The effect of chelating agents on the formation of manganese oxide (MnO) in the synthesis of sodium manganese oxide (Na$_2$Mn$_3$O$_7$)

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Abstract. This current study successfully synthesized Na$_2$Mn$_3$O$_7$ in two steps. Firstly, the synthesis of MnO from NaCl and MnCl$_2$.4H$_2$O precursors. NaCl was mixed with citric acid as a chelating agent, while MnCl$_2$.4H$_2$O was mixed with two types of chelating agents (citric acid and 1% chitosan). The solutions of [NaCl-a chelating agent] and [MnCl$_2$.4H$_2$O-a chelating agent] were stirred for ±2 hours. The solutions were hydrothermally heated at 150°C for 6 hours and then calcined at 800°C for 1 hour in a nitrogen condition. The MnO presence was then analyzed using an XRD method. As a comparison, another sample was water leached. Then, it was examined by an XRD method. Secondly, the synthesis of Na$_2$Mn$_3$O$_7$ from MnO and Na$_2$CO$_3$ powder was carried out through a solid method. The calcination was carried out at 800°C for ±3 hours in an oxidizing atmosphere. The XRD results showed the presence of Na$_2$Mn$_3$O$_7$ in the final products of both samples. Based on these experimental results, the sample [NaCl-citric acid; MnCl$_2$.4H$_2$O-1% chitosan] showed higher purity than the sample [NaCl-citric acid; MnCl$_2$.4H$_2$O-citric acid], so that it had a higher intensity of the MnO and Na$_2$Mn$_3$O$_7$ formed. Besides, the Cl$^-$ ions removal after calcination greatly affected the intensity of the MnO and Na$_2$Mn$_3$O$_7$ formed.

1. Introduction
In order to achieve current and future energy needs, humans need electrical energy. Energy resources such as wind, sun, coal, nuclear, and ocean waves do not meet the competent, permanent, consistent, and inexpensive energy storage requirements [1]. As an alternative, electrochemical energy storage systems answer these challenges by providing a constant and economical distribution of energy [2-4].

Due to its high energy density and long life cycle, lithium ion batteries (LIB) is considered the most popular electrochemical energy storage system. However, the lack of availability of their raw
materials limits the application of LIB [5]. For this reason, another ion batteries with high abundance and low cost raw materials are required, such as sodium ion batteries (SIB) which attract great attention as alternative energy storage systems [6–8].

Several cathode materials with high energy densities to improve SIB performance have been investigated [7–13]. However, the most interesting thing to study is manganese oxide (MnO) because it is non-toxic and low cost, and it strongly influences high energy density. Therefore, it is ideal for SIB cathode application and the development of SIB [8].

Various Na$_2$MnO$_2$ structures are found with changes in the value of x. Generally, a compound with the x value lower than 0.44 has a fully layered structure. A compound with the mixture of tunnels and layered structures is formed when x value lower than 0.66. Besides that, a compound with the x value lower than or equal to 1 has a fully layered [14]. These structures affect the cathode performance. The S-type tunnel structure of Na$_{0.4}$MnO$_2$ or Na$_2$MnO$_4$ has a three-dimensional structure which is advantageous for Na-ion transfer. However, theoretically the capacity is only 96 mAh g$^{-1}$ [15] while the capacity of the Na$_{0.7}$MnO$_2$ structure is 171 mAh g$^{-1}$ [16]. Recently, the large capacity with a value of 245 mAh g$^{-1}$ that supports a high energy density was obtained from the Na$_2$Mn$_3$O$_7$ with triclinic structure [17,18].

Herein, we synthesized Na$_2$Mn$_3$O$_7$ through a solid method from MnO and Na$_2$CO$_3$. MnO was prepared through the hydrothermal process using citric acid and 1% chitosan as the chelating agents. The chelating agent acts as a dispersant [19]. The purpose of this study was to determine the effect of the chelating agents and to determine the effect of the presence of NaCl in the synthesis of MnO and Na$_2$Mn$_3$O$_7$.

2. Materials and methods

Synthesis of Na$_2$Mn$_3$O$_7$ in this study was conducted in two steps. The initial step was the formation of MnO from MnCl$_2$.4H$_2$O. Then, the reaction between the MnO and Na$_2$CO$_3$ produced Na$_2$Mn$_3$O$_7$. The 10 mmol NaCl (Merck Pro Analysis ≥ 99.5%) solution was stirred with 10 mmol of citric acid as a chelating agent under stirring for ± 15 minutes. Meanwhile, 10 mmol of MnCl$_2$.4H$_2$O (Merck Pro 99% Analysis) was stirred with different chelating agents (10 mmol of citric acid and 1% chitosan). The solutions of [NaCl-chelating agent] and [MnCl$_2$-chelating agent] were stirred under vigorous stirring for ± 2 hours. Code A was labeled for sample [NaCl-citric acid; MnCl$_2$-citric acid], while code B for [NaCl-citric acid; MnCl$_2$-1% chitosan]. Each sample was put into an autoclave, and the hydrothermal process was carried out at 150°C for ± 6 hours [5], [6]. Then the calcination process was conducted in the nitrogen condition at 800°C for ± 1 hour. MnO phase was analyzed using an XRD instrument. As a comparison, the Cl$^-$ ions in sample B were removed using aquadest [5,20,21]. Furthermore, in the preparation of Na$_2$Mn$_3$O$_7$, each MnO powder produced from Samples A and B was mixed with Na$_2$CO$_3$ powder (Merck Pro Analysis 99.5%) through a solid method. The calcination was also carried out at 800 °C for ± 3 hours in an oxidizing atmosphere. Characterization using XRD was carried out to determine the phases formed in Samples A and B.

3. Results and discussion

3.1. X-Ray identification on MnO phases

Figure 1 demonstrates the result of XRD analysis of any phases formed in Sample A and Sample B. The mineral phases in Sample A consists of NaCl according to PDF2 number 77-2064, MnO according PDF2 number 89-4835, and Na$_2$Mn$_3$O$_7$ according to PDF2 number 78-0193. Based on PDF2 number 77-2064, NaCl appears to be a predominant phase in sample A as shown by the highest intensity (around 1000 counts per second (cts)) from the main peak of NaCl at a diffraction angle 20 of 31.68°, corresponding to the main crystal plane (200) of the cubic structure of sodium chloride. The high intensity of NaCl is indicated to occur because the Cl$^-$ ions were not removed after calcination in the synthesis of MnO samples [5,20,21].
According to PDF2 number 89-4835 [22], the composition of MnO of Sample A has a lower main intensity compared to the main NaCl (around 408.3 cts) at a diffraction angle 2θ of 40.62° according to the main crystal plane (200) of the cubic structure manganese oxide. In addition, according to PDF2 number 78-0193, the Na₂Mn₃O₇ phase is also detected in this sample, showing the lowest peak intensity (around 44.98 cts) at a diffraction angle 2θ of 15.71° according to the main crystal plane (-110) of the triclinic structure of sodium manganese oxide (according to PDF2 number 78-0193) [17], [23]. This proves that the Na₂Mn₃O₇ phase began to form in the synthesis of MnO sample A.

The result of XRD analysis of any phases formed in Sample B is displayed in Figure 1. According to PDF2 number 89-4835 [22], the MnO compounds appear to be the only phase that has a primary intensity of about 1000 cts at a diffraction angle 2θ of 40.62° according to the main crystal plane (200) of the cubic structure of manganese oxide. In contrast to the synthesis of MnO Sample A, the Na₂Mn₃O₇ phase is not detected during the synthesis of MnO Sample B. Likewise, NaCl is lost due to the Cl⁻ ions removal after calcination [5,20,21].

Based on Figure 1, it was indicated that the use of citric acid as a chelating agent in the synthesis of MnO Sample A produced intensity of diffraction peak of MnO which was lower than the use of 1% chitosan as a chelating agent in the synthesis of MnO Sample B. This was assumed to occur because NaCl decreased the MnO intensity in Sample A. The existence of a phase with high concentrations in a sample will result in high peak intensity and causes minor phases that had low peak intensity or even
did not appear. If the major phase is removed, the minor phase will appear as a single phase with a higher intensity than before [24]. In addition, the MnCl$_2$ precursor in Sample A during the synthesis process was strongly bonded ionically with citric acid. Citric acid is a strong metal complexing agent, and the coordination compound produced is quite stable. However, the decomposition process of Mn-citrate compounds did not require extra energy or higher temperatures to break the bonds that occurred between Mn$^{2+}$ ions and citrate. At temperatures above 175 °C, Mn-citrate decomposed into Mn-oxaloacetate [25]. Then, it decomposed gradually during the calcination process. The Mn-citrate decomposition process will occur at a relatively lower temperature than Mn-chitosan [26].

Some of MnO compounds formed at relatively lower temperatures would then react with a number of NaO produced from the decomposition of Na-citric acid precursors at a certain temperature, resulting in the Na$_2$Mn$_3$O$_7$ compounds at a diffraction angle 2θ of 15.71° according to the main (110) of the triclinic structure of sodium manganese oxide (according to PDF2 number 78-0193) [17,23]. However, the above phenomenon did not occur in Sample B. Although the Mn precursors in Sample B covalently bound to each functional group of the chitosan polymer chain, that was the hydrogen bonds between OH from Mn with NH$_2$ and OH functional groups from chitosan, and covalent coordination between O atoms of chitosan ethoxy groups with Mn metal center [27,28], the decomposition process of Mn-chitosan compounds required a relatively longer time and a relatively higher temperature [29] because of high molecular weights of chitosan [30]. Thus, the MnO crystallization process from the Mn-chitosan decomposition process was relatively slower [31]. Therefore, the MnO phase produced was likely to react with NaO (from the citric acid precursor) at a relatively higher temperature. This phenomenon was supported by the results of the XRD analysis in Sample B, that the MnO phase had a higher peak intensity than the peak intensity of MnO in Sample A. Besides, the NaMnO phase was not detected in Sample B.

![Figure 2](image_url)

**Figure 2.** The XRD identification on the Na$_2$Mn$_3$O$_7$ phase of Sample A and Sample B.
3.2. X-Ray identification on Na$_2$Mn$_7$O$_7$ phases

The result of XRD identification on the Na$_2$Mn$_7$O$_7$ phase of Sample A and Sample B is shown in figure 2. In Sample A, according to PDF2 number 78-0193, the intensity of the main Na$_2$Mn$_7$O$_7$ increases to around 553.90 cts at a diffraction angle 20 of 15.71° according to the main crystal plane (-110) of the triclinic structure of sodium manganese oxide [17,23]. However, according to PDF2 number 77-2064, NaCl is still detected [5,20,21] at a diffraction angle 20 of 31.68° according to the main crystal plane (200) of the cubic structure of sodium chloride with increasing intensity to about 1000 cts. Meanwhile, according to PDF2 number 89-4835 [22], the intensity of the major MnO decreases to around 124.57 cts at a diffraction angle 20 of 35.98° according to the main crystal plane (200) of the cubic structure of manganese oxide. In addition, there are unidentified phases at a diffraction angle 20 of around 31.90° and 44.74°.

In comparison to the synthesis of Na$_2$Mn$_7$O$_7$ Sample A, according to PDF2 number 78-0193 the intensity of Na$_2$Mn$_7$O$_7$ produced in the synthesis of Na$_2$Mn$_7$O$_7$ Sample B appears to be higher, which is around 996.54 cts at a diffraction angle 20 of 15.71° according to the main crystal plane (100) of the triclinic structure of sodium manganese oxide [17,23]. The Na$_2$Mn$_7$O$_7$ peaks produced are also more numerous than Sample A. However, similar to Na$_2$Mn$_7$O$_7$ Sample A, in Na$_2$Mn$_7$O$_7$ Sample B there are still unidentified phases found at a diffraction angles 20 of around 31.90° and 44.74°.

4. Conclusions

The Na$_2$Mn$_7$O$_7$ phase was obtained through the mixing of MnO and Na$_2$CO$_3$ precursors. Meanwhile, the MnO precursor was obtained through the mixing of [NaCl-chelating agent] and [MnCl$_2$.4H$_2$O-chelating agent]. Citric acid was used as a chelating agent in NaCl, while the chelating agent in MnCl$_2$.4H$_2$O consisted of two types, namely citric acid and 1% chitosan. In the mixing of [NaCl-citric acid; MnCl$_2$.4H$_2$O-citric acid], it produced an MnO phase with a lower peak intensity than that of the mixing of [NaCl-citric acid; MnCl$_2$.4H$_2$O-1%chitosan]. This further influenced the peak intensity of Na$_2$Mn$_7$O$_7$ formed in both samples. The sample [NaCl-citric acid; MnCl$_2$.4H$_2$O-1%chitosan] showed a higher intensity of the Na$_2$Mn$_7$O$_7$ phase than that of sample [NaCl-citric acid; MnCl$_2$.4H$_2$O-citric acid], which was 996.54 cts at a diffraction angle 20 of 15.71°. In addition, the Cl$^-$ ions removal after calcination in MnO synthesis not only greatly affected the intensity of MnO, but also affected the intensity of Na$_2$Mn$_7$O$_7$ formed and affected its impurities.

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