Thermal behavior, mineral phase, and microstructure characteristics of Na$_2$Mn$_3$O$_7$ synthesized from MnO$_2$ and MnCl$_2$ via a low-cost, simple conventional mixing method

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Sodium manganese oxide plays an important role in the cathode application of sodium ion batteries. In this study, sodium manganese oxide Na$_2$Mn$_3$O$_7$ (NMO) with a triclinic structure was successfully synthesized via a low-cost, simple conventional mixing method. NaMnO materials were synthesized by mixing Na$_2$CO$_3$ precursors and the two different types of Mn precursors, namely MnO$_2$ by a solid method (the sample C) and MnCl$_2$ by a sol–gel method (the Sample D). The calcination of both samples was carried out at 800 °C for 3 h. The results shown that the thermal behavior and crystal characteristics of the Sample D are slightly better than another one. Nevertheless, the Sample C exhibits a better microstructure, showing rod-like particles more dominant than particular particles. In addition, the Sample C reveals a little bit larger surface area than the Sample D.

Key-words : Na$_2$Mn$_3$O$_7$, MnO$_2$, MnCl$_2$, Sol–gel method, Solid method

1. Introduction

In recent years, the emergence of vehicles and portable devices with an energy efficient storage technology has become a more interesting research throughout the world.$^{1,2}$ In the several energy storage devices, lithium ion batteries are the most commercialized because of energy density, long life cycle, safety, less pollution, and cost effectiveness.$^{3,4}$ However, limited lithium resources will cause the possibility of soaring prices that restrain the application of lithium itself.$^{5,6}$ As an alternative, researches on sodium ion batteries were extensively explored because their characteristics resemble to lithium ion batteries.$^{7-10}$ The size of the Na atom radius affects the performance of the sodium ion battery.$^{11,12}$ Therefore, the exploration of cathode materials with an efficient energy density and a high capacity prepared by an effective methodology plays an important role in efforts to increase the sodium ion battery device, which subsequently plays a role in increasing its commerciality as the latest generation energy storage.$^{13}$ The several types of sodium ion battery cathode materials such as oxide-layered and tunnels structures,$^{14}$ hexacyanoferate,$^{15}$ polyanion,$^{16}$ and organic compounds$^{17}$ have been studied. The structure of oxide-layered based transition metal -manganese oxides- on the sodium ion batteries or referred to as sodium manganese oxide (Na–Mn–O) is interesting to study because the material is non-toxic, inexpensive, and has weak interaction characteristics between layers, which allows diffusion of sodium in its empty space to generate high capacity values.$^{18-20}$

Recently, the Na–Mn–O layered structure with lattice parameters of the tricinic cell unit Na$_3$Mn$_2$O$_7$ began to be re-examined after its first discovery.$^{21}$ Na$_3$Mn$_2$O$_7$ is interesting because it can be charged at 4.7 V and exhibit a high capacity of around 250 mAh g$^{-1}$, so it supports its application as a cathode on a sodium ion battery device.$^{22}$ Based on the Density Functional Theory Computation, Na$_3$Mn$_2$O$_7$ has a voltage window of 3.6–3.1 V and a
theoretical capacity of 124 mAh g$^{-1}$ so that it is very potential as a high-level cathode material with ideal ionic and electronic conductivity capabilities.\textsuperscript{23)} Although Na$_2$Mn$_3$O$_7$ is very potential as a sodium ion battery cathode, the researches on the synthesis of Na$_2$Mn$_3$O$_7$ with an efficient and effective method were barely explored. Adamczyk et al. prepared a reversible capacity NMO with a capacity of 160 mAh g$^{-1}$ through a hydrothermal method; however, the process was carried out in retentive periods of about 7 days.\textsuperscript{18)} Song et al. and Zheng et al. synthesized Na$_2$Mn$_3$O$_7$ via a conventional solid-state method using NaNO$_3$ and MnCO$_3$ as the precursors which were expensive precursors.\textsuperscript{22,24)}

In this study, the synthesis of NMO (Na$_2$Mn$_3$O$_7$) with a triclinic structure via a low-cost, simple conventional mixing method is reported. The NMO materials were synthesized by mixing Na$_2$CO$_3$ precursor and the two different types of Mn precursors, such as MnO$_2$ and MnCl$_2$. The NMO characteristics such as thermal behavior, a crystal phase, and a microstructure, of the two different Mn precursors were evaluated in this study.

2. Methods

2.1 Materials

The materials used in this study were MnCl$_2$·4H$_2$O (Merck Pro Analysis 99%), Na$_2$CO$_3$ (Merck Pro Analysis 99.5%), MnO$_2$ (Merck Pro Analysis 89%), and NaOH from a local market. All chemicals were used without further purification.

2.2 Synthesis of sodium manganese oxide (Na$_2$Mn$_3$O$_7$)

In this study, the synthesis of Na$_2$Mn$_3$O$_7$ consists of two conventional methods, namely the solid method and the sol–gel method. In the solid method, MnO$_2$ powder (Merck Pro Analysis 89%) was mixed with Na$_2$CO$_3$ powder (Merck Pro Analysis 99.5%) at a stoichiometric ratio for ± 2 h (homogenizing the mixture). Then, the powder mixture was calcined at 800 °C for 3 h in an oxygen atmosphere. Code C was given for this sample.

Whereas, in the sol–gel method, the synthesis of Na$_2$Mn$_3$O$_7$ was initiated by adjusting the pH of MnCl$_2$: 4H$_2$O solution (Merck Pro Analysis 99%) to the pH 13 with the addition of the NaOH solution under heating at ≤ 60 °C and stirring for 90 min, resulting in a concentrated gel. Then, the gel was washed with aquadest and filtered for several times in order to remove the Cl$^-$ ions in the gel. The next, the gel were mixed with a Na$_2$CO$_3$ solution (Merck Pro Analysis 99.5%) in a stoichiometric ratio under heating at ≤ 60 °C and stirring for 2 h. The sample mixture was then calcined at 800 °C for 3 h under an oxygen atmosphere. Code D was labeled for the second sample.

2.3 Characterization

The Fourier Transform Infra Red (FT-IR) spectroscopy is a spectroscopy infrared equipped with Fourier transform to determine the functional group. The study was conducted to characterize the IR spectra of the as-synthesized samples. Thermogravimetric-Differential Thermal Analyses (TG–DTA) was performed to evaluate the thermal behavior of the two as-synthesized samples of Na$_2$Mn$_3$O$_7$. Mineralogy characteristics of the calcined samples were investigated using a PANalytical X’Pert PRO X-ray diffractometer (XRD) at 40 kV with a Cu/K$\alpha$ radiation source ($\lambda = 1.54060$ Å, 1 Å = 0.1 nm), the diffraction patterns were scanned from 10 to 70° (2$\theta$) with an angular step of 0.02°. The typical microstructures of the calcined samples were observed using a scanning electron microscope (SEM, Hitachi SU3500) and transmission electron microscopes (LRTEM Hitachi HT7700 and HRTEM Hitachi H9500). The Brunauer–Emmett–Teller (BET) was used to analyze the surface area of materials through physical adsorption of gas molecules on solid surfaces.

3. Results and discussion

3.1 Synthesis of sodium manganese oxide (Na$_2$Mn$_3$O$_7$) via a low-cost, simple conventional mixing method

In this research, Na$_2$Mn$_3$O$_7$ synthesis was carried out by a low-cost, simple conventional mixing method. In the synthesis of Na$_2$Mn$_3$O$_7$, using Na$_2$CO$_3$ and MnO$_2$ precursors (Sample C), Na$_2$CO$_3$ and MnO$_2$ precursors were mixed according to stoichiometry by the solid method. Both the Na$_2$CO$_3$ precursor and MnO$_2$ precursor are reactive to produce Na$_2$Mn$_3$O$_7$. However, MnO$_2$ is hygroscopic or absorbs H$_2$O molecules. The initial reaction in sample C is shown by reaction 1, as follows.

\[ \text{MnO}_2 \cdot \text{H}_2\text{O} + \text{Na}_2\text{CO}_3 \rightarrow \text{MnO}_2 + \text{NaOH} \] (1)

Furthermore, at temperatures above 200°C MnO$_2$ loses oxygen.\textsuperscript{25)} At temperatures above 535°C, the conversion of MnO$_2$ into Mn$_2$O$_3$ and at temperatures above 700°C, the conversion of Mn$_2$O$_3$ to Mn$_3$O$_4$.\textsuperscript{25} While NaOH decomposes into Na$_2$O and H$_2$O at temperatures above 170°C.\textsuperscript{26} So that at temperatures above 770°C, Na$_2$O and Mn$_3$O$_4$ form the crystalline phase Na$_2$Mn$_3$O$_7$ as shown by the following reaction 2.

\[ \text{Na}_2\text{O} + \text{Mn}_2\text{O}_3 + \text{O}_2 \rightarrow \text{Na}_2\text{Mn}_3\text{O}_7 \] (2)

Whereas in the synthesis of Na$_2$Mn$_3$O$_7$ using Na$_2$CO$_3$ and MnCl$_2$ precursors (Sample D), the precursors were mixed according to stoichiometry by the sol–gel method. In this sol–gel method, the reaction in its synthesis is more reactive than the use of the solid method (Sample C). The initial process, the pH of the MnCl$_2$ solution is adjusted to 13 by adding NaOH solution. The initial reaction is shown by reaction 3 as follows.

\[ \text{MnCl}_2 + 2\text{NaOH} \rightarrow 2\text{NaCl} + \text{Mn(OH)}_2 \] (3)

Next, the Cl$^-$ ions was removed using aquadest. Then, the resulting product in the form of a gel was mixed with a stoichiometric solution of Na$_2$CO$_3$. At temperatures around 400°C 2 phenomena occur, namely the decomposition of NaOH to Na$_2$O\textsuperscript{26} and the decomposition of MnO(OH) to MnO$_2$\textsuperscript{25} as shown by reactions 4 and 5.
\[2\text{NaOH} \rightarrow \text{Na}_2\text{O} + \text{H}_2\text{O} \quad (4)\]

\[3\text{Mn}(	ext{OH})_2 \rightarrow 2\text{MnO(OH)} + \text{MnO}_2 + 2\text{H}_2 \quad (5)\]

\(\text{MnO}_2\) transforms into \(\text{Mn}_2\text{O}_3\) at above 450 °C. Above a temperature of 700 °C re-oxidation reaction occurs, where \(\text{Mn}_2\text{O}_3\) transforms into \(\text{Mn}_3\text{O}_4\). Furthermore, \(\text{Na}_2\text{O}\) and \(\text{Mn}_3\text{O}_4\) react to form \(\text{Na}_2\text{Mn}_3\text{O}_7\) crystals at temperatures above 770 °C as reaction 2.

### 3.2 The FT-IR study on \(\text{MnO}_2\) material and the as-synthesized samples of \(\text{Na}_2\text{Mn}_3\text{O}_7\)

**Figure 1** describes the characteristics of the FT-IR spectra of \(\text{MnO}_2\) material and the as-synthesized samples of \(\text{Na}_2\text{Mn}_3\text{O}_7\). The FT-IR spectra for all those samples in Fig. 1 demonstrate the transmission bands in the range of 4500–400 cm\(^{-1}\), indicating the vibration modes of chemical bonds on \(\text{MnO}_2\) material and the as-synthesized samples.

The FT-IR analysis result on the pure \(\text{MnO}_2\) material identifies the existence of a wide peak of the hydrogen bond at 3468 cm\(^{-1}\), assuming the stretching vibration of \(\text{OH}\) bonds from the bonds of the absorbed moisture. This phenomenon is corroborated by the presence of very low peaks at regions 1381 and 1092 cm\(^{-1}\) that are assigned to the vibration of \(\text{OH}\) bonds from the bonds of the coordinated water and \(\text{Mn}–\text{OH}\), respectively. This the FT-IR result surely indicating \(\text{MnO}_2\) material is a hygroscopic material, as shown in reaction (1). However, the vibration modes of the manganese metal and oxygen bonds in \(\text{MnO}_2\) could be observed at the transmission bands in the regions 603, 552, and 446 cm\(^{-1}\).

The as-synthesized sample C of \(\text{Na}_2\text{Mn}_3\text{O}_7\) prepared by a conventional mixing method, shows more complex and overlap peaks, which are assigned to the unique vibration modes of both \(\text{MnO}_2\) and \(\text{NaOH}\) precursors (reaction 1). The bands at 3451, 2978, 1449, 903, and 866 cm\(^{-1}\), are attributed to any vibration modes of the chemical bonds in \(\text{NaOH}\) precursor. Nevertheless, a specific band that detected at 3252 cm\(^{-1}\) is strongly assumed as the intermolecular hydrogen bonding between \(\text{MnO}_2\cdot\text{H}_2\text{O}\) and \(\text{NaOH}\). In addition, a band at 1688 cm\(^{-1}\) is probably attributed to the hydroxyl groups (–OH) on the surface of the manganese oxide.

Comparing to the as-synthesized sample C of \(\text{Na}_2\text{Mn}_3\text{O}_7\), the FT-IR result of the as-synthesized sample D prepared by a sol–gel method shows similar spectrum to that indicated by the as-synthesized sample C in Fig. 1, with slightly band shifts. The vibration modes of the chemical bonds in \(\text{Mn}(	ext{OH})_2\) precursor are found at 3462, 1067, 617, and 513 cm\(^{-1}\). However, the band of the intramolecular hydrogen bonding in –OH groups at about 3400 cm\(^{-1}\) seems to be wider and has a higher intensity than the one that shown by the as-synthesize sample C. Whereas, the vibration modes of the chemical bonds in \(\text{NaOH}\) precursor are noticed at 3462, 1450, 1190, 943, and 853 cm\(^{-1}\). Moreover, the bands of intermolecular hydrogen bonding and the hydroxyl groups (–OH) on the surface of the metal in the as-synthesized sample D, are spotted at 3038 and 1659, respectively.

### 3.3 Thermal analysis of the as-synthesized sodium manganese oxide (\(\text{Na}_2\text{Mn}_3\text{O}_7\))

**Figure 2** shows the (TG–DTA) curve of the as-synthesized Sample C and (b) the as-synthesized Sample D in the oxygen atmosphere. According to Fig. 2(a), the DTA shows an endothermic peak at the temperatures in the range of 100–159 °C in Sample C that is most probably related to the elimination of volatile compounds. The phenomenon should be the decomposition of \(\text{NaOH}\) into \(\text{Na}_2\text{O}\) and \(\text{H}_2\text{O}\), as shown by the reaction 6.

\[2\text{NaOH} \rightarrow \text{Na}_2\text{O} + \text{H}_2\text{O} \quad (6)\]

This was followed by a weight loss of around 3 % which was showed by thermal gravimetric analysis (TGA) at the temperatures ranging from 100 to 200 °C. \(\text{MnO}_2\) starts releasing \(\text{O}_2\) at a temperature around 259 °C. Furthermore, endothermic peaks at the temperatures around 306–345, 394–450, 450–485, 485–550, and 550–556 °C can be observed as the conversion of \(\text{MnO}_2\) to \(\text{Mn}_2\text{O}_3\) as indicated by reaction 7. However, there was no significant of gradual weight losses in this phenomenon.

\[2\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 + \frac{1}{2} \text{O}_2 \quad (7)\]
Furthermore, the endothermic peak is recognized at the temperatures around 485–556 °C. The peak could be assigned as the reduction reaction of MnO₂ to birth Mn₂O₃ [25] as shown by the reaction 8.

\[
2\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 + \text{O}_2 \tag{8}
\]

Another endothermic peak is noticed at the temperatures around 683–706 °C. This peak could be attributed to the conversion of Mn₂O₃ to Mn₃O₄, [25] as given in the reaction 9.

\[
3\text{Mn}_2\text{O}_3 \rightarrow 2\text{Mn}_3\text{O}_4 + 1/2 \text{O}_2 \tag{9}
\]

Furthermore, an exothermic peak is observed at the temperature range of about 774–802 °C, indicating the solid-state reaction between Na₂O and Mn₃O₄, [25] as shown by the reaction 10.

\[
\text{Na}_2\text{O} + \text{Mn}_3\text{O}_4 + \text{O}_2 \rightarrow \text{Na}_2\text{Mn}_3\text{O}_7 \tag{10}
\]

An endothermic peak in the temperature range of 100–173 °C as shown by the DTA graph Fig. 2(b) is related to the elimination of volatile compounds. At the temperatures around 175–253 °C, an endothermic peak is observed, which could probably be associated with the decomposition of NaOH and the decomposition of Mn(OH)₂ as indicated by reaction 11 and reaction 12, respectively. Those phenomena are followed by the gradual weight losses of 5%, as indicated by the TGA graph at around 100–200 °C.

\[
\begin{align*}
2\text{NaOH} & \rightarrow \text{Na}_2\text{O} + \text{H}_2\text{O} \\ 3\text{Mn(OH)}_2 & \rightarrow 2\text{MnO(OH)} + \text{MnO}_2 + 2\text{H}_2
\end{align*} \tag{11, 12}
\]

At the temperature above 253 °C, the partial decomposition of MnO(OH) becoming MnO₂ occurred, [25] as shown by the following reaction 13.

\[
2\text{MnO(OH)} \rightarrow 2\text{MnO}_2 + \text{H}_2 \tag{13}
\]

An endothermic phenomenon occurs at around 305–346 °C that is attributed to the conversion of Mn₂O₃ to Mn₃O₄, as shown by the following reaction 17.

\[
3\text{Mn}_2\text{O}_3 \rightarrow 2\text{Mn}_3\text{O}_4 + 1/2 \text{O}_2 \tag{17}
\]

Meanwhile, a solid-state reaction between Na₂O and Mn₃O₄ is assumed to be occurred at 780 °C, as shown by the reaction 18.

\[
\text{Na}_2\text{O} + \text{Mn}_3\text{O}_4 + \text{O}_2 \rightarrow \text{Na}_2\text{Mn}_3\text{O}_7 \tag{18}
\]

3.4 Analysis of X-ray diffraction on mineralogical characteristics of sodium manganese oxide (Na₂Mn₃O₇)

A PANalytical X’Pert PRO XRD was used to investigate the mineralogy characteristics in the calcined samples C and D. Figure 3 shows the results of XRD analysis for samples C and D. Based on PDF2 number 78-0193, the phase formed in the those samples is the single phase of the Na₂Mn₃O₇ compound. The diffraction peaks of Na₂Mn₃O₇ from Samples C and D shown in Fig. 3 are noticed at the diffraction angles 26 of 15.71, 24.97, 26.40, 32.13, 36.18, 37.81, 45.35, 65.31° with the main peak at an angle of 26 15.71° corresponding to the crystal plane main (-110) of the triclinic structure of Na₂Mn₃O₇ [18,27] group P1° with the following parameters, a = 6,636 Å,
b = 6,854 Å, c = 7,548 Å, α = 105.76°, β = 106.86°, γ = 111.6°, and volume cell = 276.48 Å³.

Although the TG–DTA analysis results from both samples C and D show that Na₂Mn₃O₇ from those samples formed at almost the same temperature (i.e. around 700–800 °C), a slightly difference was shown by the main peak of the diffraction pattern of sample D, exhibiting a higher intensity than sample C. This is probably due to the use of the MnCl₂ precursor through the sol–gel method for its more reactive reaction during Na₂Mn₃O₇ synthesis, as previously mentioned in the synthesis and analysis section of TG–DTA.

3.5 Microstructure analysis of sodium manganese (Na₂Mn₃O₇)

The microstructures of Samples C and D was observed using scanning and transmission electron microscopes. The SEM results of Samples C and D are shown in Fig. 4. According to Fig. 4(a), sample C has a microstructure of rod-like particles although some others seem to be lumpy. Meanwhile, Fig. 4(b) demonstrates the SEM results of Sample D. Sample D shows an elongated cylindrical microstructure, although it looks more lumpy in some spots than Sample C.

Microstructural characterization using a transmission electron microscope (TEM) is shown in Fig. 5. Figure 5(a) presents the results of LRTEM and HRTEM observation on the Sample C, showing that various microstructures of rod-like shapes, shorter cylinders, and other shapes are visible in the Sample C. The microstructure of sample C in a rod-like shape is seen at around 50 nm.

Figure 5(b) presents the results of LRTEM and HRTEM observation on the Sample D. The Sample D has more clumping microstructure than Sample C. However, there is spot that shows a rod microstructure. Agglomerate particles consisting of small shorter cylinder particles can be observed in the sample. This is indicated by the red circles that looks horizontal and yellow circles that looks vertical.

3.6 The specific surface of sodium manganese oxide (Na₂Mn₃O₇) by BET method

The surface areas of the calcined Samples C and D were measured through the BET method. The surface area of the calcined Sample C is about 11.262 m²/g with a total pore volume of 0.0402 cc/g. The surface area of the calcined Sample D is quite smaller than that of Sample C, which is around 7.598 m²/g with a total pore volume of 0.0305 cc/g. The results of the BET characterization of both the samples are in accordance with the results of the TG–DTA and XRD identification mentioned in the previous discussion.

The TG–DTA show that the formation temperature of Na₂Mn₃O₇ in the sample D (reaction 18) occurs at 780 °C a little bit lower than the one that shown in the sample C (reaction 10). Sample D thus will have faster growth in their crystals and particles than sample C. It is confirmed by the results of the XRD analysis, sample D shows slightly a higher intensity of the main peak of Na₂Mn₃O₇ than sample C. Since a material exhibit a low crystallization temperature, its crystals and particles will grow...
faster, lead to the formation large particles and a smaller surface area. Therefore, the surface areas of Na$_2$Mn$_3$O$_7$ in samples C and D are directly comparable to the formation temperature of Na$_2$Mn$_3$O$_7$. The high formation temperature of Na$_2$Mn$_3$O$_7$ in sample C leads to a little bit slower formation of the Na$_2$Mn$_3$O$_7$ phase, thus producing a slightly larger surface area.

4. Conclusions

In this study, Na$_2$Mn$_3$O$_7$ with a triclinic structure was successfully synthesized via a low-cost, simple conventional mixing method using MnO$_2$ precursor by the solid method (Sample C) and MnCl$_2$ precursor by the sol–gel method (Sample D). Na$_2$Mn$_3$O$_7$ forms at a calcination temperature of around 800 °C for 3 h in the oxygen atmosphere. The results shown that the thermal behavior and crystal characteristics of Sample D are slightly better than others. Nevertheless, the Sample C exhibits a better microstructure, showing rod-like particles more dominant than particular particles. Besides, the Sample C reveals a little bit larger surface area than the Sample D.

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