Effects of the calcination atmosphere and pre-heating treatment on the characteristics of sodium titanate nanorods synthesized from titanium tetraisopropoxide-sodium chloride precursors assisted by organic templates

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In this study, the effects of atmosphere firing and pre-heating treatment on the characteristics of sodium titanates were investigated. The materials were successfully prepared from titanium tetraisopropoxide-sodium chloride (TTIP-NaCl) precursors assisted by organic templates (ethylene glycol and citric acid) via facile templating and hydrothermal methods. Sodium titanates were initially prepared by mixing a sodium precursor solution with a titanium precursor solution at a stoichiometric mole ratio of 1.6:1 under vigorous stirring. This was followed by pre-heating treatment via a hydrothermal method at 150 °C for 6 h and then calcination at 800 °C for 1 h in two different atmospheres including reduction and oxidation conditions. The same process was carried out in the synthesis of the other samples without the preheating treatment. The thermal behaviors of all the as-synthesized samples were evaluated. Meanwhile, the mineralogy and microstructures of all calcined samples were investigated. Both atmosphere firing and pre-heating treatment influenced the thermal behaviors of the as-synthesized sodium titanates, resulting in various sodium titanate types with different microstructures. To prepare the sodium titanates from TTIP-NaCl precursors, the pre-heating treatment and the reduction firing seemed to be the optimum conditions for the formation of sodium titanate, in order to produce Na₂Ti₆O₁₃-type sodium titanates with rod-like particles in nanometer sizes.

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1. Introduction

Sustainable alternative energy sources have become a global demand over the past decades. The increasing demand for energy has triggered a paradigm shift from fossil fuels to renewable energy sources. The technology of renewable energy has the potential to provide solutions to energy problems currently faced by developing countries. Overall, electric energy storage technology is very important to sustainable energy. Integrating renewable energy into the electricity networks using an energy storage technology is essential to cope with inadequate electricity conditions. One highly used energy storage technology is the electrochemical secondary battery, preferred due to its simple maintenance, rechargeable abilities, and high energy conversion efficiency.

Lithium-ion batteries (LIB) are a type of electrochemical secondary batteries. In recent decades, the technological advances in LIB have improved living conditions throughout the world. LIB are used in most cellular electronic devices and non-emission electronic vehicles. The success of LIB is attributed to its high energy density, long life cycle, and affordable cost. Besides, the lithium ion’s small radius facilitates rapid diffusion in the crystal structure. However, the future application of LIB on large
scale renewable energy storage can be hampered because lithium resources in the earth’s crust are relatively low and the distribution of lithium sources is uneven. These factors can eventually lead to increases in lithium prices and limit the development of LIB.11,12

Recent studies have focused on alternative energy storage systems such as sodium-ion batteries (SIB). The costs and the supply problems of lithium are the reasons behind the growing interest in the development of SIB. Compared to LIB, SIB is a battery system that is a more cost-effective because of abundant sodium resources as well as its low cost and durability. In addition, SIB has chemical properties that are similar to Li; this feature suggests that SIB can be applied in large scale energy storage systems in the near future.11,12 The larger Na radius produces more intercalation material than Li, whereas Na diffusion is faster than Li in most host structures.13

The key to the success of SIB researches is finding a material with a large capacity for the sodium ion input process. Several alternative anode materials have been studied, but the most promising option currently is titanate which is an intercalation compound that can accept sodium ion input at low potential values of electrical voltage. Titanium oxide has good chemical stability, is easily synthesized, non-toxic, cheap and has a good supply.14 The development of SIB has also been carried out by several researchers, including the synthesis and characterization of Na2Ti6O13/ Na2Ti3O7 through hydrothermal synthesis and followed by calcinations.15,16 Seo et al. (2005) successfully synthesized Na2Ti6O13 and TiO2 with whisker microstructures from TiOCl2 and ammonium hydroxide solutions by hydrothermal processing.17 Meanwhile, Hayashi et al. (2016) successfully synthesized sodium titanate nanosheets using a supercritical flow reaction system from titanium dioxide and sodium hydroxide via the hydrothermal method.18 Zhang et al. (2016) successfully synthesized another sodium titanate-type of cube-shaped Na2Ti6O13 from titanium tetraisopropoxide (TTIP), NaOH, and H2O2 by hydrothermal processing and used it as anode electrode material in SIB.13 Liu et al. (2019) synthesized Na2Ti3O7 nanowires via a hydrothermal method. They reported that the transmission electron microscope (TEM) results revealed the sodium titanate to have a good aspect and dispersion ratio, with more than 20 μm in length.19 Another study reported the preparation of nanorod and nanoparticles of sodium titanates from TTIP, NaOH, and H2O2 via a microwave assisted hydrothermal synthesis.20

In the present study, we investigate a simple and environmentally friendly method of synthesizing sodium titanate nanorods without using the toxic oxidizing agent of hydrogen peroxide. Sodium titanate was synthesized from sodium chloride (NaCl) and TTIP precursors assisted by respective organic chelating agents such as citric acid (CA)19 and ethylene glycol (EG)20 via facile templating and hydrothermal methods. Nevertheless, the usage of organic compounds as templates in the synthesis of sodium titanates nanorods through a hydrothermal method have yet to be done. In addition, the calcination processes of as-synthesized sodium titanate precursors were conducted in two different atmospheres of oxidation and reduction firing. This intended to evaluate the effects of atmosphere firing on the characteristics of the resulting sodium titanate. This study focuses on the thermal behavior of the as-synthesized sodium titanate, mineral phases, and microstructures of the resulting sodium titanate.

2. Methods

2.1 Materials

The materials used in this study were NaCl (Merck KGaA for analysis), TTIP (Aldrich chemistry, ≥97.0%), CA, and EG (PA Bratachem). All materials were used without further purification.

2.2 Synthesis of sodium titanate

The synthesis of sodium titanate via facile templating and hydrothermal methods was initiated by preparing precursor solutions. The sodium precursor solution was prepared by dissolving 2.3 g NaCl in 20 ml of distilled water and then mixed with 7.6 g of CA in 20 ml of distilled water. Meanwhile, the titanium precursor was prepared by mixing 0.12 mol of TTIP with 0.12 mol of EG. Next, the TTIP solution was mixed with NaCl solution by vigorously stirring with a magnetic stirrer for 30 min.

After that, the precursor solution mixture was transferred to a teflon-coated stainless-steel autoclave. The sodium titanate precursor was preheated by the hydrothermal method at 150 °C for 6 h before it was cooled to a room temperature in the air for several hours. The preheated precursor was dried in an oven at 80 °C for 6 h. Then, the as-synthesized solids formed were calcined at 800 °C in two different atmospheres, which were reduction and oxidation conditions. The same process was carried out to synthesize the other samples without preheating treatment at 150 °C in an autoclave. The sample preheated in an autoclave was then calcined in a reduction atmosphere and labeled as HR, whereas the un-preheated sample was labeled as THR. Meanwhile, the preheated and un-preheated samples that were calcined in an oxidation atmosphere were labeled as HO and THO, respectively.

2.3 Characterization

The thermogravimetric and differential thermal analysis (TG/DTA) instrument (96 Line TGA-DTA/DSC Setaram) was used to analyze the thermal behaviors of all as-synthesized sodium titanates. In this study, the mineralogy characteristics of the resulting sodium titanates were investigated using a PANalytical X’Pert PRO X-ray diffractometer at 40 kV with a Cu/Kα (λ = 1.54060 Å) radiation source. The diffraction patterns were scanned from 10 to 80° (2θ) with an angular step of 0.02°. The typical microstructures of the resulting sodium titanates were observed using a scanning electron microscope (SEM, Hitachi SU3500) and a TEM (Hitachi HR-9500). However, SEM and TEM studies were only conducted on the HR, THR, and HO samples.
3. Results and discussion

3.1 Synthesis of sodium titanates by a facile templating method

In the synthesis of sodium titanates by a facile templating method, titanium tetra-isopropoxide \([\text{Ti(O-i Pr)}_4]\) was used as a titanium precursor. It is a reactive precursor that easily produces TiO\(_2\) when in contact with water, as described in reaction (1).

\[
\text{Ti(O-i Pr)}_4 + 4 \text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4 \text{HO} + 0_2 \quad (1)
\]

However, under normal conditions, the produced TiO\(_2\) is slow to react with another precursor such as NaCl during the synthesis of sodium titanates. Therefore, since the synthesis of sodium titanates in this study was carried out in a water-based solvent, the \([\text{Ti(O-i Pr)}_4]\) precursor initially reacted with EG, thus resulting in a water-soluble compound of titanium ethylene glycolate\(^{21)(23}\) and iso-propanol as explained in reaction (2). The metal organic compound was quite reactive and used as the titanium precursor in this study.

\[
\text{Ti(O-i Pr)}_4 + 2\text{EG} \rightarrow \text{Ti(EG)}_2 + 4\text{IP}_\text{OH} \quad (2)
\]

Besides, another precursor used in the synthesis of sodium titanate in this study was NaCl as the Na precursor. Meanwhile, the organic compound of CA was used as a templating agent to bind the Na\(^+\) ions in the form of sodium citrate, as shown in reaction (3).

\[
3 \text{NaCl} + \underbrace{\text{CA}}_{\text{Citrate}} \rightarrow 3\text{HCl} + \text{(Na)}_3\text{Citrate} \quad (3)
\]

Binding the Na\(^+\) ions by CA before the synthesis aims to minimalize free or unreacted Na\(^+\) ions that may be produced in a further reaction during the synthesis of NaTiO.

Hence, the total reaction that occurred during the synthesis of NaTiO from the TTIP and NaCl precursors with the presence of organic templates may be written as the following reaction.

\[
\text{TTIP} + 2\text{EG} \rightarrow \text{Ti(EG)}_2 + 4\text{IP}_\text{OH} \quad (4)
\]

\[
3\text{NaCl} + \text{CA} \rightarrow (\text{Na})_3\text{Citrate} + 3\text{HCl} \quad (5)
\]

\[
\text{Ti(EG)}_2 + (\text{Na})_3\text{Citrate} \xrightarrow{N_2/O_2, T 1000 °C} \text{sodium titanates} + \text{H}_2, \text{CO}_2, \text{H}_2\text{O} \quad (6)
\]

3.2 Thermal behavior of the as-synthesized sodium titanates

The thermal behavior of the as-synthesized samples calcined at 1000 °C in the reduction (a) and oxidation (b)
atmospheres by TG–DTA measurement is expressed in Fig. 2.

Figure 2(a) demonstrates the TG–DTA results of the preheated as-synthesized (HR) and the un-preheated as-synthesized (THR) samples calcined at 1000 °C in the reduction atmosphere. Based on the TG–DTA results in Fig. 2(a), endothermic peaks were found at around 171 °C (HR), 175 °C (THR), 334–394 °C (HR), 340–395 °C (THR), 442–460 °C (THR), 445–523 °C (HR), 644 °C (THR), 558–658 °C (HR), and 682–698 °C (HR), as well as exothermic peaks at around 200–213 °C (THR), 205–228 °C (HR), 301–318 °C (THR), 302–334 °C (HR), 420–431 °C (HR), 527–556 °C (THR), 810–835 °C (HR), and 884–923 °C (HR). The first endothermic reactions noted in Fig. 2(a) at both 171 °C (HR) and 175 °C (THR) were closely associated with the elimination of volatile products. The phenomena were followed by the exothermic reactions at 200–213 °C (THR) and 205–228 °C (HR), which were closely related to the initial decomposition of titanium ethylene glycolates. The exothermic peaks at 301–318 °C (THR) and 302–334 °C (HR) were strictly attributed to the initial decomposition of sodium citrates. These exothermic effects were simultaneously followed by the endothermic effect at 334–394 °C and another the exothermic effect at 420–431 °C (HR), and the endothermic effects at 340–395 and 442–460 °C (THR) that could probably be associated with the reduction of the residual organics into the amorphous carbon. Interestingly, different thermal behavior was observed in the as synthesized HR and THR samples at a temperature over 400 °C. A similar phenomenon also occurred at a temperature over 500 °C. An endothermic peak was identified in the as synthesized HR sample at 445–523 °C while an exothermic peak was detected in the as synthesized THR sample at 527–556 °C. Nevertheless, both of the effects were closely related to the initial solid-state reaction of sodium oxides and titanium oxides. The peaks at 558–658, 682–698, 810–835, 884–923 °C in the as synthesized HR sample and the peaks at 637–644 °C in the as synthesized THR sample, are possibly associated with the crystal structure alteration of sodium titanates. Significant endothermic peaks with drastic slopes were observed in the DTA results of the as synthesized HR and THR samples at around 799 °C, indicating the melting process of a product. The phenomena are closely related to the melting process of free NaCl molecules whose melting point of about 800 °C.

![Fig. 2](image-url)

**Fig. 2.** The TG–DTA results of the as-synthesized samples calcined at 1000 °C in the reduction (a) and oxidation (b) atmospheres.

| Thermal Behavior | Temperature (°C) | Weight Loss (°C) |
|------------------|-----------------|-----------------|
| Synthesis Product | HR | THR | HR | THR |
| Calcination of Volatile Products | 171 | 175 | 20% (<200) | 7.5% (<200) |
| Product Decomposition | | | | |
| 205–228, the initial decomposition of Ti(EG)₂ | 200–213, the initial decomposition of Ti(EG)₂ | 20% (200–500) | 15% (200–500) |
| 302–334, the initial decomposition of (Na₃)Citrate | 301–318, the initial decomposition of (Na₃)Citrate | | |
| 334–394, 420–431, the reduction of the residual organics | 340–395, 442–460, the reduction of the residual organics | | |
| 445–523, the initial solid-state reaction | 527–556, the initial solid-state reaction | | |
| Crystallization | — | 527–556 |
| Melting Point | 799 (NaCl) | 799 (NaCl) |
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The TGA results in Fig. 2(a) show gradual weight losses of about 20 and 7.5% in the respective as-synthesized HR and THR samples after having heating treatment up to around 200 °C, thus denoting the vaporization of volatile species such as H₂O, Cl₂, isopropanol, etc. The as-synthesized HR sample then lost 20% weight during heating from around 200 °C to about 500 °C, as confirmed by the TGA curve in Fig. 2(a). Meanwhile, the as-synthesized THR sample lost 15% weight during heating at those temperature ranges. However, the weight loss of the as-synthesized samples is connected with the decomposition of organic compounds, the process of reducing organic residues to amorphous carbon, and a solid state reaction.

Figure 2(b) expresses the TG–DTA results of the preheated as-synthesized (HO) and the un-preheated as-synthesized (THO) samples calcined at 1000 °C in the oxidation atmosphere. According to the blue-line of the DTA curve in Fig. 2(b), the as-synthesized HO sample shows an endothermic reaction at 168 °C that is closely related to the removal of volatile products such as H₂O, Cl₂, and isopropanol. This endothermic effect was followed by a gradual weight loss of about 20% during the heating up process to around 200 °C, as confirmed by the green-line of the TGA curve in Fig. 2(b). In addition, some exothermic and endothermic peaks were obviously noticed in the DTA curve of the as-synthesized HO sample during heating from approximately 250 °C to about 500 °C. Those peaks are possibly associated with the initial decomposition of metal–organic compounds and the oxidation of the residual organic compounds to gaseous species. These phenomena are confirmed by the weight loss of the as-synthesized HO sample of about 28% during heating from 200 °C up to around 500 °C, as presented by the blue-line of the DTA curve in Fig. 2(b). Besides, an endothermic peak was observed at 445–468 °C, and this could be assigned to the initial of a solid-state reaction between sodium oxides and titanium oxides. An exothermic peak was observed at 519–619 °C, and this could be attributed to the crystallization of sodium titanate. A drastic slope of the endothermic peak at around 796 °C was discovered in the DTA results of the as-synthesized HO sample, confirming the melting process of a material. Nevertheless, another exothermic peak was detected at 886–919 °C, and could be attributed to the crystal structure transformation of sodium titanates.

The brown- and purple-lines of the TG–DTA curve in Fig. 2(b) demonstrate the thermal behaviors of the as-synthesized THO sample during heating up to 1000 °C. Based on the brown-line of the DTA curve in Fig. 2(B), an endothermic reaction at 174 °C is most nearly concerned as the elimination process of volatile products such as H₂O, Cl₂, and isopropanol. The reaction was followed by a 12% weight loss during heating up to around 200 °C, as confirmed by the purple-line of the TGA curve in Fig. 2(b). Furthermore, the as-synthesized THO sample reveals exothermic activities as indicated by peaks at 201–240, 301–356, 425–436 °C and an endothermic peak at 481–550 °C. These peaks could possibly be related to the decomposition of titanium ethylene glycolates, sodium citrates, and the oxidation of the residual organic compounds, respectively. These exothermic effects are confirmed by the wide peak in the purple-line of the TGA curve at the temperatures from 200 to 500 °C with a 32% weight loss of the as-synthesized THO sample. In addition, an exothermic peak at 572–651 °C and an endothermic peak at 691–701 °C and could be associated with the initial of solid-state reaction between sodium oxides and titanium oxides, and the crystallization of sodium titanates, respectively. However, a significant endothermic effect was found at 804 °C, indicating the melting process of a material exhibiting a low melting point. Another exothermic peak was spotted at 816–854 °C, suggesting a change in the crystal structure of sodium titanates.

Based on Figs. 2(a) and 2(b), both the atmosphere firing and pre-heating treatment has influenced the thermal behaviors of the as-synthesized sodium titanates. Therefore, the profiles of the TG–DTA results of the as-synthesized samples with temperatures are mostly different.

| Thermal Behavior | Temperature (°C) | Weight Loss (%) |
|------------------|-----------------|-----------------|
|                  | HO   | THO  | HO   | THO  |
| Calcination of Volatile Products | 168  | 174  | 20% (<200) | 12% (<200) |
| Product Decomposition | 207–253, the initial decomposition of Ti(EG)_2 | 201–240, the initial decomposition of Ti(EG)_2 |
|                    | 292–306, the initial decomposition of (Na)_2–Citrate | 301–356, the initial decomposition of (Na)_2–Citrate |
|                    | 315–364, the decomposition of the residual organics | 384–396, 425–436, the decomposition of the residual organics |
|                    | 409–420, the self-auto combustion of the residual organic compounds | 481–550, the self-auto combustion of the residual organic compounds |
| Solid State Reaction/Crystallization | 445–468 | 572–651 |
|                  | 519–619 | 691–701 |
| Melting Point | 796 (NaCl) | 804 (NaCl) |
| Phase Transformation | 886–919 | 816–854 |
to those indicated by Fig. 2, leading to the formation of various sodium titanates with different mineralogy characteristics. However, all the as-synthesized samples show the same peculiarity at the temperature range of 795 to 805 °C, revealing a significant endothermic effect that is closely related to the material melting process. The material is mostly considered as free NaCl with a melting point of about 800 °C.

According to the results of the TG–DTA investigations in Fig. 2(a), both the as-synthesized HR and THR samples experienced a solid-state reaction at a temperature range of 500 to 700 °C. Whereas, no endothermic or exothermic peaks related to further alteration of the resulting sodium titanates were observed from temperatures of 700 to 900 °C. Therefore, the calcination process of the as-synthesized HR and THR samples were conducted at 800 °C in this study. The same temperature was applied in the calcination process of the as-synthesized HO and THO samples.

3.3 X-ray diffraction (XRD) analysis in the mineralogy characteristics of sodium titanates

The results of the XRD analysis of all the calcined samples at 800 °C are shown in Fig. 3.

According to Fig. 3(a), two mineral phases appears in the XRD pattern of the HR sample calcined at 800 °C. The phases are identified as NaCl and Na$_2$Ti$_6$O$_{13}$-type sodium titanate, as referring to the PDF2 data of 772064 (NaCl), as well as 370951 and 731398 (Na$_2$Ti$_6$O$_{13}$). Sodium chloride was detected by the appearance of the main NaCl peak at a diffraction angle, 2θ, of 31.68°, and corresponded to the main (200) crystal plane of the NaCl cubic structure. Meanwhile, the mineral phase of Na$_2$Ti$_6$O$_{13}$-type sodium titanate in the HR sample was observed at a diffraction angle, 2θ, of 11.85°, corresponding to the main (200) crystal plane of the Na$_2$Ti$_6$O$_{13}$ monoclinic structure. However, the preheating treatment was conducted on the HR sample via a hydrothermal method. A different treatment was applied during synthesis of the THR sample in which no preheating was carried out, resulting in a different type of sodium titanate. Based on Fig. 3(a), Na$_{0.23}$TiO$_2$-type sodium titanate is recognized as the sodium titanate phase in the THR sample. It is indicated by the appearance of its peaks at diffraction angles, 2θ, of 14, 24, 29, 44, 44 and 47°, which correspond to the (001), (110), (002), (003), (-601), and (020) crystal planes of the Na$_{0.23}$TiO$_2$ monoclinic structure, respectively.

Different phase transformations were found in the XRD profiles of the samples calcined in the oxidation atmosphere, as demonstrated in Fig. 3(a). Sodium chloride was the only crystalline phase that identified in both the HO and THO samples, as shown by the appearance of the main NaCl peak at a diffraction angle, 2θ, of 31°. Nevertheless, wide peaks with very low intensities could be observed at diffraction angles, 2θ, of approximately 25, 44, and 48°. These peaks could be attributed to the amorphous mineral phases consisting of Na and Ti metals.

Regarding to the XRD identification results in Fig. 3(a), NaCl seems to be the dominant or major phase in all samples calcined at 800 °C. This phenomenon is possibly due to a few Na-precursors interacting with CA during synthesis, generating many free Na-precursors on the surface of the as-synthesized sodium titanates. This leads to strong detection during the XRD measurement, resulting in a NaCl peak of very high intensity. Nevertheless, NaCl is a water-soluble compound. Hence, the dissolution of NaCl in all calcined samples was carried out using water. After the cleaning treatment, all calcined samples were characterized with an XRD method. Figure 3(b) demonstrates the XRD identification results on the calcined samples after water leaching.

Based on Fig. 3(b), the peak of the NaCl halite mineral did not appear in the XRD patterns of all calcined samples after water-leaching, thus suggesting that the mineral was completely removed. Not only that, the peaks of sodium titanate in the XRD patterns of the HR and THR samples were more visible and showed higher intensities. Further-
more, wide peaks with very low intensities in the XRD patterns of the HO and THO samples at diffraction angles, 2θ, of approximately 25, 44, and 48° in Fig. 3(a) are clearly noticeable after the leaching treatment as demonstrated in Fig. 3(b). However, these wide peaks belong to the sodium titanate and anatase phases. The sodium titanate phase was distinguished out by peaks at diffraction angles, 2θ, of 25, 30, and 48°, corresponding to the (110), (200), and (020) crystal planes of the Na2Ti6O13 monoclinic structure, respectively. Meanwhile, the anatase existence was shown by overlapping peaks with sodium titanate peaks at diffraction angles, 2θ, of 25.18 and 47.51°, corresponding to the (101) and (200) crystal planes of the anatase tetragonal structure, respectively.

Based on the study findings, the atmosphere firing in the calcination process obviously affected the mineralogy characteristic of the resulting sodium titanates, as shown in Fig. 3(b). The redox firing undoubtedly triggered better and faster crystallization of the as-synthesized sodium titanates during calcination process than the oxidation firing, resulting in sodium titanate with a better crystallinity. This was illustrated by the XRD patterns of the HR and THR samples in Fig. 3(b). The calcination process of the as-synthesized sodium titanates in the oxidation atmosphere required more oxygen to break down and remove the organic residues that attached the metals into gaseous species. Nevertheless, this process took time during the calcination process, delayed the process of formation, nucleation, and crystallization of sodium titanate, and allowed some titaniaoxy species to transform into a titania polymorph phase before reacting with sodium oxide molecules. Thus, the tetragonal anatase phase was identified as a free titania polymorph phase in the HO and THO samples [see in Fig. 3(b)]. A different finding was observed in the XRD analysis results of the HR and THR samples. Sodium titanate was the only mineral phase that was identified in the samples and revealed quite high intensity peaks [Fig. 3(b)]. However, the calcination process of the as-synthesized sodium titanates in the reduction atmosphere did not need oxygen to decompose the organic residues, because they were converted into amorphous carbon. While the decomposition of the organic residues occurred, a solid-state reaction between sodium oxide and titanium oxide happened at the same time to create sodium titanates. Thus, the titanium oxide molecules had no chance of interacting which each other, prohibiting the alteration of a titania polymorph phase. Therefore, the nucleation and the crystallization of the sodium titanate phase in the reduction firing were faster than in oxidation firing.

In addition, the effects of the preheating treatment through a hydrothermal method on the as-synthesized sodium titanates were evaluated in this study. The preheating treatment of the as-synthesized aimed to establish a complete reaction between TTIP-EG and NaCl-CA by means of accelerating the reaction between TTIP with EG to produce titanium ethylene glycolates and isopropyl alcohol, as well as the reaction between NaCl and CA to result in sodium citrate. Then, both of the metal organics were simultaneously reacted with each other under hydrothermal heating, resulting in gelatinous as-synthesized products. By contrast, the unpreheated treatment showed different as-synthesized products in the solid foam. This difference produced various types of sodium titanates in the final product, as clearly shown by the HR and THR samples in Fig. 3(b).

As the previous explanation in section 1, the reaction equations of (1)–(6) generally occurs during synthesis the NTO precursors before preheating treatment and further calcination were applied. Nevertheless, the formation mechanism of NTO in the HR and THR samples is most probably influenced by the preheating treatment. Based on the XRD results, the preheated precursor shows higher titanium and oxygen contents in its calcined sodium titanate structure. The preheating treatment allowed the complete reaction between TTIP-EG precursor and NaCl-CA precursor. However, a such reactive TTIP precursor easily forms TiO2 when interacts with moisture molecules. Thus, the hydrothermally preheating treatment was conducted to drive the reaction between TTIP with EG immediately, forming titanium glycolates and releasing isopropyl alcohol (b.p. 82.5°C). In advance, the metal organic precursor then reacted with Na-Citrate during calcination at elevated temperatures, resulting in sodium titanates (Na2Ti6O13). By contrast, the unpreheated precursor might produce a risky titanium precursor. When TTIP experienced heating in the drying at 80°C, it suddenly changed to TiO2 amorphous that was less reactive to join with Na-citrate precursor, producing a distinct sodium titanate structure of Na8O23TiO2.24

### 3.4 Microstructure analysis of sodium titanates

Figure 4 shows the typical microstructures of all the samples calcined at 800°C using a SEM instrument. According to the SEM results in Fig. 4(a), many rod-like particles were obviously found in the HR sample. Besides, some amorphous regions were observed in the surface morphology of the HR sample, related to the existence of the amorphous carbon produced from the decomposition of organic residues during the calcination process. Similar microstructures such as rodlike particles are also found in the THR sample, as illustrated in Fig. 4(b). Figure 4(c) demonstrates the results of SEM characterization in the typical microstructures of the HO sample. Based on Fig. 4(c), the amorphous regions dominate the morphology of the calcined HO sample. However, some aggregates consisting of very fine growth particles could be found in the calcined HO sample, as shown in Fig. 4(c). This finding is supported by the XRD identification on the HO sample in Fig. 3(c), which demonstrate wide peaks with very low intensities at diffraction angles, 2θ, of approximately 25, 44, and 48° and indicate the existence of very fine crystallites surrounded by the amorphous phase in the sample.

TEM investigations were conducted on the HR, THR, and HO samples to validate and ensure the SEM results.
in their microstructures. Figure 5(a) presents the typical TEM micrographs of the HR sample calcined at 800 °C, showing rod-like particles with wide range particle sizes from nano to micron. Many growing particles were obviously observed and an amorphous region was found in the microstructures of the HR sample. Rod-like particles that were long with some growing particles and some amorphous regions were observed in the calcined THR sample, as shown in Fig. 5(b). However, different microstructures were significantly expressed by the TEM analysis results in the calcined HO sample, as shown in Fig. 5(c). Some grew very fine particles (below 20 nm in size) and certain amorphous regions had microstructures that could be observed in the calcined HO sample.

However, a better microstructure was obtained by sodium titanates that was calcined in the reduction firing, showing rod-like particles and no amorphous regions of sodium titanates as proven by the XRD results in Fig. 3. Meanwhile, a different finding was obtained in the microstructure of sodium titanates that calcined in the oxidation
firing, indicating amorphous regions. This result is also supported by the XRD results of HO and THO samples in Fig. 3, showing some amorphous phases and very low intensity and broadened peaks at certain diffraction angles 2 theta.

4. Conclusions

In this study, facile templating and hydrothermal methods were used to synthesize sodium titanates using TTIP and NaCl as precursors assisted by EG and CA as templates. Then, the effects of the atmosphere firing and pre-heating treatment on the characteristics of the resulting sodium titanates were evaluated. The results of the TG–DTA analysis show that both atmospheric firing and pre-heating treatments influence the thermal behaviors of the as-synthesized samples, generating various sodium titanate types with different microstructures. In the calcination process with a reduction atmosphere at 800 °C, the pre-heated as-synthesized sample created Na2Ti6O13-type sodium titanate as the final product, while the unpreheated process produced Na0.25TiO2-type sodium titanate that lacked TiO2 content. Meanwhile, Na2Ti6O13-type sodium titanate and anatase phases were identified in both the pre-heated and unpreheated samples that calcined at a oxidation atmosphere of 800 °C. Different microstructures were also found in the as-synthesized samples that calcined in the different atmospheres. The as-synthesized samples that calcined in the reduction atmosphere showed rod-like particles with various particle sizes from nano to micron. In contrast, the as-synthesized samples that calcined in the oxidation atmosphere revealed very fine particles that were less than 20 nm in size as well as some amorphous regions. Based on the experimental results, compared to oxidation firing, the reduction firing undoubtedly triggers better and faster crystallization, and produces a better microstructure of sodium titanate during the calcination process.

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References

1) W. Ren, Z. Zhu, Q. An and L. Mai, Small, 1604181, 1–31 (2017).
2) C. Vaalma, D. Buchholz, M. Weil and S. Passerini, Nat. Rev. Mater., 3, 18013 (2018).
3) W. Zhang, F. Zhang, F. Ming and H. N. Alshareef, J. Energy Chem., 1, 100012 (2019).
4) A. S. Rawea and S. Urooj, Renew. Sustain. Energ. Rev., 82, 1655–1663 (2017).
5) C. Liu, Z. G. Neale and G. Cao, Biochem. Pharmacol., 19, 109–123 (2016).
6) J. Hwang, S. Myung and Y. Sun, Chem. Soc. Rev., 46, 3529–3614 (2017).
7) L. P. Wang, L. Yu, X. Wang and Z. J. Xu, J. Mater. Chem. A, 3, 9353–9378 (2015).
8) H. Hou, X. Qiu, W. Wei, Y. Zhang and X. Ji, Adv. Energy Mater., 7, 1–30 (2017).
9) W. Zhang, J. Ming, W. Zhao, X. Dong, M. N. Hedhili, P. M. F. J. Costa and H. N. Alshareef, Adv. Funct. Mater., 1903641, 1–10 (2019).
10) H. Kim, J. C. Kim, M. Blanchini, D. Seo and J. Rodriguez-garcia, Adv. Energy Mater., 1702384, 1–19 (2017).
11) H. Pan, Y. Hu and L. Chen, Energy Environ. Sci., 8, 2245–2550 (2013).
12) O. Cech, K. Castkova, L. Chladil, P. Dohnal, P. Cudek, J. Libich and P. Vanysek, J. Energy Storage., 14, 391–398 (2017).
13) Y. Zhang, H. Hou, X. Yang, J. Chen, M. Jing, Z. Wu, X. Jia and X. Ji, J. Power Sources, 305, 200–208 (2016).
14) M. M. Doeff, J. Cabana and M. Shirpour, J. Inorg. Organomet. P., 24, 5–14 (2014).
15) D. Seo, H. Kim and J. Lee, J. Cryst. Growth, 275, 2371–2376 (2005).
16) H. Hayashi, T. Nakamura and T. Ebina, J. Ceram. Soc. Jpn., 124, 74–78 (2016).
17) L. Liu, Y. Ding, B. Zhou, N. Jia, K. Wang and Z. Zhang, Appl. Sci., 9, 1673 (2019).
18) K. C. O. Cech, P. Vanysek and L. Chladil, ECS Trans., 74, 331–337 (2016).
19) R. Septawendar, A. Nuruddin, S. Sutardi, L. A. T. W. Asri and E. Maryani, Mater. Res. Express., 6, 065037 (2019).
20) R. Septawendar, B. Sunendar, S. Sutardi and N. Sofyaningsih, J. Ceram. Process. Res., 13, 343–348 (2012).
21) X. Jiang, Y. Wang and Y. Xia, J. Mater. Chem., 14, 695–703 (2004).
22) V. N. Krasil, A. P. Shtin, O. I. Gyrdasova, E. V. Polyakov and G. P. Shveikin, Russ. J. Inorg. Chem., 53, 1065–1069 (2008).
23) Y. Wei, J. Zhu, Y. Gan and G. Cheng, Adv. Powder Technol., 29, 2289–2311 (2018).
24) Z. Noer, T. Sembiring, K. Sebayang, M. N. Nasruddin, R. Septawendar and B. Sunendar, AIP Publishing., 2221, 110027 (2019).