A Layered Lithium Nickel Manganese Oxide as Environmentally Friendly Cathode Material for Secondary Batteries

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ABSTRACT: Cobalt-free cathode material development is considered necessity to assure the sustainability of Li-ion batteries. Cobalt is always considerably expensive and unsafe for both human and environment. LiNi₀.₅Mn₀.₅O₂ (LNMO) is a layer structured cathode material that has similar features to LiCoO₂ (LCO). A simple and fast processing of LNMO is proposed. A precipitation of nickel manganese oxalate was obtained in a batch reactor under atmospheric condition. The as-obtained homogenous oxalate precursor was converted to LNMO via high temperature lithiation. Based on the XRD result, a crystalline product with layer structure is successfully obtained. The presence of impurities such as residual Li can be detected from the FTIR spectra. SEM Images confirmed quasi-spherical particles with grain size of less than 10 micrometer. The charge-discharge analysis of LNMO containing cell delivers a capacity of 42 mAh/g. In spite of its promising report, continuous improvement is necessary to obtain cell with better electrochemical performance.

Keywords: Li-ion battery, cobalt-free cathode, crystallization, sintering.

1. Introduction

Energy storage technology is a crucial part for electric vehicles. New and renewable energy generation is also relied on energy storage system which assists to provide electricity with good power quality. Today, the most reliable energy storage is Li-ion batteries (LIBs) [1][2]. In comparison to the other secondary energy storage, LIBs have several advantages such as high energy density, high power density, long cycle life, compatible for numerous applications, and safety. There are four main parts in a LIBs, namely: cathode, anode, electrolyte and separator [3]. In the uncharged state, cathode material contains lithium that can be extracted during the charging process, and vice versa. This prove that cathode is the crucial part of a cell and can determine the cell behavior and performance [4][5].
Since the first commercialization of Li-ion batteries by SONY, a layer structured material is preferable due to its high capacity and high voltage operation[6]. However, the first commercialized cathode material, LiCoO$_2$, is not promising to be used for electric vehicles and stationary energy storage because it is considered expensive and toxic or harmful for both human and environment. Several studies have been employed to reduce the content of cobalt[7][8]. Two decades ago, transitional metal substitutes have been investigated. Lithium nickel cobalt aluminum oxide (NCA) and lithium nickel cobalt manganese oxide (NCM) are developed and successfully penetrates the LIB markets[9]. However, as time goes by, the presence of cobalt is still hinder the full commercialization of LIBs and therefore, most researchers focused on full elimination of cobalt in the cathode material [10].

LiNi$_{0.5}$Mn$_{0.5}$O$_2$ (LNMO) cathode material is a layer structured cobalt-free cathode material. It has equimolar mixture of Ni and Mn [11]. The synthesis of LNMO can be performed by several methods such as solid-state method, sol-gel, and precipitation. Precipitation can be performed using various precipitating agents, i.e. hydroxides, carbonates, and oxalates[12]. Oxalate precipitation offers various benefit such as stability upon atmospheric condition, and excellent homogenous and particle size distribution[13]. Therefore, we report a batch and atmospheric precipitation technique for the synthesis of LNMO. The sintering process were performed in order to obtain high crystalline product. The precursor and products are thoroughly analyzed and applied as cathode material.

2. Experimental Method
2.1 Material
The materials used are nickel chloride hexahydrate (NiCl$_2$·6H$_2$O) (Zenith, Brazil), manganese sulfate monohydrate (MnSO$_4$·H$_2$O) (Merck, Germany), Oxalic Acid dihydrate (C$_2$H$_2$O$_4$) (Merck, Germany), Sodium hydroxide (NaOH) (Asahimas, Indonesia) and Lithium Carbonate (Li$_2$CO$_3$, Sichuan Brivo Chemical Co. Ltd, China).

2.2 Methodology
2.2.1 Synthesis of Ni$_{0.5}$Mn$_{0.5}$C$_2$O$_4$.
The first step is to mix 238 grams of NiCl$_2$·6H$_2$O and 188 grams of MnSO$_4$·2H$_2$O were dissolved in 1L distilled water. Then the solution mixture was stirred and heated at 60ºC for 4 hours. Simultaneously added 1 M oxalic acid solution and 2 M NaOH solution slowly. The mixed solution was then precipitated and washed with water until the pH was neutral. After that, the solution was filtered and dried in an oven to form Nickel Manganese Oxalate. The second step was the nickel manganese oxalate precursor was calcined at 500°C for 5 hours. Then after the material has been calcined, a lithiation process is carried out by adding lithium carbonate using a mortar and pestle. After that, the material was sintered at 800°C for 8 hours. Product LiNi0.5Mn0.5O2-C2O4 then grind until smooth and filtered 200 mesh.

2.2.2 Characterization of materials and electrochemical performance test.
Powder X-ray diffraction (XRD) was used to evaluate the crystal structure of the obtained powder materials. These three samples were tested using a mini diffractometer (MTI, USA) with CuK$\alpha$ radiation = 1.5418 in the range of 17-67°. SEM (Scanning Electron Microscope) testing was also carried out at 5000 x magnification (JEOL, Japan). The Fourier transfer infrared (FTIR) test was also applied to samples operating with a wavelength range of 400-4000 cm$^{-1}$ at room temperature (Shimadzu, Japan). Electrochemical performance tests were evaluated on a 18650 cylindrical battery. The anode sheet was prepared by coating graphite on both sides of Cu foil. Moreover,
the cathode sheet was prepared by coating a mixture of LiNi_{0.5}Mn_{0.5}O_{2}: CMC: AB: SBR = 9:2:5:3 in aqueous solvent on both sides of Al foil, with a thickness of 300 µm. The products were then dried and assembled in cylindrical cells using an assembly kit (MTI, USA).

3. Results and Discussion

3.1 Characterization of the Precursors

The structure of the precursor powder of Nickel Manganese Oxalate (Ni_{0.5}Mn_{0.5}C_2O_4.2H_2O) X-ray diffraction is illustrated in Figure 1. In the turtle, no additional peaks were identified due to manganese oxalate dihydrate and no impurity peaks were detected [14], indicating that Ni and Mn were homogeneously distributed in the precursor. The precursor sample of Ni_{0.5}Mn_{0.5}C_2O_4.2H_2O has a hexagonal lattice structure of oxalate groups [15].

Figure 3. shows the morphology of the precursor of Nickel Manganese Oxalate (Ni_{0.5}Mn_{0.5}(C_2O_4).2H_2O) at magnification (a) 1000x, (b) 2500x, and (c) 5000x analyzed by Scanning Electron Microscope (SEM). From Figures 3.(a),(b), and (c) it can be seen that the morphology of the precursor particles of Nickel Manganese Oxalate (Ni_{0.5}Mn_{0.5}(C_2O_4).2H_2O) has a uniform shape which is spread evenly. At 1000x magnification (Fig. 3. (a)) it has a particle size of microns. At 2500x magnification (Fig. 3. (b)) it has a particle size of 2.45 microns. At 5000x magnification 3.85 (Fig. 3. (c)) it has a particle size of 6.75 microns.
3.2 Characterization of the Product of LiNi_{0.5}Mn_{0.5}O_2-C_2O_4.

The structure of the X-ray diffraction product Lithium Nickel Manganese Oxide – Oxalate (LiNi_{0.5}Mn_{0.5}O_2·C_2O_4) is illustrated in Figure 4. In this figure, the curve forms a sharp diffraction peak. The XRD results of the Lithium Nickel Manganese Oxide – Oxalate (LiNi_{0.5}Mn_{0.5}O_2·C_2O_4) sample are in accordance with the literature, namely ICDD No: PDF-01-080-55 [19]. The diffraction peaks on the sample curve of Lithium Nickel Manganese Oxide – Oxalate (LiNi_{0.5}Mn_{0.5}O_2·C_2O_4) form a sharp curve, and have the highest diffraction peak at peak (003). The XRD pattern of the Lithium Nickel Manganese Oxide – Oxalate (LiNi_{0.5}Mn_{0.5}O_2·C_2O_4) sample has a hexagonal structure and there are no impurities in this curve [20]. In addition, there are double split peaks that can be observed at peak (006)/(102) and (108)/(110) on both peaks indicating the presence of a high crystal structure with a layered structure [21]. The lattice constants of Lithium Nickel Manganese Oxide were shown in Table 1.

### Table 1. Lattice parameter of LNMO55.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice Constant Parameters (Å)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Nickel Manganese Oxide – Oxalate</td>
<td>2.855</td>
<td>14.115</td>
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The FTIR spectroscopy of the Lithium Nickel Manganese Oxide – Oxalate (LiNi_{0.5}Mn_{0.5}O_2·C_2O_4) product is presented in Figure 5. This curve shows that the Lithium Nickel Manganese Oxide – Oxalate (LiNi_{0.5}Mn_{0.5}O_2·C_2O_4) spectrum has a small peak at the wavelength ~2300 cm\(^{-1}\) which at this peak shows a carbonate group [22]. In addition, the absorption peak at the wavelength ~500 cm\(^{-1}\) where this peak reveals a bending mode (O–Mn–O (or) O–Ni–O) [23].
Figure 6. shows the morphology of the Lithium Nickel Manganese Oxalate (LiNi$_{0.5}$Mn$_{0.5}$O$_2$-C$_2$O$_4$) product at (a) 1000x, (b) 2500x, and (c) 5000x magnification analyzed by Scanning Electron Microscope (SEM). From Figures 3.(a),(b), and (c) it can be seen that the particle morphology of the Lithium Nickel Manganese Oxalate (LiNi$_{0.5}$Mn$_{0.5}$O$_2$-C$_2$O$_4$) product is irregularly shaped particles. At (Fig. 3. (a)) 1000x, (Fig. 3. (b)) 2500 and (Fig. 3. (c)) 5000x magnification it has an average particle size of 2.3 microns, 4.55 microns and 5.59 microns, respectively.

3.3. Electrochemical Performance Test

The electrochemical performance of LiNi$_{0.5}$Mn$_{0.5}$O$_2$-C$_2$O$_4$ obtained by oxalate coprecipitation carried out using graphite/LiNi$_{0.5}$Mn$_{0.5}$O$_2$-C$_2$O$_4$ at 20 mA/g is shown in Figure 7. Figure 7 shows that LiNi$_{0.5}$Mn$_{0.5}$O$_2$-C$_2$O$_4$ has a charge capacity of 86 mAh/g at a voltage of 0 V - 4.5 V while the discharge capacity is 42 mAh/g at a voltage of 4.5 V - 2.5 V. The charge-discharge capacity is low due to the phenomenon of cation mixing, which causes the capacity to be low, far from the theoretical capacity[24]. However, even though it has a low capacity, the LiNi$_{0.5}$Mn$_{0.5}$O$_2$-C$_2$O$_4$ sample can prove this material is functional as energy storage, but it needs improvement and innovation to produce a better capacity.

4. Conclusion

In conclusion, Lithium Nickel Manganese Oxide LiNi$_{0.5}$Mn$_{0.5}$O$_2$-C$_2$O$_4$ synthesized by co-precipitation of oxalate can be used as a functional material as an energy store. This is evidenced by the XRD results of the Lithium Nickel Manganese Oxide LiNi$_{0.5}$Mn$_{0.5}$O$_2$-C$_2$O$_4$ sample showing high crystallinity, the sample has a hexagonal structure and there are no impurities in this curve. Furthermore, LiNi$_{0.5}$Mn$_{0.5}$O$_2$-C$_2$O$_4$ show any peak carbonate groups in the FTIR results. LiNi$_{0.5}$Mn$_{0.5}$O$_2$-C$_2$O$_4$ exhibits electrochemical performance with charge-discharge capacities of 86 mAh/g and 42 mAh/g, respectively. Thus, the manufacture of Lithium Nickel Manganese Oxide by
synthesis through oxalate co-precipitation can be developed.

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Author Contributions
Firmansyah Adi Nugroho carried out the experiment. Meidiana Arinawati wrote the manuscript with support Cornelius Satria Yudha. The final report was committed by all contributors.

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