Synthesis of Na₂Ti₃O₇–based anode for sodium-ion battery using solid state reaction method

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Abstract. Na₂Ti₃O₇-based anode for sodium-ion battery was synthesized through solid-state reaction of high purity Na₂CO₃ and TiO₂. The dry and wet mixing by using ethanol assistance were used to compare the effects on their properties. Simultaneous Thermal Analysis (STA) was carried out to determine the temperature of sintering process. Precursors, both from dry and wet mixing, were sintered at 900 °C for 4 h in air. The structure and phase of the sintered samples were characterized by X-ray diffraction (XRD), while the particle size was determined using a particle size analyzer (PSA). The samples were then assembled into coin cells for performance test purposes. The electrochemical processes of all of samples were examined using an automatic battery cycler system. It is shown that ethanol assisted-wet process did not decrease the sintering temperature but it decreased the particle size of samples. Phase analysis showed that the phases for both treatments are Na₂Ti₃O₇ and Na₂Ti₆O₁₃, and they had a high crystalinity. Cyclic voltammetry shows that all samples have an unbalanced pair of redox peaks and show formation SEI layers.

1. Introduction

Energy is the most important thing in our live because everybody in entire world needs energy to do one’s activity. Almost all energy which is consumed every day is from the dirty fossil fuel energy. The fossil fuel energy has been used in some economic sectors like industry, transportation, and home. Burning fossil fuel energy every time will increase the amount of carbon dioxide in the atmosphere and will lead to global warming and climate change [1]. The way to combat these impacts to our live is by decreasing the fossil fuel energy use and replacing it with renewable energy from wind, solar, tidal, and hydro energy. To apply these renewable energy sources to the grid, electrochemical energy storage device is required. Electrochemical energy storages like lithium ion batteries are seen to be the most favorable candidate because they have high energy densities, ability to demonstrate flexible response times, portability, pollution-free operation, long cycles, and high efficiencies [1, 2].

Batteries are a collection of electrochemical cells which can convert chemical energy into electrical energy and its reverse. The three main constituents of a lithium ion cell are: an anode (which is oxidized), a cathode (which is reduced), and the electrolyte. These electrochemical devices convert electrical energy into chemical energy when the devices are charged and convert chemical energy into electrical energy when the devices are used [3].

Secondary sodium-ion batteries (SIBs), as alternative to lithium-ion batteries (LIBs), have attracted the battery researchers entire the world because sodium is more abundant and cheaper than lithium.
SIB and LIB have many technical similarities in electrodes and electrolytes. One of the similarities is anode material of Na$_2$Ti$_3$O$_7$, or called NTO in SIBs, has the same form with Li$_2$Ti$_3$O$_12$ (LTO) in LIBs [4].

Ti-based oxides have been considered as potential electrode material for their small structural expansion and applicable operating voltage [5]. As a typical insertion Ti-base oxides, Na$_2$Ti$_3$O$_7$ is a promising negative electrode for rechargeable batteries since it has a very low insertion voltage (0.6 V vs Li$^+$/Li, or 0.3 V vs Na/Na$^+$) and high specific capacity (178 mAh/g) [6, 7]. This materials, Na$_2$Ti$_3$O$_7$, is very low cost and has a good cycling stability.

In this preliminary study, we will synthesize NTO powder via solid state reaction with dry and wet mixing, determine phase via XRD, and study intercalation process via cyclic voltammetry. Like in LiBs, anode act as host for ion while intercalating and de-intercalating process so Na$_2$Ti$_3$O$_7$ also act as host for Na ion [8, 9]. We will study intercalating process in Na$_2$Ti$_3$O$_7$ powder with Li ion because Li$^+$ radius is smaller than Na$. Smaller ion will have more mobile while inserting/de-inserting process [10].

2. Experimental method
The NTO phase can be prepared easily by solid state reaction from Na$_2$CO$_3$ and TiO$_2$ by following equation [11].

$$\text{Na}_2\text{CO}_3 + 3 \text{TiO}_2 \rightarrow \text{Na}_2\text{Ti}_3\text{O}_7 + \text{CO}_2$$ (1)

NTO powder was synthesized via a ceramic route using TiO$_2$ (Sigma Aldrich) anatase as Ti sources and Na$_2$CO$_3$ (Sigma Aldrich) as Na sources. Raw materials were mixed stoichiometrically with ethanol and without ethanol-assisted or wet and dry mixing respectively to become precursor. Both precursor were tested by Simultaneous Thermal Analysis (STA) merck Linseis/PT1600 to determine the sintering temperature. The mixture was then heated in air at up to 900 °C for 4 h. The structural characterization of product was done by X-ray diffraction (XRD) using Rigaku. Particle size of powder was measured by Particle Size Analyzer (PSA) merck cila 1190 using water as dispersant medium.

The electrode was prepared with common way from slurry containing 85 wt% of Na$_2$Ti$_3$O$_7$ powder, 5wt% of acetylene black as conductive agent, and 10% of polyvinylidene fluoride (PVDF) as binder. All materials were dissolved in N,N Dimethylacetamide (DMAC) solution instead of using NMP because PVDF more soluble in DMAC than in NMP solution [12]. The paste was coated on a Cu foil by the screen printing method. The working electrode was dried at 80 °C in vacuum oven for 30 minutes and then pressed into the final thickness of 40-60 um. After they were completely dried, then the electrode sheet was cut to a 14 mm diameter. The electrodes were assembled with lithium metal, separator and electrolyte in glove box become half-cell. After that, the half cells were measured by the cyclic voltammetry using battery cycler WBCS3000.

3. Results and discussion
Figure 1 shows the results of thermal analysis using STA of precursor Na$_2$Ti$_3$O$_7$ via (a) dry and (b) wet milling. Both of patterns show identical pattern. From DSC curve, there is small endothermic peak at the range of 25-100 °C for all samples and it is associated with evaporation water content adhering on raw materials surface. The difference of both sample is the peak of second sample (wet mixing) is wider than first sample, which indicates that second sample absorb more energy because there is ethanol content in the sample. From TGA curve at the range 25-100 °C, There is no significant mass change and it indicates that there is no crystallization or formation of a new phase. In that range, relative mass increases of about 7% and 3% occur for precursor (a) and (b) respectively, and it indicates that there is oxidizing process. From DSC curve at the range 800-900 °C, there is high and sharp endothermic peak for all sample and it associated with crystallization and formation of new
phases. This endothermic process is accompanied by a drastic mass change. After 900 °C, there is no endothermic process and mass change, and it means that the crystallization process is over.

![Figure 1.](image1)

**Figure 1.** Thermal analysis using simultaneous thermal analysis (STA) of precursor Na₂Ti₃O₇ (a) dry mixing (b) wet mixing.

![Figure 2.](image2)

**Figure 2.** X-ray diffraction patterns of all samples of Na₂Ti₃O₇ (a) dry mixing (b) wet mixing.
Figure 2 shows XRD pattern of NTO with and without ethanol assistance as showed by (a) and (b) sign, respectively. The XRD patterns show that there are two dominant phases such as Na$_2$Ti$_3$O$_7$ and Na$_2$Ti$_6$O$_{16}$ which are denoted by solid circle and triangle marks, respectively [13]. Both of patterns show good XRD diagrams with high peak, sharp and narrow which indicated that these material have high crystallinity. The existence of Na$_2$Ti$_6$O$_{16}$ phase indicated that the reaction does not occur perfectly and material need more heat or longer time in sintering process. However, ethanol-assisted process before sintering can increase the Na$_2$Ti$_3$O$_7$ and decrease the Na$_2$Ti$_6$O$_{16}$ phase, it indicates that ethanol-assisted help mixing process and the precursor become more homogenous than the sample without ethanol assistance.

**Table 1.** Particle size of samples.

| Measurement | Dry mixing (μm) | Wet mixing (μm) |
|-------------|-----------------|-----------------|
| 1           | 6.12            | 3.53            |
| 2           | 5.62            | 3.70            |
| 3           | 6.36            | 3.33            |
| Mean        | 6.05            | 3.52            |

Table 1 shows that samples prepared by wet mixing have smaller particles than samples prepared by dry mixing. Sample b has particle size almost half time bigger than other because ethanol could dissolve and pulverize raw material to smaller sizes.

**Figure 3.** Cyclic voltammogram patterns of all samples of Na$_2$Ti$_3$O$_7$ (a) dry mixing (b) wet mixing.

Figure 3 shows the CV of Na$_2$Ti$_3$O$_7$ both (a) dry mixing and wet mixing in the potential range of 0.0-2.0 V (vs Li/Li$^+$) at a scan rate of 0.1 mV.s$^{-1}$. All samples show identical pattern with small pairs of oxidizing and reducing peak, which indicates that sample can be charge-discharge slowly. The second sample has a higher intensity than the first sample because it is attributed from the phase and the particle size. The second sample has higher crystallinity and smaller particle than the first sample, and therefore this material will be more active in electrochemical process. In the first cathodic scan, a weak peak at around 1.3 V could be attributed to insertion of lithium ion to the Na$_2$Ti$_3$O$_7$ structure. The small peak emerging at 1.8V could be associated with Na$_2$Ti$_6$O$_{16}$ phases [13], while the large peak ranged from 0.4 to 0.0 V correspond to the de-insertion of Li$^+$ and the formation of solid electrolyte interface (SEI) layer [5]. The oxidizing peak appearing at 1.3 V is similar with the result of an experiment that used Na reference and Na-electrolyte [8]. It indicates that Li environment can be used to analyze intercalating process in NTO powder.
4. Conclusion

Na$_2$Ti$_3$O$_7$ powder was prepared by solid state reaction with dry mixing and wet mixing. Thermal analysis shows that both sample must be sintered at 900 °C, while ethanol assistance just decreased the amount of energy. Phase analysis showed that there are co-existence of Na$_2$Ti$_3$O$_7$ and Na$_2$Ti$_6$O$_{16}$ phases but ethanol-assisted process can increase the Na$_2$Ti$_3$O$_7$ phase. Ethanol assistance also can decrease particle size from 6 micrometer to 3 micrometer on average while in sintering process. Cyclic voltammetry shows that all samples have a pair of unbalance redox peak, show two oxidizing peaks and show formation SEI layer.

Acknowledgment

The author would like to acknowledge the financial and experimental tools support from the Ministry of Research, Technology and Higher Education (Menristek-Dikti); and Research Center for Physics – Indonesian Institute of Sciences (LIPI). The author also would like to thank the Battery Research Group in Research Center for Physics – Indonesian Institute of Sciences (LIPI) for helping the battery fabrication and analysis.

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