Phase and Morphological Studies of LiCo\textsubscript{0.3}Ni\textsubscript{0.3}Mn\textsubscript{0.3}Ti\textsubscript{0.1-}\textsubscript{x}Sn\textsubscript{x}O\textsubscript{2} Cathode Materials

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Abstract. The substitution of LiCo\textsubscript{0.3}Ni\textsubscript{0.3}Mn\textsubscript{0.3}Ti\textsubscript{0.1-}\textsubscript{x}Sn\textsubscript{x}O\textsubscript{2} materials with Sn is done to investigate the effect on the phase and morphology. The materials were synthesized via a combustion method. The annealing temperature and time of the precursors was obtained at 700 °C for 24 hours. The crystalline phase and purity of the materials are studied using X-Ray Powder Diffraction (XRPD). All the materials were observed to be pure phase and good cation ordering. Field Emission Scanning Electron Microscope (FESEM) is used to assess the morphology and the crystallites size of the materials. The images showed that the materials consist of polyhedral shaped crystals and well-crystallized particles with smooth surfaces. The % calculated synthesized materials shows close stoichiometry to the % element content from the EDX measurements of the synthesized materials within experimental error.

1. Introduction
The only source that can produces electrical energy from movement of Li\textsuperscript{+} ions to and to between the cathode and anode electrode is lithium-ion battery. It is considered as a non-hazardous battery because their component can be recycled, and this made them the best power option in the near future [1]. It widely used in commercialization due to its high specific power, high specific energy, good high temperature-performance, low self-discharge, high energy density, lightest weight battery, long cycle life, no memory effect (no reconditioning process is needed) and so on [2].

High demand in batteries application for cathode layered oxides is due to its higher theoretical specific capacities which are about double from the spinels. Lithium cobalt oxide, LiCoO\textsubscript{2} (LCO) is the most common commercial cathode that use in lithium-ion batteries. It is a member of the Li transition metal oxides family [3]. Larger difference in ionic radius between Li\textsuperscript{+} and Co\textsuperscript{3+} makes LCO an ideal layered structure. Extraction and insertion of lithium ions more easily take place because it provides a two-dimensional array of interstitial sites with a rhombohedral structure. One of the advantages of LCO is good rechargeability even at high rates and easy to prepare but it suffers from three major restrictions which are toxicity, cost, and scarcity [4]. Therefore, it is logical to produce materials with less Co content for commercial applications such as LiNiO\textsubscript{2} materials.

Lithium nickel cobalt manganese oxides, LiNi\textsubscript{0.3}Co\textsubscript{0.3}Mn\textsubscript{0.3}O\textsubscript{2} (NMC) have attracted extensive attention use as a cathode material due to its excellent properties such as higher capability, safety, and
low cost [5]. It also considered as one of the promising candidates to replace LiCoO2 in lithium-ion batteries application. It is because this material can present higher capacity when charged at higher voltage. Li [6] reported that NMC gave a higher capacity of about 184 mAhg−1 in the voltage range of 2.5 – 4.6 V. However, the results show capacity fading became faster than that over the voltage range. Substitute Titanium (Ti) and Tin (Sn) [7] in the cathode material with comparable or better performance than the commercial material, LiCoO2, is the main objective in cathode materials research. However, it is not easy to find good and suitable materials for mass production. We have synthesized and prepared the novelty materials, LiCo0.3Ni0.3Mn0.3Ti0.1-xSnxO2 (x = 0.0, 0.0005, 0.001).

2. Experimental

The synthesis method used to prepare LiCo0.3Ni0.3Mn0.3Ti0.1-xSnxO (x = 0.0, 0.0005, 0.001) materials was via combustion method. This method is chosen due to easier preparation and shorter time to complete the reaction which is over in a few seconds [8]. Lithium nitrate, LiNO3, tin (II) acetate (Sn(C2H3O2)2), nickel (II) nitrate hexahydrate (Ni(NO3)2.6H2O), titanium nitrate (Ti(NO3)4), manganese (II) nitrate hexahydrate, Mn(NO3)2.xH2O, and cobalt (II) nitrate hexahydrate, Co(NO3)2.6H2O were used as starting materials. Deionized water was used as a solvent to dissolve the stoichiometric amounts of starting materials separately before mixed with a fuel, citric acid C6H8O7. The heating process of the solution mixture was done at 200 °C until it has reached its ignition conditions. The process was done in the fume cupboard and it took about five to ten minutes for the precursor to completely dry.

The annealing temperature and time of the precursors was obtained at 700 °C for 24 hours. X-Ray Diffraction on PANalytical Xpert Pro powder diffraction was using to identify the crystallographic structure and the crystalline phase of the materials. The potential and current that used are at 45 kV and 40 mA. The reflection mode was done using Cu Ka X-Ray radiation over the 20 range of 10° – 90° with 10s counting time and 0.02° step size. The materials were measured by using a Bragg-Brentano optical configuration with the spinning mode in order to minimize the preferred orientation effects. The morphologies and crystallite size of materials were determined by FESEM instrument, JEOL JSM-7600F Field Emission Scanning Electron Microscope attached to an Energy Dispersive X-Ray Spectroscopy (EDS).

3. Results and discussions

Figure 1 showed the XRD patterns of LiCo0.3Ni0.3Mn0.3Ti0.1-xSnxO2 (x = 0.0, 0.0005, 0.001) materials. It was observed that the phase obtained for all the materials were pure (no impurity peaks detected), clear and sharp in the XRD patterns. That means the substitutions of Ti+ and Sn+ ions have been successfully in the LiNi0.3Co0.3Mn0.3O2 structure. All the fingerprint peaks viz. (003), (104), (006), (012), (101), (018) and (110) are clearly observed and easily identifiable in all XRD patterns. The diffraction peaks can be indexed to the α –NaFeO2 structure (R-3m space group) based on the hexagonal crystal system.

XRD patterns of LiCo0.3Ni0.3Mn0.3Ti0.1-xSnxO2 materials are isostructural with LiNiO2 and LiCoO2 phases as compared with the XRD patterns in the ICDD database. The XRD pattern clearly shows that the material is a single phase and sharp peaks in the spectra which indicate the materials were well-crystallized. The integrated intensity ratio of (003) and (104) peaks, called RIR is taken as a measure of the cation ordering and structure stability of the materials. RIR value above 1.2 indicates good cation ordering [9]. Our result shows the RIR value for LiCo0.3Ni0.3Mn0.3Ti0.099Sn0.001O2 and LiCo0.3Ni0.3Mn0.3Ti0.0995Sn0.0005O2 materials are 1.56, 1.53 and 1.52 respectively which indicate this material has good cation ordering [10].
Figure 1. XRD patterns of (a) LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.1}$O$_2$ (b) LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.099}$Sn$_{0.0005}$O$_2$ (c) LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.099}$Sn$_{0.001}$O$_2$ and the enlargement XRD patterns from 15° to 50° for (d) LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.1}$O$_2$ (e) LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.099}$Sn$_{0.0005}$O$_2$ (f) LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.099}$Sn$_{0.001}$O$_2$ cathode material anneal at 700 °C for 24 hour.

Figure 2 show the morphologies of the LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.1}$O$_2$, LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.099}$Sn$_{0.0005}$O$_2$, LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.099}$Sn$_{0.001}$O$_2$ and LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.099}$Sn$_{0.0005}$O$_2$ materials with magnification 30K. The images showed that the materials consist of polyhedral shaped crystals and well-crystallized particles with smooth surfaces. The range of the crystallite size that shows in Table 1 is about 30 – 130 nm which is considered as nano size because the average crystallite size of LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.1}$O$_2$, LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.099}$Sn$_{0.0005}$O$_2$, and LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.099}$Sn$_{0.001}$O$_2$ materials are 79 nm, 67 nm and 59 nm respectively. The crystallite size of the materials decreases as the amounts of Sn substitution in LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.1}$O$_2$ is increased.
Figure 2. SEM images of (a) LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.1}$O$_2$ (b) LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.0995}$Sn$_{0.0005}$O$_2$ (c) LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.099}$Sn$_{0.001}$O$_2$ materials with magnification of 30000x.

Table 1. The crystallite size of LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.1-x}$Sn$_x$O$_2$ materials.

| Sample                          | Crystallite Size Range (nm) | Avg Crystallite Size (nm) |
|---------------------------------|-----------------------------|---------------------------|
| LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.1}$O$_2$ | 50 - 130                    | 79                        |
| LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.0995}$Sn$_{0.0005}$O$_2$ | 35 - 115                    | 67                        |
| LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.099}$Sn$_{0.001}$O$_2$ | 30 - 90                     | 59                        |

Figure 3 shown the EDX measurements and the % elemental composition is listed in Table 2. The % element of the calculated synthesized materials shows close stoichiometry to the % element of the synthesized materials measured by EDX within experimental error. Once again, this proves that the substitution of Sn in the LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.1}$O$_2$ samples was successful. Therefore, results from EDX support the accuracy of the cation content of the synthesized materials (Table 2).

Figure 3. EDX Spectrum of samples (a) LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.1}$O$_2$ (b) LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.0995}$Sn$_{0.0005}$O$_2$ (c) LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.099}$Sn$_{0.001}$O$_2$ material.
Table 2. % Stoichiometry of LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.1-x}$Sn$_x$O$_2$ ($x = 0.0, 0.0005, 0.001$) samples from EDX result.

| Sample ID     | LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.1}$O$_2$ | LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.0995}$ | LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.099}$ |
|---------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| Atomic % of Synthesized Ti | 10                                           | 9.95                                          | 9.9                                          |
| Atomic % of Synthesized Mn   | 30                                           | 30                                            | 30                                           |
| Atomic % of Synthesized Co   | 30                                           | 30                                            | 30                                           |
| Atomic % of Synthesized Ni   | 30                                           | 30                                            | 30                                           |
| Atomic % of Synthesized Sn   | -                                            | 0.05                                          | 0.1                                          |
| Atomic % Ti ± 0.01           | 10.63                                        | 10.03                                         | 9.80                                         |
| Atomic % Mn ± 0.01           | 27.99                                        | 26.53                                         | 25.63                                        |
| Atomic % Co ± 0.01           | 31.96                                        | 32.25                                         | 34.18                                        |
| Atomic % Ni ± 0.01           | 29.41                                        | 31.15                                         | 30.12                                        |
| Atomic % Sn ± 0.01           | -                                            | 0.04                                          | 0.09                                         |
| Synthesized Stoichiometry    | LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.1}$O$_2$ | LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.0995}$ | LiCo$_{0.3}$Ni$_{0.3}$Mn$_{0.3}$Ti$_{0.099}$ |
| Stoichiometry from EDX       | LiCo$_{0.3}$Ni$_{0.2941}$Mn$_{0.2799}$Ti$_0$. | LiCo$_{0.3}$Ni$_{0.3113}$Mn$_{0.2653}$Ti$_{0.1000}$Sn$_{0.0}$ | LiCo$_{0.3}$Ni$_{0.3102}$Mn$_{0.2563}$Ti$_0$. |
| SEM                        | 198O$_2$                                      | 004O$_2$                                      | 008Sn$_{0.0009}$O$_2$                       |
4. Conclusion
Sn substitutes in LiCo0.3Ni0.3Mn0.3Ti0.1O2 materials were successfully done synthesized using the combustion method. XRD results revealed a hexagonal structure were pure without impurity phase for all the materials. The morphologies results show the decreasing of the crystallite size with the introduction of Sn in LiCo0.3Ni0.3Mn0.3Ti0.1O2 lattice materials. The % element of the calculated synthesized materials shows close stoichiometry to the % element of the synthesized materials measured by EDX within experimental error.

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