Arch. Metall. Mater. **66** (2021), 4, 987-990

DOI: 10.24425/amm.2021.136411

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SYNTHESIS OF THE NICKEL-COBALT-MANGANESE CATHODE MATERIAL USING RECYCLED NICKEL AS PRECURSORS FROM SECONDARY BATTERIES

As the amount of high-capacity secondary battery waste gradually increased, waste secondary batteries for industry (high-speed train & HEV) were recycled and materialization studies were carried out. The precipitation experiment was carried out with various conditions in the synthesis of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ material using a Taylor reactor. The raw material used in this study was a leaching solution generated from waste nickel-based batteries.

The nickel-cobalt-manganese (NCM) precursor was prepared by the Taylor reaction process. Material analysis indicated that spherical powder was formed, and the particle size of the precursor was decreased as the reaction speed was increased during the preparation of the NCM. The spherical NCM powder having a particle size of 10 μm was synthesized using reaction conditions, stirring speed of 1000 rpm for 24 hours. The NCM precursor prepared by the Taylor reaction was synthesized as a cathode material for the LIB, and then a coin-cell was manufactured to perform the capacity evaluation.

Keywords: Secondary Battery, Nickel, Recycling, Taylor Reaction, Cathode Materials

1. Introduction

Though the use of nickel-metal hydride production use has been minimized, still, a large amount of nickel-based waste batteries is generated are worth recycling for material recovery or value-added material recovery. By recovering the valuable metals contained in the waste nickel-based battery, it is possible to simultaneously solve environmental problems caused by the efficient use of resources and disposal [1].

In our previous study reported elsewhere, waste secondary batteries were recycled through materialization. To efficiently recycle waste nickel batteries, waste batteries were crushed by a cut-mill and classified by jet-mill. Also, the acid leaching test for the recovered precursor was carried out by wet processing [2]. In this study, nickel-cobalt-manganese (NCM) material was manufactured using recycled nickel as precursors for lithium-ion batteries (LIBs).

As a cathode material that can replace lithium cobalt oxide, three-component $Ni_{1-x-y}Co_xMn_y$ material has been developed. To manufacture three-component $Ni_{1-x-y}Co_xMn_y$ cathode material, the material must be uniformly distributed and dispersible. One of the problems in the synthesis of NCM material is that productivity is low due to the long reaction time [3].

The Taylor reactor exhibits excellent mass transfer rate and agitation strength compared to conventional reactors, and it has an excellent performance in producing a homogeneous product by forming uniform donut-shaped loops by the Taylor fluid flow. It is possible to synthesize continuously uniform products without a stagnant region by reducing the residence time of the reactant because of the simultaneous injection of the raw material and discharge of the reactant [4].

In this study, for efficient waste materialization studies, a Taylor reactor was used to conduct precipitation experiments under NCM (622) materials and various conditions, and the nickel salts used were recycled raw materials from waste secondary batteries.

2. Experimental

The experimental conditions for the Taylor fluid flow reaction are shown in Fig. 1. Recycled nickel sulfate, cobalt sulfate,

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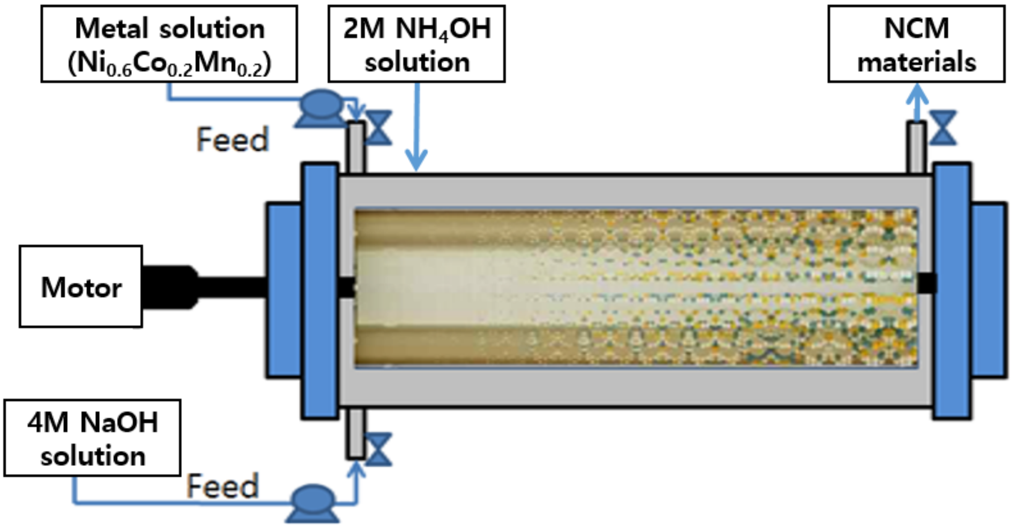

Fig. 1. The schematic diagram for the synthesis of NCM materials by Taylor reactor

and manganese sulfate were used as precursor materials. A 2M aqueous solution having a molar ratio of Ni : Co : Mn = 6 : 2 : 2 was prepared and used as a starting material. The nickel material recycled from the waste nickel batteries (Saft corporation, France) was applied in the form of a 99.9% purity nickel aqueous solution, and as impurities, Cd and Mn were each contained at 4 ppm or less. The recycled nickel is a material recovered through solvent extraction and electro-refining.

Sodium hydroxide (NaOH, ≥97%, Daejung) used as a complexing agent was prepared from a 4M aqueous solution, and ammonia solution (NH_4OH, 28~35%, Junsei) for precipitation was diluted with a 2M solution.

NCM material was manufactured using the Taylor fluid flow reactor (Laminar, LCTR-Lab II-H) which can continuously react. In this study using the Taylor reactor, in order to confirm the change according to the generation efficiency of the Taylor flow, the stirring speed was tested using 800 to 1200 rpm. To examine the effect of the aging time, an NCM material having a reaction time of 6 to 24 hours was synthesized.

The NCM precursor prepared by the Taylor reaction was synthesized as a cathode material for the LIB, and then a cell was manufactured to perform the capacity evaluation. NCM precursor and lithium hydroxide were mixed with the molar ratio of 1:1 and calcinated at 900°C for 10 h.

The positive electrode was fabricated with $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ as the active material, polyvinylidene difluoride (PVDF, Aldrich) as the binder and Super-p carbon black (SPB) as the conductive agent. The half-cell electrodes were placed in a coin cell base, followed by polypropylene separator wetted with 1.0 M $LiPF_6$ in EC/DMC = 50/50 (w/o) electrolyte, lithium foil as the counter electrode, a spacer, a spring for improved contact and the coin cell lid.

The crystal structure of the NCM material was analyzed by X-ray diffractometer (SHIMADZU, XRD-6100). A particle size analyzer (PSA) (Microtrac, S3500) and scanning electron microscope (FEI, Nova NanoSEM 200) were used to analyze the size and microstructure of the powders.

3. Results and discussion

The X-ray diffraction patterns of the synthesized NCM materials prepared by Taylor reaction for 12 hours are shown in Fig. 2. The three characteristic peaks (010), (101) and (102) were observed, indicating that the resulting powders are $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$. In the crystal phase, all three conditions of stirring speed showed NCM crystalline, and there was no significant difference. Additionally, the results of EDX analysis of the NCM sample prepared under the condition of a reaction rate of 1000 rpm were found to be Ni = 59, Co = 21, and Mn = 20(a/o).

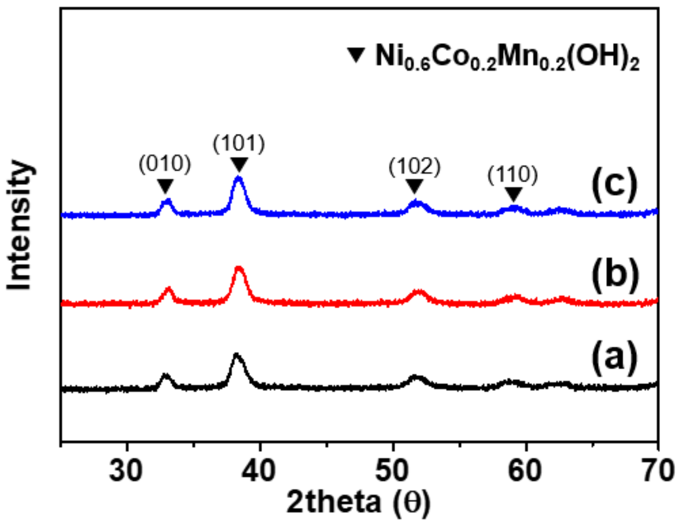

Fig. 2. XRD patterns of the NCM materials according to rpm using a Taylor reactor: (a) 800, (b) 1000, and (c) 1200 rpm

As a result of this, in the synthesis of NCM powder using the Taylor reaction, it is possible to synthesize at an agitation speed of 800 to 1000 rpm, and it seems to be most preferable to synthesize it in the condition section where the Taylor flow is formed to the minimum.

Fig. 3 shows the PSA results of the synthesized NCM powder according to the Taylor reaction time. As the reaction time increases, the average particle diameter of the NCM powder gradually increases. In addition, the particle size distribution of the NCM powder also showed a gradually narrower distribution according to the reaction time.

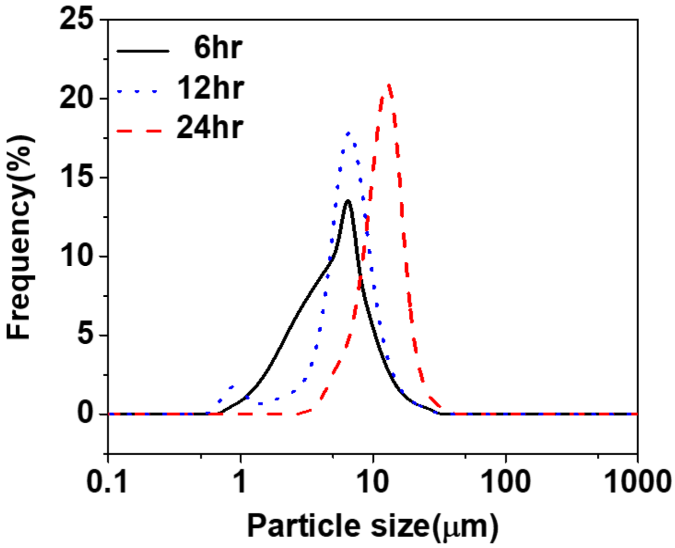

Fig. 3. Particle size distribution of the NCM material according to reaction time

NCM powder with a reaction time of 6 to 12 hours shows a relatively wide particle size distribution and appears to contain some fine particles. And as the reaction time increases, the content of the fine particle is decreasing. As the NCM solution was introduced into the initial reactor, a concentration gradient of the solution was generated inside the reactor, a crystalline seed was generated in the low concentration section, and the growth of particles appeared as the reaction time increased. As the reaction time increases, the reaction concentration is stabilized by flow, which seems to increase the size and dispersibility of the particles [3,5]

Particle growth can also be observed in the microstructure analysis results in Fig. 4. In case of the reaction proceeded for 6 hours, a microstructure in which fine particles of 1 μm or less and 8 μm size were mixed was analyzed, and as the reaction time increased to 24 hours, NCM powder of about 10 μm size was synthesized.

As the reaction time increases, the agglomeration and growth of fine particles occur, and the shape of the particles is also analyzed to change from amorphous to spherical. As the particle growth occurs, the particle size increases and the uniformity improves. This result can be seen as similar to the result of particle size distribution analysis in Fig. 3.

Using the synthesized cathode material, a coin-cell was manufactured, and charge/discharge evaluation was performed on the NCM powder prepared for 24 hours at 1000 rpm by Taylor reaction, and the results are shown in Fig. 5. In the case of the charging, CC/CV 4.3 V cut-off, in case of the discharging, CC

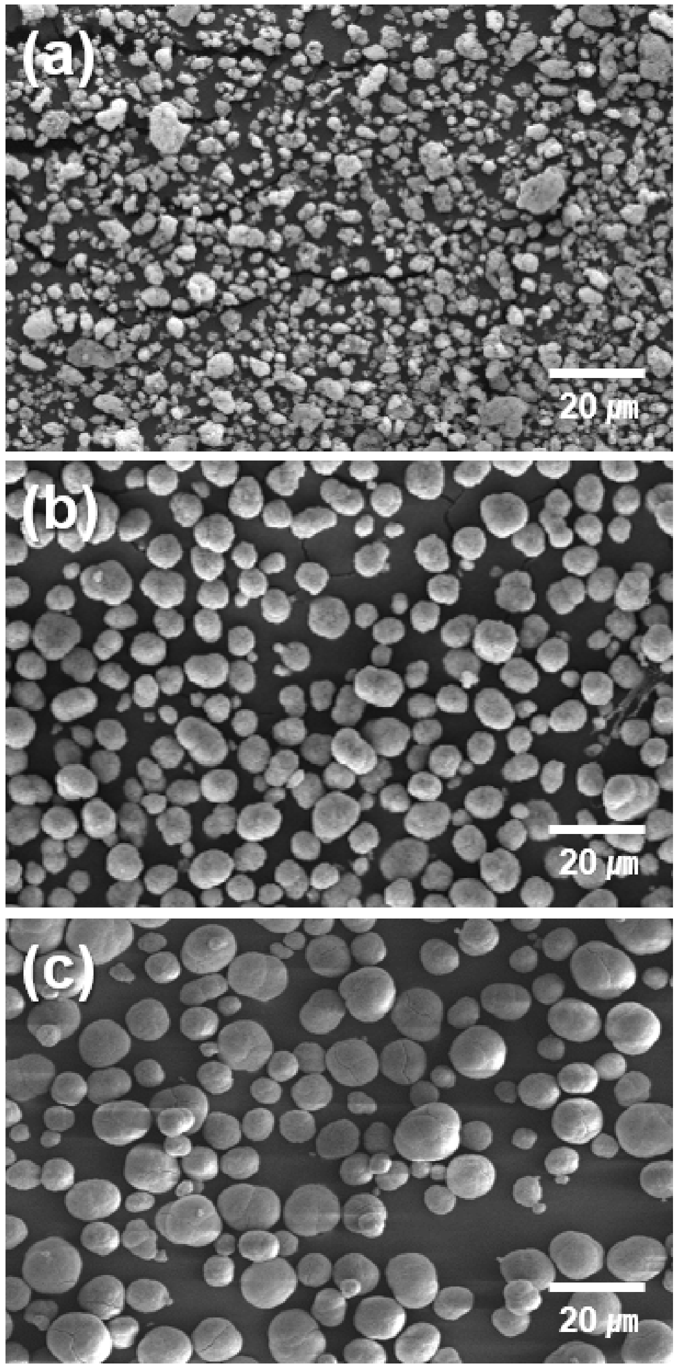

Fig. 4. Microstructures of the NCM material according to reaction time: (a) 6, (b) 12, and (c) 24 hours

3.0 V cut-off was performed. It was analyzed to have a discharge capacity characteristic of about 95% compared to the level of discharge capacity of 180 mAh/g represented by a general NCM material, and it is evaluated as a level that can be applied as a secondary battery precursor through the materialization of recycled NCM materials.

The Ni material recycled from the nickel battery contains a trace amount of Cd (<200 ppm), which is considered to have been introduced from the waste Ni-Cd battery. In addition, the NCM powder made from recycled Ni salts as a raw material also contains a very small amount of Cd less than 10 ppm. As a result of evaluating the coin cell in this study, it was confirmed that

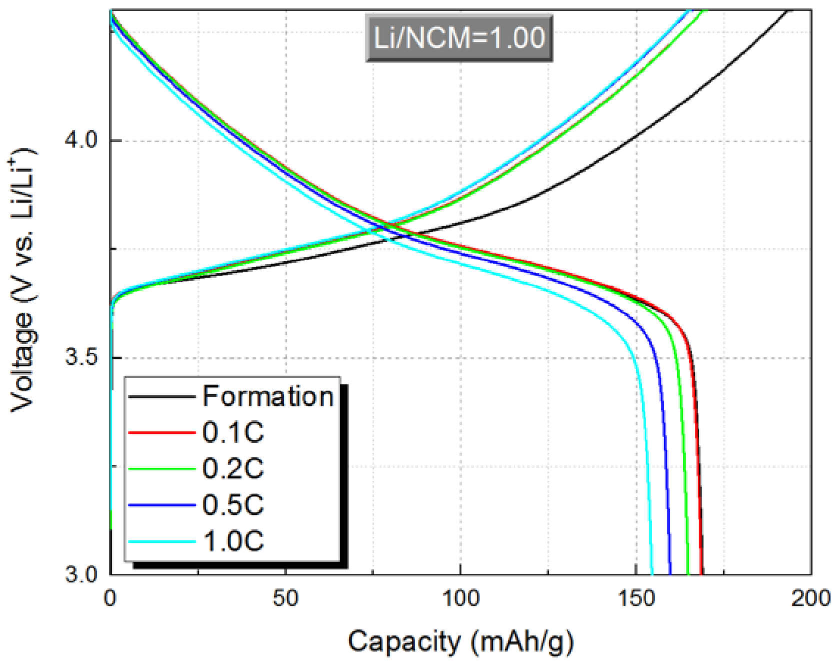

Fig. 5. Charge/discharge curve by rate of cells prepared by NCM materials

the difference in performance between NCM powder using recycled nickel and commercial NCM powder was insignificant. However, when performing a full-cell evaluation, the difference in capacity and life-time performance of commercial NCM powder and NCM powder using recycled nickel requires additional verification.

4. Conclusions

$Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ was synthesized by a Taylor reaction process using recycled nickel precursors as raw materials. As the reaction time increased, the dispersibility of the NCM particles improved and the size of particles also increased.

The spherical NCM powder having a particle size of 10 μm was synthesized under Taylor reaction conditions reacted at a stirring speed of 1000 rpm for 24 hours. As a result of battery evaluation for the Li/NCM molar ratio of 1.0 cathode material, it showed about 95% of discharge characteristics compared to commercial products.

If conditions such as the adjustment of lithium content and heat treatment are controlled, it seems that it will be possible to apply recycled nickel as a cathode material for LIBs.

Acknowledgments

This work was supported by the Industrial Strategic Technology Development Program (No. 20004128) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea)

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