

EFFECT OF CALCINATION TEMPERATURE ON THE STRUCTURAL AND ELECTROCHEMICAL PROPERTIES OF Ni-RICH MATERIALS

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Abstract

LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ layered materials were synthesized by solid-state reaction using LiOH·H₂O and hydroxide precursors of composition Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)₂ (NMC) at various calcination temperature. The final LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ products showed different physical and electrochemical properties depending on their calcination temperatures. The LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ synthesized at 800 °C for 16 h showed the best electrochemical properties with a high discharge capacity over 188 mAh/g with a capacity retention > 96 % after 50 cycles at 1C-rate in a half cell.

Keywords. Lithium ion batteries, Ni-rich material, co-precipitation, LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂.

1. INTRODUCTION

Lithium ion battery is widely used in electronic products because of its high energy density compared to other secondary batteries^{1,2}. LiCoO₂ is by far the most popular and well researched material amongst transitional metal oxides for lithium ion batteries. However it suffers several shortcomings including poor stability, inability to extract all the lithium ions and the high cost and toxicity of cobalt [3]. In recent years, the Li[Ni_{1-x-y}Co_xMn_y]O₂ material with high Ni content has emerged as alternatives to increase energy density as evidenced by the fact that more and more battery manufacture companies are actively pursuing the Ni-rich chemistry in their applications for hybrid electric vehicle. Various methods have been applied to synthesize Ni-rich such as solid state method [4], sol-gel method [5], chloride co-precipitation [6], carbonate co-precipitation [5, 7] and hydroxide co-precipitation method [8, 9]. Comparing to these synthesis methods, co-precipitation method has advantages which provide homogeneous precursor with tap-density, controllable morphology and high electrochemical properties.

In this work, the effect of calcination temperature on the physical and electrochemical properties of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ is investigated.

2. METHODS

2.1. Preparation of materials

The precursor Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)₂ was prepared by co-precipitation method [10]. At first, stoichiometric amounts of NiSO₄·6H₂O, CoSO₄·7H₂O, and MnSO₄·6H₂O were dissolved together in distilled water to get a transparent solution which was pumped into reactor (capacity 1.5 L) under N₂ atmospheric. A NaOH solution and NH₄OH solution as a chelating agent were separately added to the transition metal sulfate solution drip by drip. The spherical Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)₂ powders were washed with de-ionized water and dried vacuum at 110 °C for 24 hours. Finally the Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)₂ precursors were mixed with 5 % excess LiOH·H₂O and pre heat treatment at 480 °C for 5 h and at 760, 800 and 840 °C for 16 hours in air atmosphere to obtain the target compound of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ powders. We denote sample name are A-760, A-800 and A-840, respectively

2.1. Characterizations

The crystalline structure of samples was characterized by X-ray diffraction (XRD) measurements using a Rigaku D Max/ 2000 PC with a Cu *ka* radiation in the 2θ angular range of 10 to 80° at a scanning rate of 4° min⁻¹. The particle morphology and element composition of the

powders were observed by using scanning electron microscope (SEM, Hitachi S-4800) equipped with energy dispersive spectroscopy (EDS).

2.2. Electrochemical Characterization

Coin-type half-cell tests were conducted on samples between 3 and 4.3 V. We made the cathodes for the battery test cells from the active material, the super P carbon black (conducting agent-Timcal), and a polyvinylidene fluoride (PVDF, KF 1300 binder, KUREHA) in a weight ratio of 80:10:10. To prepare the electrodes, we coated Al foil with the cathode slurry and left it to dry at 110 °C for 2 h in vacuum oven. For electrochemical measurements, the coin-type battery test cells (CR-2016 size), each of which contained the cathode, the Li metal anode, and the microporous polyethylene separator, and 1:2 volume ratio mixture of ethylene carbonate (EC) and dimethyl-carbonate (DMC) containing 1 M LiPF₆ as the electrolyte, were prepared in a Argon-filled glove box in which oxygen and H₂O contents were maintained below 2 ppm.

The galvanostatic charge and discharge tests of the cells were performed on a cell life test system (PNE solution, KOREA) in the potential range between 3.0 and 4.3 V at different current densities from 18.5 mA.g⁻¹ (0.1C) to 1295 mA.g⁻¹ (7C) and at room temperature (25 °C).

3. RESULTS AND DISCUSSION

3.1. Characteristics of Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)₂ precursor

Fig. 1 shows the SEM images of the precursor Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)₂ powders. The particle morphology of the precursor is spherical with average secondary particle diameter about 9 μm, and the primary particle is less than 100 nm.

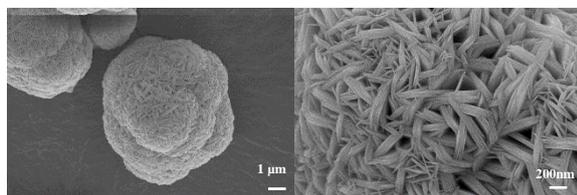


Fig. 1: SEM images of the precursor: (a) low magnification; and (b) high magnification

Characteristic of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂

Fig. 2 (a) shows the X-ray diffraction pattern of Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)₂ precursor which is similar to

the spectra of pure Ni(OH)₂ [11]. All diffraction lines are indexed to a hexagonal structure with a space group of P-3m1. The crystal lattice parameters of the layered Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)₂ precursor are a = 3.114 Å and c = 4.617 Å. Fig. 2(b) displays the XRD pattern of the A-760, A-800 and A-840 samples.

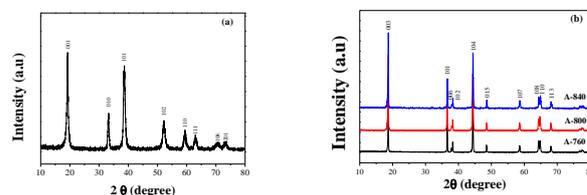


Fig. 2: The XRD pattern of the A-760, A-800 and A-840 samples

In all cases, the observed diffraction lines can be indexed based on the R-3m space group and are consistent with the layered structure of the α-NaFeO₂ structure and no impure peaks appear. When the calcinations temperature increase, the XRD pattern shows clear slip between the 006/102 and 108/110 peak which indicates that the layered LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode materials successfully synthesized at all the calcinations temperature in this experiment, and have better hexagonal structure. Cation mixing is known to deteriorate the electrochemical performance of the layered materials. The intensity ratio of I₀₀₃/I₁₀₄ is a sensitive parameter for determining the cation distribution in the lattice of the layered oxide, and a value lower than 1.2 indicates a high degree of cation mixing which is an indication of undesirable cation mixing [12, 13]. The lattice parameter are summarized in Table 1. When the calcination temperature is not higher than 800 °C, the value of c/a and I₀₀₃/I₁₀₄ increase with increasing calcination temperature. However, the value of c/a and I₀₀₃/I₁₀₄ decrease when the calcination temperature increasing is increased to 840 °C. According to the above results, the sample calcined at 800 °C exhibits the best layered structure and the lowest cation mixing.

Table 1: Lattice parameters of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ prepared with various calcination temperature

LNMCO	a	c	c/a	Rw
A-760	2.8758	14.2206	4.9462	1.3491
A-800	2.8753	14.2287	4.9486	1.4131
A-840	2.8739	14.2133	4.9456	1.3052

The particle morphologies of the A-760, A-800 and A-840 samples are shown in Fig. 3. No distinct

difference in particle morphology and size was observed between the samples.

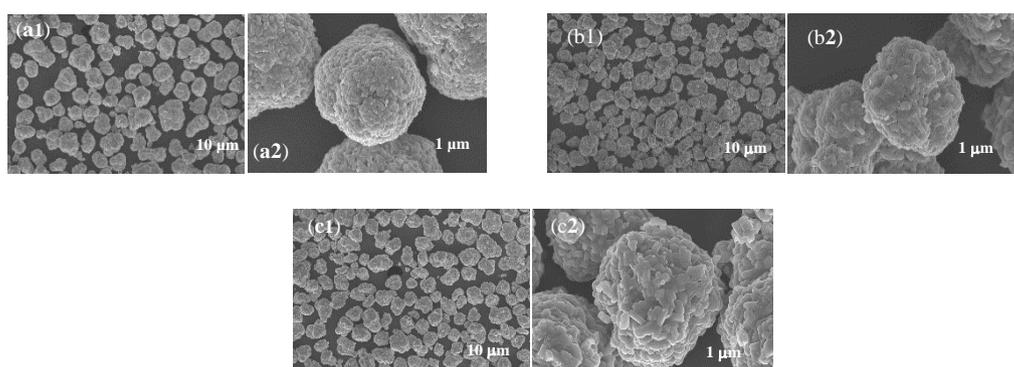


Fig. 3: SEM images (a1, a2) A-760, (b1, b2) A-800 and (c1, c2) A-840 samples. (1) low magnification (2) high magnification

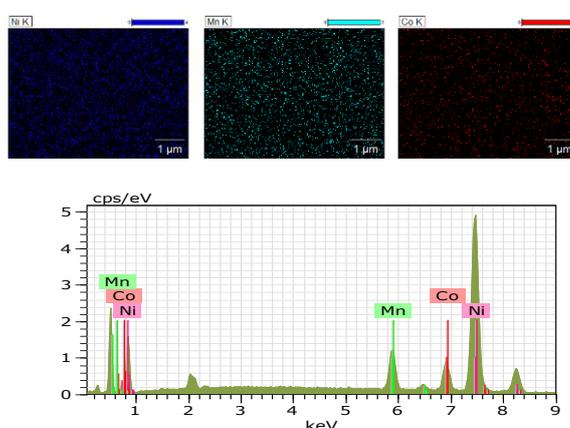


Fig. 4: Element mapping images and EDX analysis of the A-800 sample

All of the samples consist of the secondary particles which are composed of numerous primary particles whose size is approximately 300 nm. The integrity and sphericity of the particles are the best when the calcination temperature is 800 °C. Increasing the calcination temperature usually leads to a crystal growth¹⁴. Therefore, higher calcination temperature results in larger primary particles, i.e. larger crystallite size.

EDS mapping analysis was carried out to check the elemental distribution and homogeneity of element Ni, Co and Mn. As can be seen in Fig. 4, Ni, Co, Mn components were found to be homogeneously distributed over the particles. The EDX analysis confirmed that no impurities were presented in the prepared samples. The atomic ratio of Li:Ni:Co:Mn in the $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ material is determined to be 1.05:0.8124:0.105:0.0826. The particle is nearly consisted of a molar ratio of 0.8 Ni, 0.1 Co, and 0.1 Mn which is expected material.

The electrochemical performances of Li/LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cells have been preliminarily evaluated to quantify the specific capacity. The

initial charge-discharge curves of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ material were sintered at different temperatures for 16 h at a discharge rate of 0.1C in the potential range from 3.0 to 4.3 V at 25 °C, are shown in Fig. 5(a). All of the samples show the typical smooth shape of the charge-discharge curves without any plateaus. The discharge capacities increase with increasing sintering temperature from 760 to 800 °C. The observed initial discharge capacity for the sample sintered at 760, and 800 °C are 181.742 and 184.117 mAhg⁻¹, respectively. However, the discharge capacity decreases to 180.772 mAhg⁻¹ when the sintering temperature reaches 840 °C.

The cycling performance of A-760, A-800 and A-840 samples was also investigated, as shown in Fig.5 (b). The cells were cycled at 1C rate between 3.0 and 4.3V.

The sample sintered at 800 °C showed the highest specific discharge capacity. The cell delivers a capacity of 165.232 mAhg⁻¹ at 1st cycle and 160.035 mAhg⁻¹ at 50th cycle with 96.85 % of capacity retention, while capacity of 161.552, and

162.217 mAhg⁻¹ at 1st cycle and 146.910, 153.836 mAhg⁻¹ at 50th cycle with 90.93, and 94.83 % of capacity retentions of sample A-760, and A-840, respectively. The low initial discharge capacity and

fast capacity fading of the sample calcined at 760 °C can be attributed to its low crystallinity. Therefore, the optimum calcination temperature can be confirmed as 800 °C.

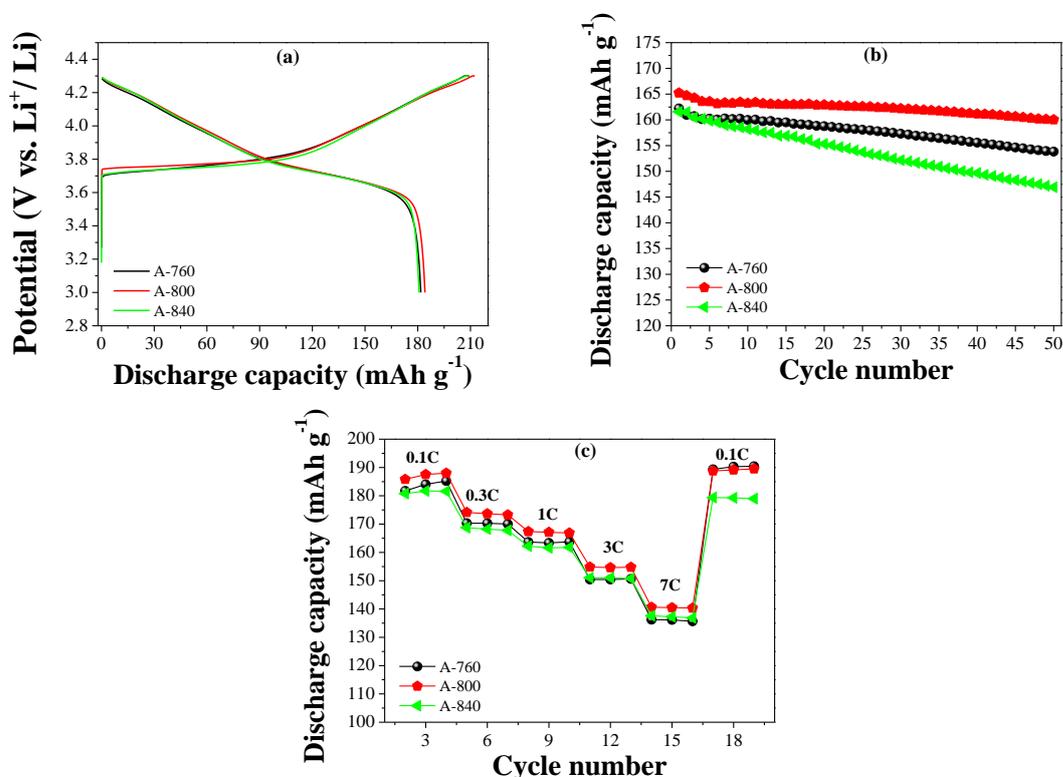


Fig. 5: Electrochemical properties of samples in a voltage window of 3.0-4.3V at 25 °C: (a) Initial charge- discharge capacity at a rate of 0.1C and (b) discharge capacity vs (b) cycle number at a rate of 1C and (c) rate capability at various C-rates

Table 2: Specific discharge capacity at various C-rates of A-760, A-800 and A-840 samples

LNMCO	0.1C	0.5C	1C	3C	7C
A-760	181.74	170.31	163.67	150.41	136.22
A-800	185.79	174.12	167.36	154.85	140.62
A-840	180.77	168.73	162.19	151.04	137.61

It is well known that rate capability can be affected strongly by surface area of cathode material (primary particle size). Fig. 5(c) shows the rate performance of the samples with various current densities between potential limits of 3.0-4.3 V. The cell is charged at a current density of 92.5 mA g⁻¹ (0.5 C) before each discharge test. The cells are first cycled at 0.1 C (18.5 mA g⁻¹) and then at 0.5 C (92.5 mA g⁻¹), 1 C (185 mA g⁻¹), 3 C (555.5 mA g⁻¹) and 7 C (1285 mA g⁻¹) for every discharge cycles. The cells deliver discharge capacity as shown in Table 2. The A-800 electrode delivers a discharge capacity of

185, 174, 167, 154, 140 mAhg⁻¹, whereas the A-760 and A-840 electrodes deliver lower discharge capacity than that of A-800 electrode. Even when discharged at 7 C, a capacity as high as 140 mAhg⁻¹ is achieved, indicating that the LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ material synthesized in the optimal conditions has superior rate capacities which are not reported in the previous research [15].

4. CONCLUSION

The spherical LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode materials with high homogeneity, spherical morphology and high capacity have been successfully synthesized by hydroxide co-precipitation method in the optimum conditions. The sintering temperature strongly affects the structure and the electrochemical performance. From electrochemical experiments, the layered LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode material are synthesized at 800 °C for 16 h exhibit highest discharge capacity

(184.117 mAhg⁻¹ at 0.1C), as well as excellent cycling stability and rate capability. We conclude that 800 °C is an optimal calcinations temperature in this experiment.

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