

PAPER • OPEN ACCESS

Synthesis of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ cathode material by hydrothermal method for high energy density lithium ion battery

To cite this article: Hendri Widiyandari *et al* 2019 *J. Phys.: Conf. Ser.* **1153** 012074

View the [article online](#) for updates and enhancements.



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Synthesis of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ cathode material by hydrothermal method for high energy density lithium ion battery

Hendri Widiyandari¹, Atika Nadya Sukmawati², Heri Sutanto², Cornelius Yudha³, Agus Purwanto³

¹ Department of Physics Faculty of Mathematics and Natural Science Sebelas Maret University Ir. Sutami 36 A Surakarta Indonesia

² Department of Physics Faculty of Science and Mathematics Diponegoro University Prof. H. Soedarto, SH Semarang Indonesia.

³ Department of Chemical Engineering Faculty of Engineering Sebelas Maret University Ir. Sutami 36 A Surakarta Indonesia

E-mail: hendriwidiyandari@staff.uns.ac.id

Abstract. The synthesis of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (LNMC) material had been performed via hydrothermal method. LNMC materials as Li-ion battery cathode is chosen because it has many advantages, such as the availability of abundant materials, low cost, high capacity and superior performance of the battery. In this research, hydrothermal method is chosen because it can increase the size of crystallite with good structure hence the crystal quality is improved which is advantageous to improve battery capacity and cycle performance. The novelty of this study is the use of nickel sulfate, manganese sulfate and cobalt sulfate as the transitional metal source of LNMC. The hydrothermal temperature was varied between 160°C – 190°C. Based on X-ray Diffraction test (XRD), LNMC material has crystallite size in the range 45.37 – 46.74 nm. While based on the charge-discharge test, the resulting LNMC cathode battery has a capacity value in the range 0.0453 – 1.199 mAh/g. The highest capacity was obtained on batteries using LNMC cathode electrodes synthesized at 190° C hydrothermal (LNMC H-190 samples). This could be caused by large crystallite size of the sample. As the size of the crystal increases, the Li^+ ion intercalation pathways will be wider hence the storage capacity is also greater.

1. Introduction

Advanced technologies have been applied in many aspects of human lives. Most of these technologies require flexibility in terms of using them. Flexible items powered with electrical energy need energy storage to allow them operate wirelessly. Therefore, energy storage becomes one of important technology especially in these millennia. Batteries as energy storage have become a technology of choice on wireless tools due to its ability to store electrical energy in the form of chemical energy. Among different kinds of batteries, lithium ion (Li-ion) Battery is preferred owing to its recharge ability, high energy and power density and safety. Every Li-ion battery cell operates at relatively higher voltage than lead acid battery or



NiCd battery. The main component responsible for the high capacity is electrode, specifically the cathode. Intercalation cathode provides series of network where the guest ion, Li^+ , could be stored and de-stored[1]. The cathode of Li-ion battery developed since late 20th century. The first commercially success cathode material is layer structured LiCoO_2 or lithium cobaltate (LCO) with specific energy density of 0.98 Wh/g and specific volumetric density of 5,10 g/cm³[2]. However, the presented capacity (140 mAh/g) is only half of its theoretic value (280 mAh/g). The high cobalt content also raises its harmfulness and tend to explode when the Co^{4+} element is formed[3].

Nickel rich cathode namely LiNiO_2 become interesting subject due to its availability, feasibility and safety properties. However, high nickel content cathode material suffers poor cycle ability because the occurrence of Ni^{2+} which form ion blockade during the cycle which hindering Li-ion transport[4]. On the other hand, Doped LiNiO_2 with various atoms become the solution of its poor electrochemical performance[5].

$\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ is novel cathode materials with superior performance compared to LiNiO_2 and LiCoO_2 . It has large market share and projected to be increased till 2025[6]. Recently, the $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) is being developed by Tesla as domestic electrical energy storage due to its high capacity and superior electrochemical performance. It has longer cycle life compared to LiNiO_2 due to the presence of Co and Mn doping and high conductivity[7]. Extensive studies on NMC811 have been performed and reported. NMC811 could be synthesis via solid state reaction, sol-gel and coprecipitation. The solid-state reaction from individual element requires long mixing, milling and sintering process to obtain homogenous particle. Sol-gel reaction need organic metal source such as metallic acetate which increases the production cost. The coprecipitation method requires large control during the process due to dependency on variables such as stirring, flowrate, temperature, pH and atmosphere[8].

The aim of this study is to synthesize NMC811 via simple hydrothermal method from transitional metal sulfate salts which is non-conventional. These sulfate salts are cheaper sources with high solubility and high availability especially in developed countries compared to other source such as nitrate and acetate. The hydrothermal method has numerous advantages among other methods such as lower reaction temperature, avoid unusual oxidation process, dissolution of oxide impurities at higher temperature, highly crystalline material and narrow particle distribution[9]. As far as we concern, such approach has never been reported before.

2. Experimental Methods

Nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), Manganese sulfate mono hydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) and cobalt sulfate hepta hydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) were used as TM source; ammonium bicarbonate was used as precipitant; ethylene glycol and demineralized water were used as the solvent; Li_2CO_3 was used as lithium source. Figure 1 shows the flowchart synthesis of NMC811.

First, the transitional metal sulfate were dissolved in ethylene glycol-demineralized water mixture (EG:DI = 2:1) with molar ratio Ni:Mn:Co of 8:1:1 and greenish colloidal solution was obtained. The solution was transferred into Teflon-lined stainless steel autoclave and heated to 160 °C-190 °C for 12 hours. The sample obtained denoted as LNMC H-160, LNMC H-170, LNMC H-180 and LNMC H-190 were each represents the temperature during hydrothermal synthesis. The obtained particle were washed and mixed with Li_2CO_3 using mortar and pestle. The precursor were calcined at 450 °C for 1 hour and sintered at 800 °C for 10 hours. Last, obtained particle is ground using ball mill for an hour.

The crystal structure of each sample were measured using X-ray diffractometer ($\text{CuK}\alpha$ $\lambda = 1.54056 \text{ \AA}$, $10 \leq 2\theta \leq 80$). The crystallite size was determined by debye-scherer's equation. Electrochemical performance of each sample was tested using galvanostic test of half-cell. The electrodes were assembled by mixing the as prepared sample with PVDF and AB with the ratio of 8:1:1 in NMP solvent to form slurry. The slurry was coated on Al-foil using doctor blade method. The coated slurry was dried in oven overnight. The electrode were pressed and punched into disc with diameter of 16 mm. CR2032 coin cells were assembled

inside argon-filled glove box where Li metal and LiPF_6 1 M dissolved in EC:DC:DMC 1:1:1 were used as the counter anode and electrolyte respectively. The test were performed at 3-4.3 V and 1/20 C (1 C= 180 mA/g) in room temperature.

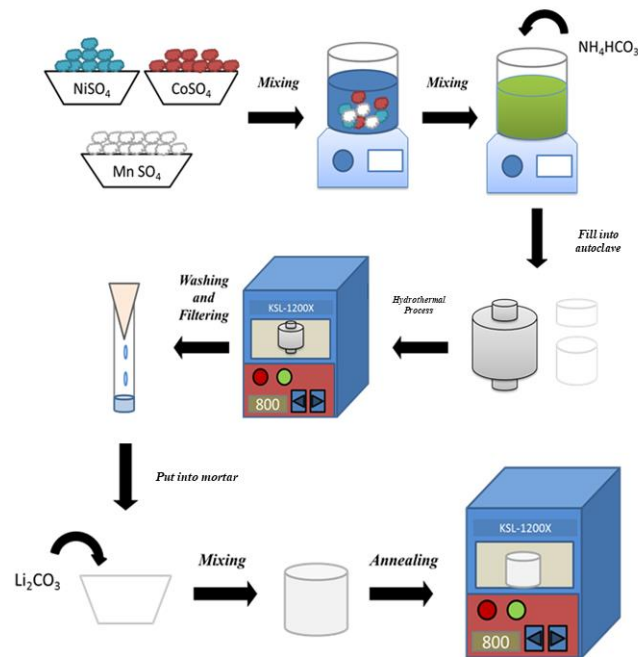


Figure 1. Flowchart of NMC811 synthesis via hydrothermal method



Figure 2. As prepared samples of LNMC-H-T (T=160;170;180;190 °C)

3. Result and Discussion

3.1 Characterization by XRD

The obtained powder can be seen in figure 2 is characterized by XRD. The X-ray diffraction pattern is presented in figure 3. There are no significant differences among LNMC H-160, LNMC H-170, LNMC H-180 and LNMC H-190 X-ray diffraction patterns. The highest peak can be seen in the LNMC H-190 sample specifically located at 2θ of 43.2316° . There are 5 main peaks that could be indexed to JCPDS card no. 09-0063, 32-0581 and 20-0781. These peaks is well-match with the reference at particular order 2θ of 18.80° ;

23.839°; 38.300°; 44.406°; and 64.373° with miller index of (003); (111); (012); (104); and (440), respectively[10].

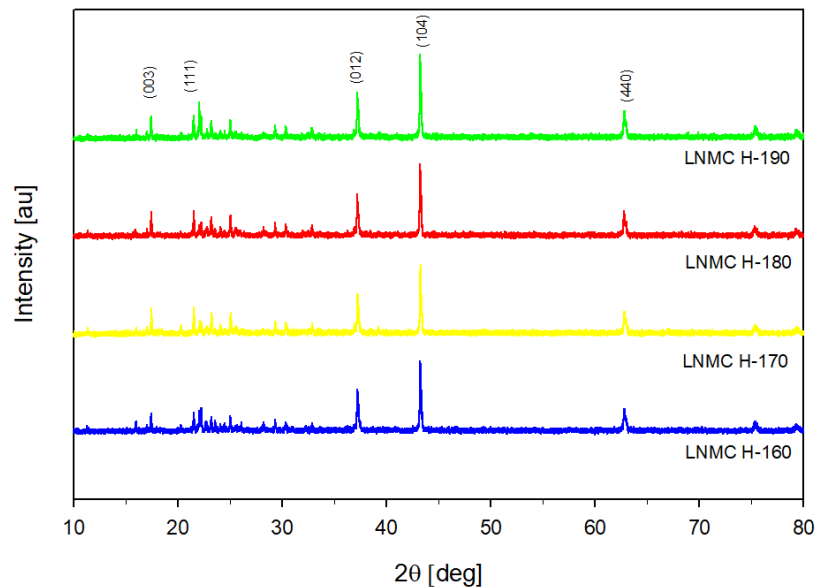


Figure 3. X-ray diffraction patterns of LNMC samples

The value of 2θ and Full Width at Half Maximum (FWHM) based on XRD characterization could be used to determine the crystallite size (D_{XRD}) of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ using schere's equation. Since the highest peak located at 43.2316° , the crystallite size of each sample at the selected diffraction plane was firstly calculated.

Table 1. Crystallite size of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ at diffraction plane (104)

LNMC samples	D_{XRD} (nm)
H-160	45,37
H-170	45,79
H-180	45,96
H-190	46,74

Table 1 shows the crystallite size of LNMC samples at diffraction plane (104). The D_{XRD} value is within the range of 45.37 – 46.74 nm. The mean crystallite size of each sample and at different diffraction planes is presented in figure 4. The value of mean crystallite size is increased as the hydrothermal process temperature is increased. This could be caused by the crystal growth process which depends on temperature of process. Based on what figure 4 shows, the highly crystalline particle is obtained at temperature of 190 °C[9], [11]. Based on previous study, higher crystalline material means higher lithium ion diffusivity due to broadening intercalation pathways of the ions. Thus, the capacity and the diffusion kinetics are improved[12].

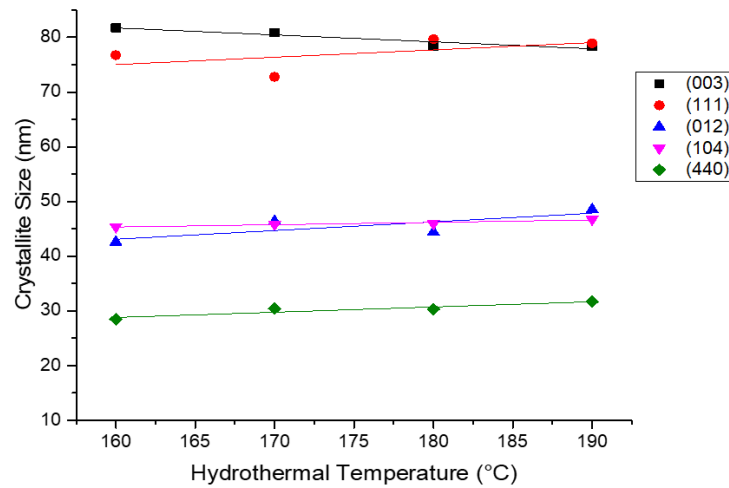


Figure 4. The effect of hydrothermal process temperature on the crystallite size of as-prepared LNMC samples

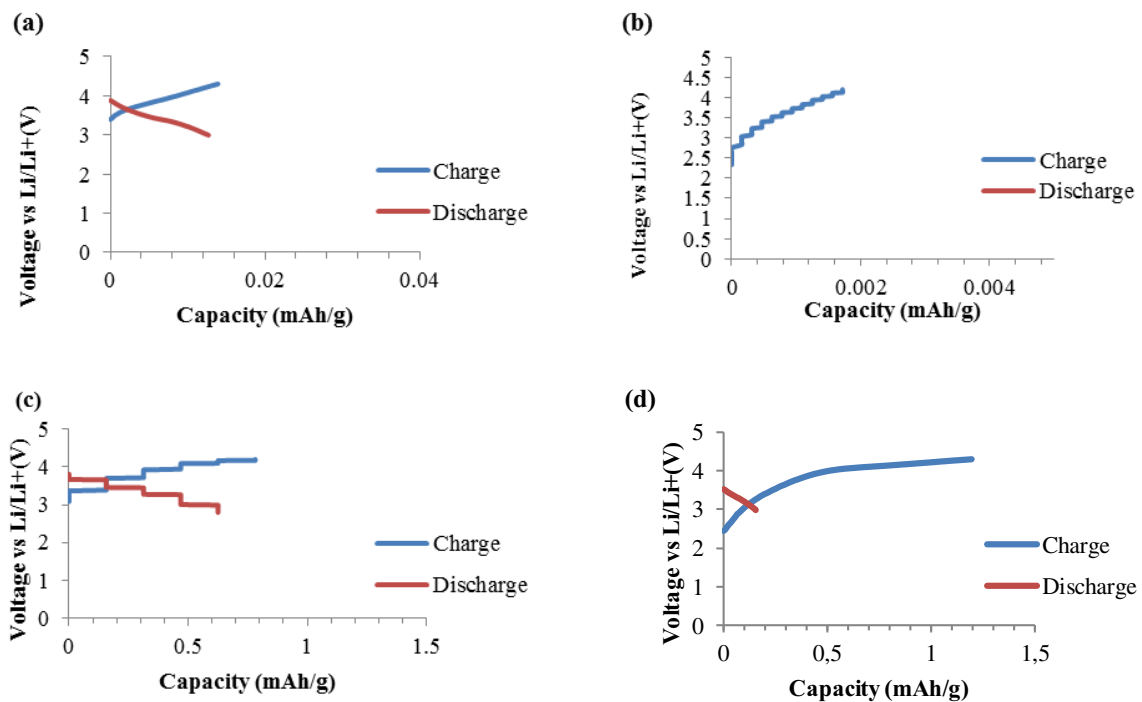


Figure 5. Initial Charge-discharge curve of (a) LNMC H-160, (b) LNMC H-170, (c) LNMC H-180, (d) LNMC H-190 samples

3.2 Electrochemical Performance Analysis

The galvanostatic test or charge-discharge test results are presented in figure 5. The specific charge capacity of LNMC H-160, LNMC H-170, LNMC H-180 and LNMC H-190 is 0.0453 mAh/g, 1.041 mAh/g, 1.041 mAh/g and 1.199 mAh/g respectively. The increasing capacity could be related with the XRD result. The highest capacity is exhibited by LNMC H-190 sample which has the highest patterns peaks compared to other samples and highest crystallite size.

The highest capacity is exhibited by the LNMC H-190. The cycle performance of each sample is presented in figure 6. LNMC H-160 sample experienced capacity drop at the second cycle. LNMC H-170 and LNMC H-180 experience capacity drop at the third cycle while LNMC H-190 experienced high capacity drop at the second cycle. The significant capacity drop of LNMC H-190 sample is caused by its highly crystalline structure and characteristics which promote various redox process which severe the performance of the sample. The sample LNMC H-190 could have highly agglomeration particle due to high temperature of hydrothermal process which lowers the conductivity of the material. The instability of the performance could be the result of oxygen loss during the cycle. The oxygen loss occurs at high voltage operation and causing irreversible capacity loss[13][14][15].

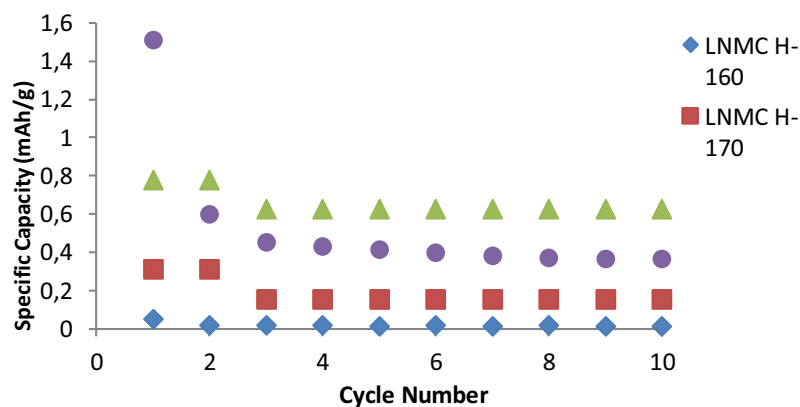


Figure 6. Cycling performance of LNMC H-160; LNMC H-170; LNMC H-180; LNMC H-190 at 1/20C rates

4. Conclusion

Based on our study, hydrothermal process synthesis of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) at temperature of 160, 170, 180 and 190 °C produce particles with crystallite size value in the range of 45.37 – 46.74 nm. Higher hydrothermal process temperature produces higher crystallite size value. The highest crystallite size is obtained at the temperature of 190 °C which also has the highest specific capacity of 1.199 mAh/g.

5. Acknowledgements

We acknowledge to PERTAMINA for funding this research. This paper also partially supported by USAID through Sustainable Higher Education Research Alliance (SHERA) Project Prime Award: AID-497-A-16-00004.

6. References

- [1] J. M. Tarascon and M. Armand, "Issues and challenges facing rechargeable lithium batteries," *Nature*, vol. 414, no. 6861, pp. 359–367, 2001.
- [2] K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, " Li_xCoO_2 ($0 < x \leq 1$): A new cathode material for batteries of high energy density," *Solid State Ionics*, vol. 3–4, no. C, pp. 171–174, 1981.
- [3] J. Dahn, E. Fuller, M. Obrovac, and U. Vonsacken, "Thermal-Stability of Li_xCoO_2 , Li_xNiO_2 and Li_xMnO_2 and Consequences for the Safety of Li-Ion Cells," *Solid State Ionics*, vol. 69, no. 3–4, pp. 265–270, 1994.
- [4] X. Li *et al.*, "Enhancing cycle stability and storage property of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ by using fast cooling method," *Electrochim. Acta*, vol. 227, pp. 225–234, 2017.
- [5] P. Kalyani and N. Kalaiselvi, "Various aspects of LiNiO_2 chemistry: A review," *Sci. Technol. Adv. Mater.*, vol. 6, no. 6, pp. 689–703, 2005.
- [6] C. Pillot, "Battery Market Development for Consumer Electronics, Automotive, and Industrial: Materials Requirements and Trends," *5th Isr. Power Sources Conf.*, vol. 33, no. 0, pp. 1–39, 2015.
- [7] Z. Xiao, Y. Zhang, and Y. Wang, "Synthesis of high-capacity $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode by transition metal acetates," *Trans. Nonferrous Met. Soc. China*, vol. 25, no. 5, pp. 1568–1574, 2015.
- [8] Z. Qiu, Y. Zhang, S. Xia, and Y. Yao, "A facile method for synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode material," *Solid State Ionics*, vol. 307, no. April, pp. 73–78, 2017.
- [9] H. Zhao *et al.*, "A simple, low-cost and eco-friendly approach to synthesize single-crystalline LiMn_2O_4 nanorods with high electrochemical performance for lithium-ion batteries," *Electrochim. Acta*, vol. 166, pp. 124–133, 2015.
- [10] D. Pant and T. Dolker, "Green and facile method for the recovery of spent Lithium Nickel Manganese Cobalt Oxide (NMC) based Lithium ion batteries," *Waste Manag.*, vol. 60, pp. 689–695, 2017.
- [11] C. Te Hsieh, H. H. Hsu, J. P. Hsu, Y. F. Chen, and J. K. Chang, "Infrared-assisted Synthesis of Lithium Nickel Cobalt Alumina Oxide Powders as Electrode Material for Lithium-ion Batteries," *Electrochim. Acta*, vol. 206, pp. 207–216, 2016.
- [12] M. V Reddy, G. V. S. Rao, and B. V. R. Chowdari, "Preparation and Characterization of $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Co}_{0.4}\text{Al}_{0.1}\text{O}_2$ by Molten Salt Synthesis for Li Ion Batteries," *J. Phys. Chem. C*, vol. 111, pp. 11712–11720, 2007.
- [13] X. Yang *et al.*, "Suppressed capacity/voltage fading of high-capacity lithium-rich layered materials via the design of heterogeneous distribution in the composition," *J. Mater. Chem. A*, vol. 2, no. 11, pp. 3899–3911, 2014.
- [14] K. Rengsirikul *et al.*, "Biomass Yield, Chemical Composition and Potential Ethanol Yields of 8 Cultivars of Napiergrass (<i>Pennisetum purpureum</i> Schumach.) Harvested 3-Monthly in Central Thailand," *J. Sustain. Bioenergy Syst.*, vol. 03, no. 02, pp. 107–112, 2013.
- [15] E. M. Erickson *et al.*, "Review—Recent Advances and Remaining Challenges for Lithium Ion Battery Cathodes," *J. Electrochem. Soc.*, vol. 164, no. 1, pp. A6341–A6348, 2017.