Al doped LiNi$_{0.6}$Co$_{0.3-x}$Ti$_{0.1}$Al$_x$O$_2$ cathode material via combustion method

Wan Aida Hazwani Wan Azizan$^{1,2}$, Muhd Firdaus Kasim$^{1,2}$*, Roshidah Rusdi$^{1,3}$ and Kelimah Elong$^{1,2}$

$^1$Centre for Nanomaterials Research, Institute of Science, Universiti Teknologi MARA, Malaysia.
$^2$School of Chemistry and Environment, Faculty of Applied Sciences, Universiti Teknologi MARA, Malaysia.
$^3$School of Physics and Material Studies, Faculty of Applied Sciences, Universiti Teknologi MARA, Malaysia.

*muhdfir@salam.uitm.edu.my

Abstract. Aluminium (Al) was doped into cobalt sites of LiNi$_{0.6}$Co$_{0.3}$Ti$_{0.1}$O$_2$ (LNCT) material, producing LiNi$_{0.6}$Co$_{0.29}$Ti$_{0.1}$Al$_{0.01}$O$_2$, LiNi$_{0.6}$Co$_{0.27}$Ti$_{0.1}$Al$_{0.03}$O$_2$ and LiNi$_{0.6}$Co$_{0.25}$Ti$_{0.1}$Al$_{0.05}$O$_2$ cathode materials denoted as LCA1, LCA3 and LCA5 respectively. The synthesis of those materials were using self-propagating combustion method. The doping of Al is done to reduce the toxicity of Co element and to stabilize the cathode structure in order to increase the initial discharged capacity of the lithium-ion battery system. The characterization of the materials was done by using X-Ray Diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM). Based on the XRD results, all materials showed a single phase structure. Meanwhile, FESEM results revealed that all materials are polyhedral like shape but the Al doped materials have smaller crystallite size than the undoped material. The electrochemical performance of the battery system using the synthesized cathode were tested. According to the battery testing results, the initial discharged capacity of the Al doped battery were successfully increased.

1. Introduction

The demand of portable electronic devices increases the usage of energy storage system such as battery. Lithium-ions battery is the most preferred system since it gives high energy density and low self-discharge rate [1–3]. The important role of cathode material in the battery system had attracted researchers to improvise the material so that a better battery will be produced. Currently, the commercialize cathode material used is LiCoO$_2$ [1, 4]. LiCoO$_2$ is chosen due to its well-ordered layered crystal structure that serve a high theoretical specific capacity of 274 mAh/g [5]. However, the cobalt element in the LiCoO$_2$ material is a major concern since cobalt is toxic and expensive [6]. Therefore, researchers are trying to substitute the cobalt with another safer and cheaper element.

Apparently, LiNiO$_2$ has become a promising material to replace LiCoO$_2$ since nickel is cheaper and less toxic than cobalt [7, 8]. However, its electrochemical performance decreases during lithium deintercalation process [7]. Thus, the nickel element is being partially substituted with cobalt or any other suitable element in order to maintain its good performance.

A research on Ni rich materials of LiNi$_{0.6}$Co$_{0.3}$Ti$_{0.1}$O$_2$ had been done [9]. This material shows initial specific discharge capacity of 100 mAh/g. However, this material is quite big (micron) crystallite size.
that lead to longer Li⁺ pathway and small interfacial contact area with the liquid electrolyte. Some research had been done, showing that aluminium (Al) doped materials serve higher discharge capacity and improved cycling stability [10–12]. Besides, Al is cheaper and less toxic than Co and Ni [6]. Thus, we improvise the material by doping Al into cobalt sites of \( \text{LiNi}_{0.6}\text{Co}_{0.3-x}\text{Al}_x\text{Ti}_{0.1}\text{O}_2 (x=0.01, 0.03, 0.05) \) by using combustion method. This method was used due to its short synthesis time and the crystallite size of the product formed is uniform [13]. The performance of the synthesized materials was measured in term of their crystal structure, morphology and electrochemical performance.

2. Methodology

LNCT, LNA1, LNA3 and LNA5 were synthesized by self-propagating (SPC) combustion method. The starting materials used were lithium nitrate (LiNO₃), nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O), cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), titanium nitrate (Ti(NO₃)₄) and aluminium (III) nitrate nonahydrate (Al(NO₃)₃·9H₂O). The calculated stoichiometry amount of starting materials needed were dissolved in deionized water and mixed with citric acid. The solution was combusted and precursor was obtained. The precursor was then being annealed at 700 °C for 24 hours to obtain the final product (cathode material) [14–16].

The characterization of the cathode materials was done by using X-ray Diffraction (XRD). The XRD data was obtained by using PANalytical Xpert Pro powder diffraction equipment. The measurement was done using Cu Kα X-ray radiation over 2 range of 10° – 90°. As for the morphology study, Field Emission Scanning Electron Microscopy (FESEM) was used. The FESEM images were obtained using JEOL JSM-7600F instrument.

The fabrication process of the cathode material was done by mixing 80% of active material, 10% of carbon as conducting agent and 10% of polytetrafluoroethylene (PTFE) as a binder. The mixture was then being pressed onto a stainless steel grid and allowed to dry at 200 °C for 24 hours. The fabricated cathode was assembled under argon gas atmosphere in glovebox (Mbraun Labmaster). The battery system uses lithium metal as the anode, fabricated cathode and 1M LiPF₆ in EC/DMC (1/1 v/v) from Mitsubishi Chemicals as the electrolyte. The electrochemical charge-discharge performance was tested using WonaTech WBCS 3000 (Korea) battery tester, at a constant current of 1.0 mA and cycled at a voltage range of 2.5 to 4.3 V [17, 18] for 50 cycles.

3. Results and discussion

Figure 1 shows the XRD pattern of undoped cathode material LNCT and Al doped LNCT; LCA1, LCA3 and LCA5. Based on the portrayed pattern, all materials show pure, layered and rhombohedral structure, tally with LiNiO₂ structure with ICDD database pattern number of 01-070-4310. These results indicate that Al is successfully substituted into LNCT crystal lattice.

Referring to the XRD peaks, (003) diffraction peak has the highest peak, indicating highest crystallinity (well-ordered atoms in cell). XRD pattern (a) shows that the doublet peaks of (006) and (012), (018) and (110) are asymmetry peaks, meaning that the two peaks are not split completely. Meanwhile, XRD patterns (b), (c) and (d) show complete merge of those duplet peaks. That combined peaks specify that there is cation mixing [19]. There was also a research done revealing that cation mixing helps to stabilize the active materials’ structure, slower the voltage decay and capacity fading for long-term cycling [20]. However, the portion of cation mixing give great different in the battery performance. According to Lee et. al, too much cation mixing reduce the electrochemical performance since the Li⁺ migration will be blocked by other cations [21]. The degree of cation mixing in the materials can be determined based on the calculated intensity ratio \( I_{003}/I_{104} \) (RIR value). Based on Table 1, LCA1 has the highest RIR value, meaning that LCA1 has the lowest degree of cation mixing [22]. Besides, Kim et. al (2016) stated that, the RIR value also expresses the degree of cation ordering [23]. High RIR value indicates uniform cation ordering due to low cation mixing between octahedral layers [23]. This phenomenon is believed to give LCA1 a higher electrochemical performance since the Li⁺ migration will not be disturbed or blocked by other cations [21]. The \( R \) factor results eventually support
the RIR results. Referring to Table 1, all samples have $R$ factor value of 1.0, indicating good cation ordering [22].

![XRD patterns](image)

**Figure 1.** XRD patterns of (a) LNCT (b) LCA1 (c) LCA3 (d) LCA5 annealed at 700°C for 24 hours.

From the (003) peaks, the FWHM of LNCT, LCA1, LCA3 and LCA5 were measured using Scherer equation. The increased value of FWHM (broaden peak) of the Al doped samples indicate that the crystallites become smaller [14]. Smaller crystallites promote better strain for structural transformation upon continuous lithiation and delithiation process [24]. Figure 2 shows the illustration of Al doped structure. Further details of the electrochemical performance of the materials is discussed in battery testing analysis.

| Cathode material | $RIR$ | $R$ factor | FWHM | Crystallite size (nm) | Strain (%) |
|------------------|-------|------------|------|-----------------------|------------|
| LNCT             | 1.15  | 0.92       | 0.42 | 344.6                 | 0.24       |
| LCA1             | 1.17  | 0.87       | 0.47 | 159.2                 | 0.56       |
| LCA3             | 1.03  | 0.89       | 0.45 | 265.4                 | 0.43       |
| LCA5             | 1.02  | 0.88       | 0.45 | 265.4                 | 0.43       |

**Table 1.** $RIR$, $R$ factor, FWHM, crystallite size and strain values for LNCT, LCA1, LCA3 and LCA5.
Figure 2. Illustration of Al doped into Co site of LNCT.

Figure 3. FESEM images at 50k magnification of (a) LNCT (b) LCA1 (c) LCA3 (d) LCA5 annealed at 700°C for 24 hours.

Figure 3 shows the surface morphology of LNCT, LCA1, LCA3 and LCA5 observed using FESEM at 50k magnification. Based on the captured figures, all samples show polyhedral like shape crystals. In addition, the particle size of LCA1 (60 nm to 120 nm), LCA3 (60 nm to 140 nm) and LCA5 (60 nm to 160 nm) are smaller than LNCT (120 nm to 200 nm) and the average particle size of LCA1, LCA3, LCA5 and LNCT are 84 nm, 94 nm, 90 nm and 152 nm respectively. Therefore, it is proven that partial substitution of Al in LNCT material has reduce the particle size of the materials. The reduction of particle size indicates increased contact area of the material. The increase in contact area, increases lithium ions exchange and at the same time, the intercalation/deintercalation rate of Li ions will increase as well [25]. Therefore, the performance of the batteries will be improved with the increase in intercalation/deintercalation rate of lithium ions. The charge-discharge capacity of all materials are discussed in the battery testing analysis.
Figure 4 shows the initial specific discharged capacity patterns and the cycling performance of LNCT, LCA1, LCA3 and LCA5 cathode materials. Further details of the electrochemical performances of the four samples was tabulated in Table 2. Referring to Table 2, the initial specific discharged capacity of LNCT, LCA1, LCA3 and LCA5 cathode materials are 150.5 mAh/g, 238.6 mAh/g, 242.6 mAh/g and 172.9 mAh/g respectively. The initial specific discharged capacity of all Al doped materials were successfully increased. However, they suffer from high capacity fading upon 50th cycle. This phenomenon is well agreed as mention in the XRD results discussed earlier. The doping of Al apparently is to stabilize the cathode structure since Al is expected to hold the structure from collapse during lithiation/delithiation process, but due to too much cation mixing, the structure is not stable. In addition, non-transition metal (Al) is electrochemically inactive. The addition of large amount of this non-transition metal cause the reversible capacity of the batteries become low [26]. In consequence, the performance of the battery keeps dropping throughout the 50th cycle. Thus, an improvement of the material will be further investigated for future work.

Table 2. Discharged capacity and capacity fading of LNCT, LCA1, LCA3 and LCA5.

| Cathode material | 1st discharged capacity (mAh/g) | 50th discharged capacity (mAh/g) | Capacity fading (%) |
|------------------|---------------------------------|----------------------------------|---------------------|
| LNCT             | 150.5                           | 132.4                            | 12.0                |
| LCA1             | 238.6                           | 92.8                             | 61.1                |
| LCA3             | 242.6                           | 49.2                             | 79.7                |
| LCA5             | 172.9                           | 6.7                              | 96.1                |

4. Summary
Aluminium doped cathode materials were prepared and pure, layered compound were successfully synthesized. Partial substitution of Al into LNCT material has decrease the crystallite size of the doped materials. As the result, the initial discharged capacity of the doped materials is higher than LNCT. However, they suffer from very high percentage of capacity fading due to inactivity of Al, making the performance low upon 50th cycle. Therefore, future works will be done in order to overcome this problem, making Al doped LNCT materials a higher potential to replace the commercialized cathode materials.
Acknowledgement
The authors would like to thank the Ministry of Education for the grants (FRGS/1/2017/STG01/UIJT/03/13) and Centre for Nanomaterials Research, Institute of Science, Universiti Teknologi MARA, Shah Alam, Malaysia for their support to this work.

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