage range from 3.0 to 4.3 V at 25 °C. Both samples display a flat and stable voltage plateau without polarization. The La modified sample has an initial capacity of 210.6 mAh/g, and the pristine sample has an initial capacity of 205.8 mAh/g, which is slightly inferior compared La modified sample. It can be elucidate that small amount of La modification produces thin La coating layer, enabling smooth and fast lithium and electron kinetics, on the surface of  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  cathode resulting in superior electrochemical activity<sup>[9-11]</sup>.

The rate capabilities of both samples are measured in order to verify the possibility of fast charge-discharge application, as shown in

Fig. 4. At low C-rate of 0.5 C and 6.0 C, both samples have very similar capacity retentions. However, as the C-rate increases, the capacity retention tends to decrease. As shown in Fig. 4, it can be seen that the pristine sample deteriorates more severely than the La-modified sample. In the case of a pristine sample without a coating layer, an unwanted solid electrolyte interphase (SEI) layer is generated by reaction with the liquid electrolyte [12]. It is widely known that SEI layer prevents the movement of lithium ions and electrons due to low conductivity. On the contrary, La modification, with relatively good conductivity and chemical stability, effectively inhibits the formation of SEI, enabling high mobility of lithium ions and electrons during rapid charge - discharge rates. The La-modified sample has capacity retention of 95.5 %, 91.6 %, 82.9 % and 52.5 % at 1.0 C, 2.0 C, 4.0 C and 6.0 C respectively. It can be seen that these values are superior to the capacity retention of the pristine sample (95.4 % (1.0 C), 90.9 % (2.0 C), 80.1 % (4.0 C) and 42.3 % (6.0 C)).

The cycle stabilities of both samples are displayed in Fig. 5. Both samples experience capacity fading and become faster as the number of charge/discharge increases. The reasons for such capacity fading include i) elution of transition metals, ii) phase transition from layered structure to rock-salt structure on the surface, and iii) micro-cracking due to side reaction with electrolyte. In the case of the pristine sample, since there is no physical/chemical barrier on the surface, the above-mentioned problems occur seriously due to the low chemical stability of  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  [13-14]. Therefore, the transfer of lithium ions and electrons becomes slow, leading to rapid capacity fading. On the contrary, in the case of the La modified sample, La acts as a physical barrier in the form of a uniform and ultra-thin film which suppresses formation of thick SEI, and La can effectively inhibit the unwanted reaction with the electrolyte due to its strong chemical stability [13]. For these reasons, structural degradation of Ni-rich  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  can be minimized, and thus has relatively superior long-term electrochemical performance. After 50 cycles, the La modified sample has a capacity retention of 89.9 % compared to the initial discharge capacity, and the pristine sample shows a lower capacity retention of 71.1 % under same condition. This can be explained by the increase in charge-transfer resistance due to the SEI layer on the surface of the pristine sample with a large contact area with the electrolyte [14].

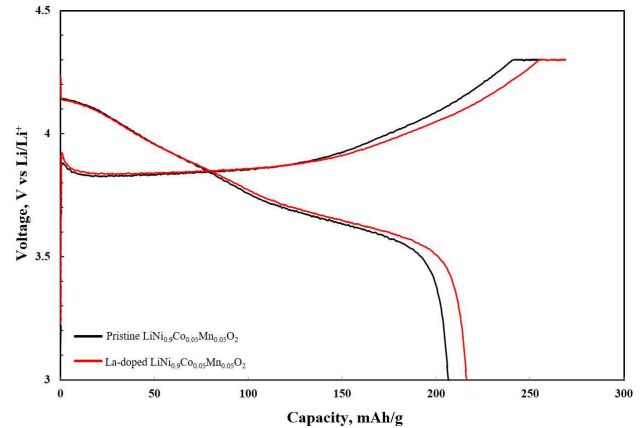


Fig. 3 Initial charge-discharge profiles of La modified and pristine  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$

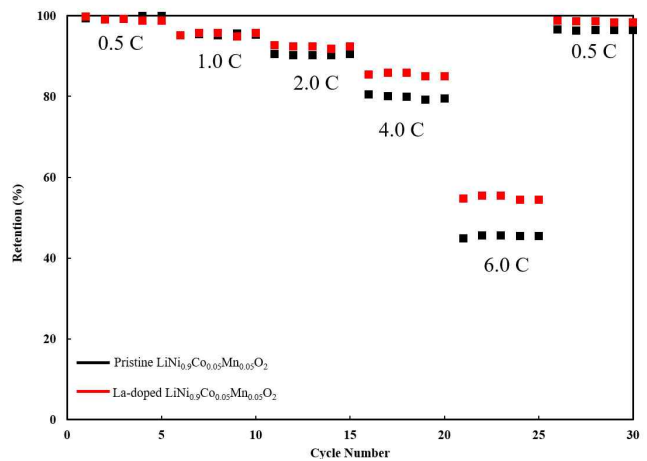


Fig. 4 Rate performances of La modified and pristine  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$

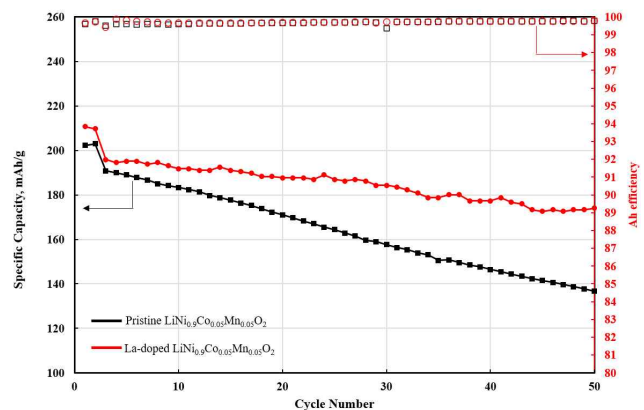


Fig. 5 Cycle performances of La modified and pristine  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$

### 3. Experimental

The  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  powders with spherical morphology were prepared via co-precipitation method. The  $\text{Ni}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}(\text{OH})_2$  precursor was synthesized by nickel sulfate hexahydrate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ), Cobalt sulfate heptahydrate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ), Manganese sulfate monohydrate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . The precipitating material was fabricated with  $\text{NH}_4\text{OH}$  and  $\text{NaOH}$  solution. The  $\text{Ni}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}(\text{OH})_2$  precursor with spherical shape mixed with Li source ( $\text{LiOH} \cdot \text{H}_2\text{O}$ ) in a molar ratio 1.05 : 1. After that, the mixture was calcined at 500 °C and 750 °C for 5 h, 15 h, respectively in the furnace under the  $\text{O}_2$  atmosphere. The La-modification was performed on  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  via the  $\text{La}_2\text{O}_3$  powder in a mole ratio of La : NCM = 0.05 : 1. Subsequently, the powders were annealed at 500 °C for 6h in atmosphere.

A cathode was prepared via La modified  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  powder (95 wt %), Super P (2.5 wt %) and polyvinylidene fluoride (PVDF) (2.5 wt %). In order to prepare cathode slurry, N-methyl-pyrrolidinone (NMP) solution was supplemented. The prepared slurry was coated on the Al foil and dried at 100 °C for 24 h in an oven. The CR 2032 cells were fabricated with Li foil as an anode in glove box filled with Ar gas. 1M  $\text{LiPF}_6$  in dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and ethylene carbonate (EC) (with a volumetric ratio 1 : 1 : 1) were applied as an electrolyte.

X-ray diffraction (XRD, X'pert MPD DY1219) and field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) were used to confirm the structural properties of powders. The TOSCAT-3100 (Toyo system) equipment was used to evaluate the electrochemical performances.

### 4. Conclusion

In this paper, we successfully fabricated La modified samples and investigated their structural and electrochemical properties. Compared to the pristine sample, the La modified sample showed high crystallinity and low cation disordering. Based on such high structural stability, it exhibited high initial discharge capacity, rate capability and cyclability. This can be explained by the fact that La effectively prevented structural collapse due to penetration of the electrolyte and provided a rapid lithium ion and electron path.

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## 대표저자소개

이 승 환(Seung-wan Lee)



- 2008년 2월 : 광운대학교 전자재료공학과 (공학사)
- 2010년 2월 : 광운대학교 전자재료공학과 (공학석사)
- 2015년 8월 : 광운대학교 전자재료공학과 (공학박사)
- 2018년 8월 : University of Maryland (Faculty Assistant)
- 2022년 2월 : 대전대학교 신소재공학과 (조교수)
- 2022년 3월 ~ 현재 : 강원대학교 재료공학전공 (부교수)

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