Synthesis and characterization of NaCo\(_{(1-x)}\)Mn\(_{x}\)O\(_2\) solid electrolyte using sol-gel method: the effect of milling speed variations

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Abstract. Battery is a device that converts chemical energy into electrical energy through electrochemical process. Further research on the synthesis of cathode of Na-ion battery that has good conductivity to maximize the battery performance needs to be conducted. One of the production steps of the NaCo\(_{(1-x)}\)NaCo cathode synthesis in the Na-Ion battery was a ball-milling process, in which by the ball-milling process, the crystal size of NaCo\(_{(1-x)}\)Mn\(_{x}\)O\(_2\) cathode can be minimized. The purpose of this study was to determine the effect of variation of ball-milling speed to the characteristics of resulting product including the oxide types composing NaCo\(_{(1-x)}\)Mn\(_{x}\)O\(_2\) cathode, surface morphology, and conductivity. The main ingredients used were sodium acetate, manganese acetate, cobalt acetate with molar ratio of 0.7: 0.66: 0.22, respectively and citric acid as chelating agent with the M/CA ratio of 1: 1. The variations of milling speed were 0, 300, 400, 500, 600 and 700 rpm. Characterization of the product was conducted using XRD, SEM-EDS, and conductivity meter (LCR-meter). The result showed that a solid electrolyte of NaCo\(_{(1-x)}\)Mn\(_{x}\)O\(_2\) consisting of NaMnO\(_2\), NaO\(_2\), CoO, Co\(_2\)O\(_3\), MnO\(_2\) components was successfully synthesized. The observation on the milling speed at 400 rpm showed that the solid electrolyte produced had the highest conductivity i.e. 4.08 x 10\(^{-6}\) Scm\(^{-1}\) with a homogeneous surface morphology and had a spinel formula NaCo\(_{0.65}\)Mn\(_{0.35}\)O\(_2\).

Keywords: Ball milling, Sodium Battery, Sol-gel, Solid Electrolytes

1. Introduction

Battery is a device that can generate electrical energy. Battery performance is transferring electrons from negative electrode (anode) to positive electrode (cathode) as to generate electric current and potential difference. Battery based on the operating principle is categorized into 2 types, namely, primary and secondary batteries. Primary battery production can only be applied for single use hence once discharged, it is discarded. On the other hand, secondary battery can be used to convert chemical energy into electrical energy through an electrochemical process. This electrochemical process takes place in reversible way therefore this battery is also called rechargeable battery [1].

The electrolyte or ionic conductor is the medium for transferring ions, which are between the anodes and the cathode in the cell. Currently the use of electrolyte tends to switch to solid electrolyte form. This trend is based on safety, leak-free media, easy to use, and can be made with smaller dimensions in sheet form [1].
The research on Na-ion batteries was conducted by Bucher et al. [2] which reported that $\text{Na}_{0.7}\text{Co}_{0.11}\text{Mn}_{0.89}\text{O}_2$ cathode material was synthesized by combustion synthesis method that was in accordance with the research conducted by Cheng and colleagues [3] which the product was $\text{Na}_{2/3}\text{Co}_{2/3}\text{Mn}_{1/3}\text{O}_2$ by co-precipitation method. According to Datta et al. [4], there was an effect of milling time on the character of $\text{NaMn}_2\text{O}_4$ cathode with milling condition using ball weight and sample ratio 10:1. According to research conducted by Lu et al. [5], the ball milling process helped to reduce the crystal size of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ cathode material, which increased the conductivity of the material. While Doubaji et al. [6] reported that $\text{Na}_x\text{Co}_{2/3}\text{Mn}_{2/9}\text{Ni}_{1/9}\text{O}_2$ cathode could be synthesised by sol-gel method followed by ball milling process and calcination at 800°C.

Panabière et al. [7] performed variation on milling speeds i.e. 200, 500 and 700 rpm for 1 h and generated the best retention capacity in the negative $\text{Li}_3\text{Mn}_4$ electrode for Lithium ion batteries, producing the best capacity of 250 mAhg$^{-1}$ in ball-milled with the speed of 500 rpm. The stable capacity was also obtained at 200 and 700 rpm; however, the retention capacity was smaller which were of 220 mAhg$^{-1}$ and 205 mAhg$^{-1}$ respectively. The resulting product ($\text{NaCo}_{1-x}\text{Mn}_x\text{O}_2$) was then characterised using LCR, XRD and SEM-EDS.

This study investigated the effect of milling speed variations conducted at 0, 300, 400, 500, 600 and 700 rpm in producing electrode material that had the best electrical conductivity. The electrodes were synthesised via sol-gel method using sodium acetate, manganese acetate, cobalt acetate and citric acid as chelating agent and continued by characterization using XRD and SEM-EDS.

2. Experimental Method

2.1. Material.
Sodium acetate trihydrate p.a. [CH$_3$COONa.3H$_2$O (Merck)], cobalt acetate tetrahydrate p.a. [Co(CH$_3$COO)$_2$.4H$_2$O (Merck)], manganese acetate tetrahydrate p.a. [Mn (CH$_3$COO)$_2$.4H$_2$O (Sigma Aldrich)], aquabidest p.a., and citric acid monohydrate [C$_6$H$_8$O$_7$.H$_2$O (Merck)].

2.2. Tool
Glass, porcelain, spatula, digital balance, Thermolyne furnace 47900, High Energy Milling (HEM) E3D, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) - Energy Dispersive X-ray Spectroscopy (EDS), LCR HI HIOKI Tester 3532-50.

2.3. Synthesis of $\text{NaCo}_{1-x}\text{Mn}_x\text{O}_2$ Solid Electrolyte
25 mL of CH$_3$COONa 0.7 M, Co(CH$_3$COO) 0.66 M and Mn(CH$_3$COO)$_2$ 0.22 M were mixed into C$_6$H$_8$O$_7$ citric acid solution, then stirred constantly with magnetic stirrer for 2 hours continued by evaporation at 80°C until the gel formed. The formed gel was dried in an oven at 110°C. Further, the result was milled by a ball milling with the speed variations of 300, 400, 500, 600 and 700 rpm for 3 hours at room temperature. The ratio of powder and ball milling used was 1:10. Then, the result in the form of powder was calcined at 800°C for 12 hours.

2.4. Characterization of results
The powder was made into pellet and performed its conductivity using LCR meter to know the ability of solid in conducting electricity. The powder obtained from the calcination was also characterised using XRD and SEM-EDS.

3. RESULTS AND DISCUSSION

3.1. Product Characterization using LCR meter
Figure 1 shows the solid electrolyte conductivity of $\text{NaCo}_{1-x}\text{Mn}_x\text{O}_2$ as function of milling speed. It can be seen that milling speed of 400 rpm, the solid electrolyte had the highest conductivity of 4.08 x 10$^{-6}$ Scm$^{-1}$, whilst the lowest conductivity owed by the $\text{NaCo}_{1-x}\text{Mn}_x\text{O}_2$ solid electrolyte with a milling speed
of 300 rpm which was $0.963 \times 10^{-6}$ Scm$^{-1}$. This indicates that variations in milling speed produced the best electrical conductivity at milling speed of 400 rpm. The electrical conductivity increased 4-fold at a milling rate of 300 rpm to 400 rpm and decreased gradually thereafter. Thus, the milling process of a solid electrolyte should be applied at a given milling speed to produce the highest conductivity. This result may be due to at a given milling speed produced the highest number of holes hence the conductivity increases.

![Figure 1. Graph of effect of milling speed on conductivity](image)

3.2. Product Characterization using XRD

To confirm the effects of milling speed on the crystal structure of NaCo$_{(1-x)}$Mn$_x$O$_2$, XRD observations were carried out and displayed in Figure 2. All the XRD patterns of NaCo$_{(1-x)}$Mn$_x$O$_2$ samples display a set of narrow peaks, which reflect good crystallinity of these materials and all samples have been well prepared. However, the XRD pattern shows the noise that may be caused by by-products on the spinel making process or the formation of low-concentration amorphous materials mixed with the crystal structure. In general, all XRD diffractograms produced similar peak patterns that indicated that the formed solids had the same structure. However, the relative intensity of one peak with another peak were different. These results indicate that the speed of milling does not affect the resulting crystal structure and crystal of NaCo$_{(1-x)}$Mn$_x$O$_2$ structure was not destroyed during milling process.

![Figure 2. XRD diffractogram of NaCo$_{(1-x)}$Mn$_x$O$_2$ solid electrolyte (a) un-milled (b) 300rpm (c) 400rpm (d) 500rpm (e) 600rpm (f) 700rpm](image)
According to the Scherrer formula, the average crystal size for each sample was calculated to be 19.42, 1.04, 1.02, 3.47, 0.74 and 0.84 nm for un-milled sample, samples milled at 300, 400, 500, 600 and 700 rpm respectively. This indicated that the particle size decreased with the increasing milling speed. This result is in accordance with Kar et.al. [8], reporting that the widening peak in diffractogram was associated with small crystal size or lattice strain caused by structural defects such as dislocations or defective arrays.

The peak intensity followed the same pattern as the conductivity pattern presented in Fig. 1. For non-milling samples and samples milled at 300 rpm, the peak of 2θ = 15.7° shows a low intensity. The 2θ peak of 15.7° from the sample with 400 rpm milling speed displays the highest intensity. Furthermore, the peak of 2θ = 15.7° decreases gradually with increasing milling speed. The intensity rise pattern of this diffractogram is closely correlated with the electrical conductivity pattern. These results indicate a correlation between the crystallinity of the battery samples and their electrical conductivity properties. This result is in line with what were reported [9-11] that there was a close relationship between the crystallinity of the material and the electrical conductivity. The conductivity increases with increase of crystallinity may be due to the increased crystallinity reduced the energy barrier to facilitate the diffusion of ions in the electrolyte.

3.3. Product Characterization using SEM-EDS

Further, the products were characterized using SEM-EDS. The three samples observed were non-milled sample, sample having the highest conductivity (milled at 400 rpm) and having the lowest conductivity (milled at 300 rpm) as shown in Figure 3. The electrode materials exhibit exclusively a worm-like structure for all samples. All samples have dense structures and show uniform distribution.

Figure 3a shows that the particle size of the NaCo_{(1-x)}Mn_{x}O_{2} sample was still large and the surface morphology was not homogeneous. This is because the two synthesis materials were simply mixed hence the mixing was uneven. The powder particles were not perfect to produce smaller crystalline sizes so uniform particle size has not yet taken place.

The material treated with a 300 rpm milling speed (Fig. 4b) shows a fairly high porosity. It can be seen that there was a large cavity over the distance between the particles and the presence of agglomerates. For materials treated with 400 rpm milling speed (Fig. 4c), the particle arrangement is finer and denser compared to the 300 rpm milling speed. This may be caused by repeat collision energy during higher grinding hence the particles broke up more frequently.

The compositions of solid electrolyte constituents were analysed using Energy Dispersive Spectroscopy (EDS). EDS results are presented in Table 1.
Table 1. Composition of solid electrolyte constituent elements

| Variation of speed milling | Content of Element (% Mass) | Na  | Co  | Mn  | O   |
|----------------------------|----------------------------|-----|-----|-----|-----|
| 300 rpm (I)               | 20.90                      | 48.72| 30.37| 22.65|
| 400 rpm (II)              | 25.44                      | 49.68| 24.89| 22.79|
| 0 rpm (III)               | 26.64                      | 51.63| 21.73| 22.80|

EDS results can be used to find out the value of x using the formula

\[
x = \frac{(Ar\text{Co} \times \text{mass Mn})}{((Ar\text{Mn} \times \text{mass Co} + Ar\text{Co} \times \text{mass Mn}))}
\]

The values of x obtained from the calculation for samples treated by milling speed of 300, 400 rpm and un-milled samples were 0.29; 0.40 and 0.35 respectively. Thus, the spinel formulas for sample I, sample II and standard sample were \(NaCo_{0.6}Mn_{0.4}O_2\), \(NaCo_{0.65}Mn_{0.35}O_2\) and \(NaCo_{0.71}Mn_{0.29}O_2\), respectively.

4. Conclusion

\(NaCo_{1-x}Mn_xO_2\) solid electrolyte was successfully synthesised using several mineral composers consisting of \(NaMnO_2\), CoO, \(Na_2O\), \(Co_2O_3\) and MnO_2. Treatment of sample by milling speed at 400 rpm showed the highest conductivity of \(4.08 \times 10^{-6}\) S/cm with homogeneous surface morphology and has a spinel formula \(NaCo_{0.65}Mn_{0.35}O_2\).

5. References

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