



Preparation of Mg-Mn doped LiNiO₂ via direct Indonesian Mixed Hydroxide Precipitate Lithiation

M. Rahmawati¹, E. Apriliyani¹, T. Paramitha^{1,3}, H. S. E. A. Gustiana^{1,2,*}

1. Centre of Excellence for Electrical Energy Storage Technology, Universitas Sebelas Maret, Jl. Slamet Riyadi 435, Surakarta 57146, Indonesia
2. Chemical Engineering Department, Vocational School, Universitas Sebelas Maret, Jl. Kol. Sutarto 150K Jebres, Surakarta 57126, Indonesia
3. Chemical Engineering Department, Engineering Faculty, Universitas Sebelas Maret, Jl. Ir. Sutami 36 A, Surakarta 57126, Indonesia

* corresponding author : himmahseag@staff.uns.ac.id

Received: 05-14-2022; Revised : 06-03-2022; Accepted : 06-12-2022; Published : 06-27-2022

ABSTRACT: Using local raw materials affects the development of the Li-ion batteries industry in Indonesia, which is highly important for the sustainability of electric vehicles. Cathode material affects around 40-50% of Li-ion batteries production costs. The utilization of cheap and local nickel sources for nickel rich-cathode material is a promising approach for reducing LIBs cell cost. Mixed Hydroxide Precipitate (MHP) which contain significantly high amount of nickel can serve as the nickel source for LiNiO₂ cathode material This article proposes an effective and economical method to obtain nickel rich cathode material via direct high thermal lithiation of MHP. Non negligible amount of Mn and Mg in MHP can be directly used as a dopant. Based on XRD analysis, a mixture of NiO and LNO phase can be detected. The presence of Mg and Mn impurities is not observable. The SEM images confirms the irregular shape of the as-prepared LNO. The FTIR confirm the absence of residual Li. Based on the findings, a pretreatment technique is required to be explored in the future.

Keywords: LiNiO₂, cathode, high-voltage, Batteries, Energy Storage.

1. Introduction

Indonesia is considered as a promising market for electric vehicles due to its strategic position and high population. Battery electric vehicles (BEV) and Hybrid Electric Vehicle (HEV) would likely be developed in the near future[1]. A sustainable supply chain of EV is largely affected by the economic value of battery. The battery, which is largely lithium ion based, consists of several crucial parts such

as the active materials, current collectors, separators, and electrolytes[2], [3]. The active materials properties and their chemistries affect the overall behavior of a single cells. In other words, the electrochemical performance of a cell is highly affected by the type of cathode and anode materials. Key component in determining a cell capacity is directly affected by the total mass of cathode materials. The cathode materials become the

determining factor since the Li content in the cathode material can be extracted or inserted to their lattice electrochemically. This is why, most of Li-ion cells are named based on the cathode material, i.e. LiFePO₄ battery, LiCoO₂ battery, etc[4]–[6].

Since cathode material has a large impact on the overall cost of a cell, using local raw materials for cathode material fabrications is necessary. Currently, there are two type of cathode materials that achieve a lot of attention from the industry, which are LiFePO₄ (LFP) and LiNi_xCo_yMn_zO₂ (NCM)[7], [8]. LFP is favorable due to its safety and economical aspect. However, it suffers from low energy density and poor conductivity. In the other hand, NCM provide material with high capacity and voltage which result in higher energy density compare to LFP, however, the presence of cobalt is unconsidered since it has low availability, expensive and high toxicity. The up-and-coming cathode material that are promising to be developed is LiNiO₂ (LNO). LNO can be considered identical to its predecessor such as LiCoO₂ and NCM, however, it suffers from poor electrochemical properties. However, the absence of cobalt in LNO motivates researchers to improve and overcome its shortcomings. Several approaches that can be used to improve the electrochemical performance of LNO are morphology tuning, dimension reduction, composite formation, coating or encapsulation, and atomic doping. Doping of material is the simplest way to improve the structural property of LNO.

Herein, we utilize Indonesian mixed hydroxide precipitate (MHP) as a precursor to LNO. Mixed hydroxide precipitate has a considerably high amount of nickel. However, the presence of impurities such as Mg, Mn, iron, and sulfur cannot be neglected. Fortunately, the impurity such as Mg and Mn has been used as a dopant in previous

studies and successfully improve the electrochemical performance of LNO. In the end, Mg and Mn doped LiNiO₂ with good properties is obtained via direct lithiation of MHP at high temperature [9]–[11]. Direct MHP conversion to LNO is considered as an effective, energy and utility saving approach which is highly potential for mass production. As far as our concern, this approach has never been investigated. In this study, we also investigated the characteristics of the LNO material synthesized from MHP and using different lithium sources (LiOH and Li₂CO₃). In particular, we have studied the functional group, crystal structure, and morphology of the cathode material in the presence of a lithium source after the heating.

2. Experimental Method

2.1. Material

The production of LiNiO₂ materials is prepared using several raw materials, such as, MHP (mixed hydroxide precipitate) (Gebe Industry Nickel Ltd, Gresik), Li₂CO₃ (lithium carbonate) (Brivo Shicuan Brivo Lithium Materials Co. Ltd), and LiOH·H₂O (lithium hydroxide monohydrate) (Leverton, U.K.).

2.2. Methodology

2.2.1. Synthesis methods of LiNiO₂

Lithium nickel oxide is produced via solid-state method. The amount of 18 grams of mixed hydroxide precipitate (MHP) is mixed with 7.5 grams of lithium carbonate to synthesize LiNiO₂-Li₂CO₃ sample, whereas the amount of 18 grams of MHP is mixed with 9 grams of LiOH·H₂O to synthesis LiNiO₂-LiOH sample. Both mixtures are heated at 600°C for 10 hours. The synthesis scheme of each sample is shown in figure 1. Then, the characterization properties of the samples will be observed

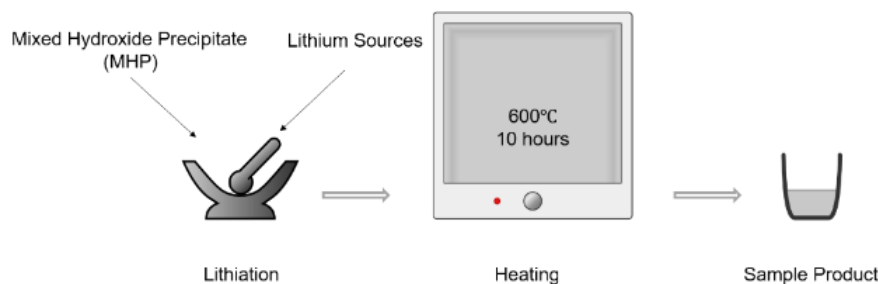


Figure 1. Scheme production of LiNiO₂ samples

2.2.2. Characterization

FT X-Ray Diffraction (XRD) testing to analyze the characteristics of the crystal sample structure. The XRD tool used to test is the MD-10 Minidiffractometer from MTI using Cu-K α radiation ($\lambda=0.15418$ nm) and a diffraction angle of 17-67°. Fourier-transformed infra-red spectroscopy (FT-IR) testing to study the functional groups of each sample and to confirm the reaction between each process. The FTIR tool used to test is the IR Spirit FTIR from Shimadzu. Meanwhile, the morphological feature of the samples was observed using Scanning Electron Microscope (SEM). The SEM tool used to test is the JCM7000 from JEOL.

3. Result and Discussion

The FT-IR spectrum of the samples is observed by Fourier Transform Infra-Red Spectroscopy which represents in figure 2. FT-IR spectrum was used to observe the functional group of the samples. Figure 2 shows that both samples were successfully synthesized. The presence of a peak at 425, 750, and 850 cm⁻¹ wavelengths indicates that the sample contains the stretching vibration of C-O-H. Whereas the bending vibrations of C-O appeared at the peak around 1000 and 1400 cm⁻¹ [10], [12].

Lithium nickel oxide with different lithium sources has been analyzed by X-ray diffraction (XRD). Figure 3 shows the XRD pattern of LiNiO₂ synthesized using a Li₂CO₃ as a lithium source compared to LiNiO₂ synthesized using LiOH·H₂O as a lithium source. The samples have a hexagonal

crystal structure that identified by the Joint Committee on Powder Diffraction Standards (JCPDS) No. 23-0362 [13]. However, some peaks don't appear in LiNiO₂ material due to the operating conditions used are not optimal, so the sample has not been formed perfectly. The split of peaks at 101 and 102 indicates that the sample has a good crystal structure [9], [13]–[15]. Strong NiO phase is also can be seen similar to LiNiO₂. This shows that the reaction between LiOH and Nickel Oxide is not occurred properly. The sample of LiNiO₂-Li₂CO₃ has a larger crystallite size than LiNiO₂-LiOH. It can be predicted that the sample of LiNiO₂-Li₂CO₃ will have higher electrochemical performance than LiNiO₂-LiOH. Even though high crystalline LiNiO₂ are achieved, a longer and higher temperature reaction is required in order to obtain pure LiNiO₂ phase materials.

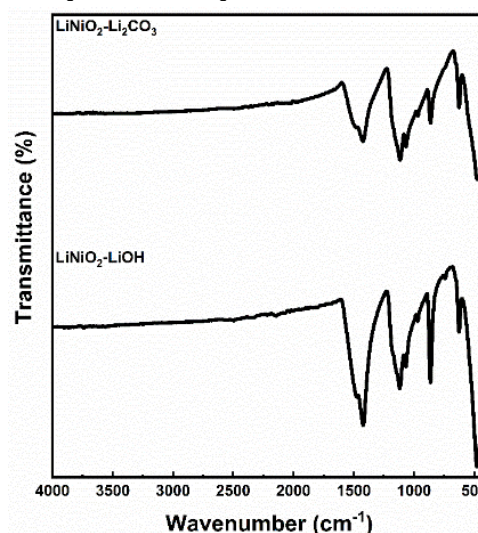


Figure 2. FT-IR Spectrum of the Lithium Nickel Oxide as-prepared samples

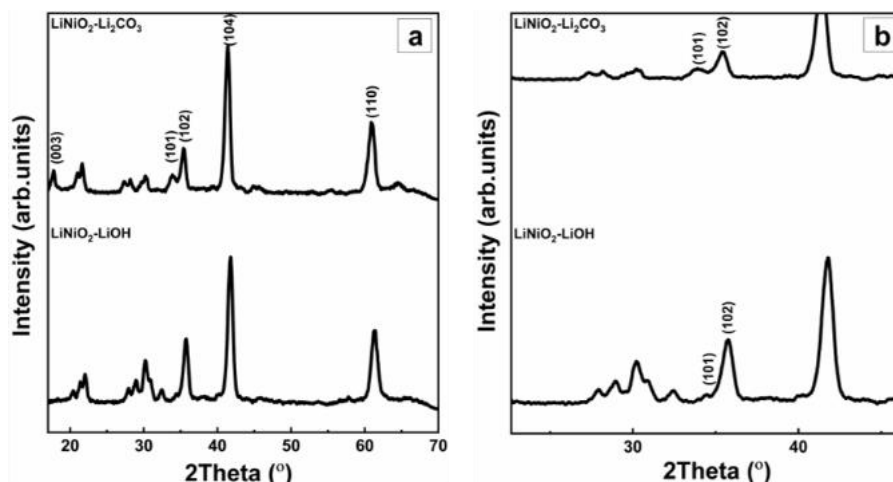


Figure 3. (a) XRD pattern of the Lithium Nickel Oxide as-prepared samples. (b) zoomed in at the peaks of 101 and 102

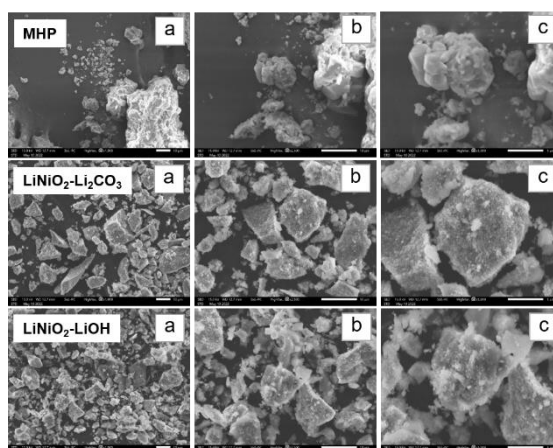


Figure 4. SEM images of the MHP and Lithium Nickel Oxide as-prepared materials at (a) 1,000x, (b) 2,500x, and (c) 5,000x magnification

The morphology of the samples has been analyzed using Scanning Electron Spectroscopy (SEM) at 1,000x, 2,500x, and 5,000x magnification. Figure 4 shows SEM images of LiNiO₂ cathodes prepared from LiNiO₂ synthesized by lithiation of the MHP with Li₂CO₃ and LiOH·H₂O. Based on the figure, it can be seen that both of the materials have an irregular morphology. The sample of LiNiO₂-Li₂CO₃ has a larger particle size than LiNiO₂-LiOH but is not overly significant, which were 2-12 microns and 1.5-10 microns, respectively. Both samples tend to retain their original shape

so that it has a similar morphology when compared to the morphology of MHP as shown in Figure 4. The components contained in the sample are also confirmed using Energy Dispersive X-ray (EDX), which is presented in table 1. Based on the EDX results, there are impurities in the samples, so it is necessary to do a post-treatment such as re-washing and re-heated to remove the Na content in the sample [16], [17].

Table 1. Energy Dispersive X-ray (EDX) of the Lithium Nickel Oxide as-prepared materials

No.	Element	Mass%	
		LiNiO ₂ -Li ₂ CO ₃	LiNiO ₂ -LiOH
1	Ni	51.60	35.06
2	O	33.80	47.77
3	Na	4.94	3.79
4	S	6.63	3.23
5	C	-	8.47
6	Mg	3.03	1.68
Total		100.00	100.00

5. Conclusions

The sample of LiNiO₂ has been synthesized by solid-state method using mixed hydroxide precipitate (MHP) as a nickel source and a different lithium source. The stretching vibrations of the C-O and C-O-H bonds are clearly seen in the FT-IR analysis. The samples have good crystal structures according to the results of the

XRD analysis. The SEM images were shown that each materials have an irregular morphology. This study showed a promising method to obtain LiNiO₂ from MHP, however the formation of pure LiNiO₂ require further investigation.

Acknowledgment: The authors expressed their gratitude to the Centre of Excellence for Electrical Energy Storage Technology (CE-FEEST), Universitas Sebelas Maret for providing the research facility and the raw material.

The authors confirm contribution to the paper as follows: study conception and design: M. Rahmawati, E. Apriliyani; data collection: M. Rahmawati, E. Apriliyani; analysis and interpretation of results: M. Rahmawati, E. Apriliyani. T. Paramitha; draft manuscript preparation: M. Rahmawati, E. Apriliyani, T. Paramitha, H.S.E.A. Gustina. All authors reviewed the results and approved the final version of the manuscript.

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