SOLID-STATE SYNTHESIS OF SODIUM HEXA-TITANATE FROM NATURAL RUTILE MINERAL

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Sodium titanates (NTOs) are emerging as promising electrode materials for advanced energy storage devices, including sodium-ion batteries (SIBs), lithium-ion batteries (LIBs), and supercapacitors, owing to their favourable structural and electrochemical characteristics. Among various NTO phases, Sodium Hexa-Titanate ($Na_2Ti_6O_{13}$) has gained particular interest due to its wide range of applications in energy storage devices. In this study, a novel, simplified, and cost-effective, greener solid-state synthesis method was developed to produce $Na_2Ti_6O_{13}$ using naturally occurring rutile mineral sourced from Pulmoddai and Na_2CO_3 as precursors. The raw materials were mixed in a 1:6 molar ratio and subjected to mechanical activation through milling, followed by calcination at 800 °C. Phase identification via X-ray diffraction (XRD) confirmed the successful formation of single-phase $Na_2Ti_6O_{13}$, indexed to JCPDS card No. 73–1398. This indicates that the chosen stoichiometric conditions and processing parameters were effective in directing the complete transformation from the rutile precursor to the $Na_2Ti_6O_{13}$ phase. Morphological analysis using scanning electron microscopy (SEM) revealed the formation of disorderly interconnected nanorods, with diameters ranging from 70 to 900 nm and lengths between 2 and 20 µm. Electrochemical performance was evaluated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The CV profile of the synthesised $Na_2Ti_6O_{13}$ displayed broad redox peaks centred at ~0.4 V (cathodic) and ~0.7 V (anodic), corresponding to the reversible insertion/extraction of Na^+ ions, while the rutile precursor showed no significant redox activity. EIS results of $Na_2Ti_6O_{13}$ demonstrated enhanced ion diffusion characteristics and higher electrical conductivity. These findings demonstrate the viability of converting locally available rutile into a functional electrode material through an environmentally friendly and scalable process. The synthesised $Na_2Ti_6O_{13}$ exhibited promising electrochemical behaviour, confirming its potential as an effective electrode material for SIBs, LIBs, and supercapacitor applications.

Keywords: Sodium titanate, rutile, value addition, energy storage

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INTRODUCTION

The sodium titanate (NTO) family has attracted considerable research interest in recent years. This group comprises various compounds, including Na_4TiO_4, Na_2TiO_3, $Na_8Ti_5O_{14}$, $Na_2Ti_3O_7$, and $Na_2Ti_6O_{13}$, each exhibiting distinct structural and electrochemical properties (Bamberger & Begun, 1987). Among them, $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$ are notable due to their widespread application as electrode materials in sodium-ion batteries (SIBs), lithium-ion batteries (LIBs), and supercapacitors (Ghosh, 2020; Ji et al., 2019; J. Li et al., 2012; P. Li et al., 2016; Zhu et al., 2017). Various synthesis routes have been employed to obtain NTO phases, particularly the $Na_2Ti_6O_{13}$ phase, including hydrothermal synthesis, chemical precipitation, sonochemical methods, and solid-state reactions (Fagundes et al., 2019).
The primary objective of this work is to develop a novel and simplified solid-state synthesis method for producing $Na_2Ti_6O_{13}$ using locally sourced rutile mineral. Unlike conventional methods such as hydrothermal, chemical precipitation, or sonochemical routes, which often involve the use of hazardous reagents, extended reaction times, and expensive analytical-grade precursors (Cao et al., 2016; Ghosh, 2020), this approach aims to provide a cost-effective and time-saving alternative. By employing a solid-state reaction facilitated through milling, this method minimizes chemical consumption and offers environmental compatibility. Furthermore, the use of naturally occurring rutile from Sri Lanka (Pulmoddai) as a TiO_2 source not only reduces raw material costs but also adds significant value to an underutilized local mineral resource. Ultimately, this will contribute to the advancement of high-performance electrode materials for next-generation energy storage systems.

METHODOLOGY

NTO was synthesized via the solid-state method using rutile obtained from Lanka Mineral Sands (Pvt) Ltd (Pulmoddai) and sodium carbonate (Na_2CO_3) as the starting materials. The reactants were mixed in a molar ratio of 1:6 (Na_2CO_3: rutile) and homogenized using a mill for 30 seconds to ensure uniform mixing and mechanical activation. The resulting powder mixture was then subjected to calcination in a muffle furnace at 800 °C for several hours to facilitate the solid-state reaction. The phase composition of the synthesized material was analysed using X-ray diffraction (XRD) with Cu Kα radiation (λ = 1.5418 Å), and the morphology of the as-prepared compound was examined by Scanning Electron Microscopy (SEM).

The electrochemical performance of the synthesized material was evaluated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The working electrode (WE) was prepared by mixing NTO, conductive carbon black, and polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) at a weight ratio of 8:1:1. The resulting slurry was uniformly coated onto aluminium foil and dried at 60 °C overnight to form the WE. Electrochemical measurements were conducted in a three-electrode configuration using a platinum sheet counter electrode, an Ag/AgCl electrode as the reference, and 1 M $NaClO_4$ dissolved in a 1:1 mixture of ethylene carbonate (EC) and propylene carbonate (PC) as the electrolyte.

RESULTS AND DISCUSSION

Structural Characterization

The crystal structures of the prepared sample and the rutile mineral were identified by recording their XRD patterns, as presented in Figure 1a. The XRD pattern of the rutile mineral exhibited characteristic peaks at 2θ values of 27.42°, 39.24°, 44.14°, 54.32°, and 56.60°, corresponding to the (110), (200), (210), (211), and (220) crystallographic planes, respectively (El-Desoky et al., 2020), which are comparable to the standard rutile TiO_2 pattern (JCPDS No. 75-1537). The XRD pattern of the synthesized sample exhibited well-defined diffraction peaks that were successfully indexed to the $Na_2Ti_6O_{13}$ phase, in accordance with the crystallographic data reported in JCPDS card No. 73–1398 (Lee et al., 2024). Therefore, these results confirmed that the adopted synthesis method and conditions successfully yielded NTO with a well-defined $Na_2Ti_6O_{13}$ crystalline phase.

The morphologies and nanostructures of the natural rutile mineral and the synthesized $Na_2Ti_6O_{13}$ are presented in the SEM micrographs shown in Figure 1b and Figure 1c, respectively. The SEM image of $Na_2Ti_6O_{13}$ reveals disorderly interconnected nanorods with diameters predominantly ranging from 70 to 900 nm and lengths between 2 and 20 µm. These morphological features are consistent with those of $Na_2Ti_6O_{13}$ nanorods reported in the literature for materials synthesized via solid-state reaction methods, suggesting successful formation of the desired nanostructure (Ghosh, 2020), via a much greener approach.

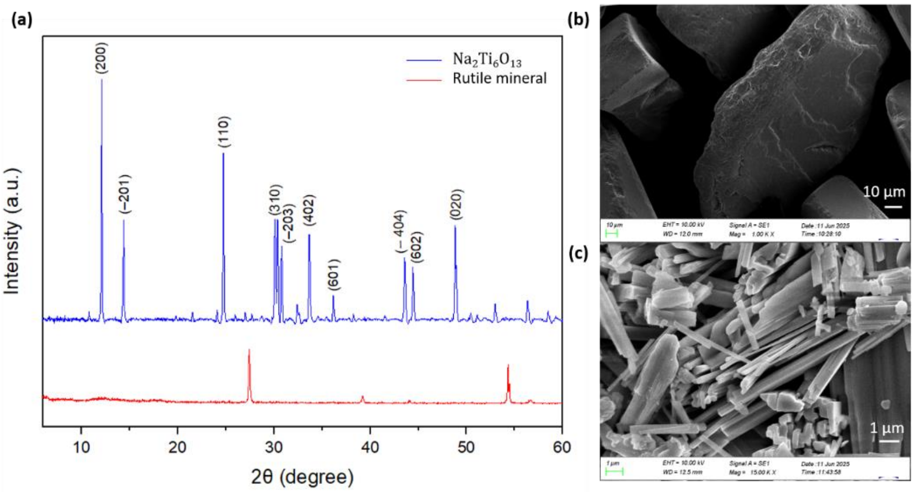

Figure 1: (a) XRD patterns of $Na_2Ti_6O_{13}$ and rutile mineral, (b) SEM image of rutile mineral (1000×), (c) SEM image of $Na_2Ti_6O_{13}$ (15000×)

Electrochemical Characterization

The redox behavior of $Na_2Ti_6O_{13}$ and rutile mineral was investigated using CV at a scan rate of 5 mV/s within a potential window of –0.3 V to 1.6 V (Figure 2a). The CV profile of NTO exhibited a pair of broad redox peaks centered at approximately 0.7 V (anodic) and 0.4 V (cathodic), corresponding to the extraction and insertion of Na^+ ions into the NTO lattice. Additionally, a minor anodic peak was observed at 1.0 V, indicating a two-step Na^+ extraction mechanism. In contrast, the CV curves of the rutile mineral did not exhibit any distinguishable redox peaks, indicating the absence of electrochemical activity related to Na^+ intercalation. However, a sudden increase in current was observed around 0.8 V, which could be attributed to a side reaction caused by impurities in the WE. According to Figure 2b, EIS results revealed that the synthesized $Na_2Ti_6O_{13}$ exhibited enhanced ion diffusion characteristics at high frequencies and demonstrated higher electrical conductivity.

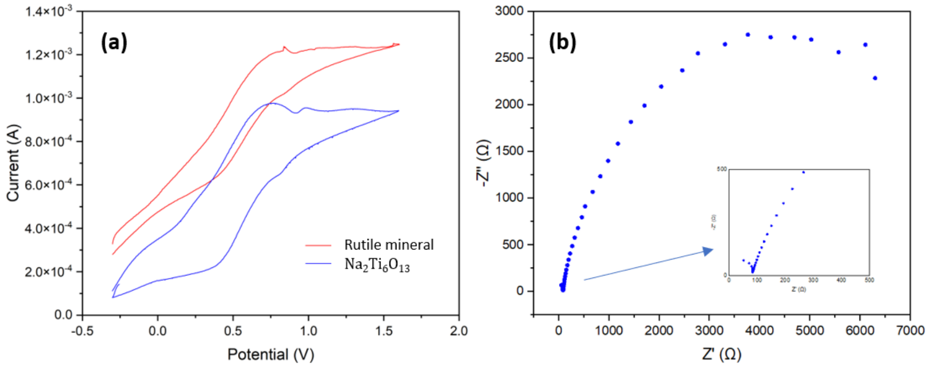

Figure 2: (a) Cyclic voltammograms of $Na_2Ti_6O_{13}$ and rutile mineral at 5 mV/s scan rate, (b) Nyquist plot of $Na_2Ti_6O_{13}$

CONCLUSIONS/RECOMMENDATIONS

NTO was successfully synthesized via a solid-state method using natural rutile mineral sourced from Pulmoddai and Na_2CO_3 as precursors. Structural characterization by XRD confirmed the formation of a well-defined $Na_2Ti_6O_{13}$ crystalline phase, while the presence of characteristic peaks in the raw rutile sample matched the standard TiO_2 rutile phase. SEM analysis revealed that the synthesized NTO consisted of disorderly interconnected nanorods, which are compatible with the previously reported $Na_2Ti_6O_{13}$ structures.
Electrochemical characterization through CV demonstrated the redox activity of the synthesized NTO, with broad and reversible Na^+ insertion/extraction peaks and evidence of a two-step Na^+ extraction mechanism. In contrast, the rutile mineral showed no redox peaks, confirming its electrochemical inactivity toward Na^+ intercalation. EIS analysis confirmed improved ion diffusion and higher electrical conductivity for the synthesized $Na_2Ti_6O_{13}$.
These findings highlight the effectiveness of this solid-state synthesis route as a value-added approach for converting natural rutile into electrochemically active NTO materials. For future work, further electrochemical characterization, such as galvanostatic charge–discharge (GCD) testing, will be carried out to comprehensively evaluate the performance of the synthesized NTO as a promising electrode material for SIBs, LIBs, and supercapacitors.

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REFERENCES

Bamberger, C. E. & Begun, G. M. (1987). Sodium Titanates: Stoichiometry and

Raman Spectra. *Journal of the American Ceramic Society*, *70*(3), C-48-C-51. https://doi.org/10.1111/j.1151-2916.1987.tb04963.x

Cao, K., Jiao, L., Pang, W. K., Liu, H., Zhou, T., Guo, Z., Wang, Y. & Yuan, H. (2016). Na2Ti6O13 Nanorods with Dominant Large Interlayer Spacing Exposed Facet for High-Performance Na-Ion Batteries. *Small*, *12*(22), 2991–2997. https://doi.org/10.1002/smll.201600845

El-Desoky, M. M., Morad, I., Wasfy, M. H. & Mansour, A. F. (2020). Synthesis, structural and electrical properties of PVA/TiO2 nanocomposite films with different TiO2 phases prepared by sol–gel technique. *Journal of Materials Science: Materials in Electronics*, *31*(20), 17574–17584. https://doi.org/10.1007/s10854-020-04313-7

Fagundes, N. G., Nobre, F. X., Basilio, L. A. L., Melo, A. D., Bandeira, B., Sales, J. C. C., Andrade, J. C. S., Anglada-Rivera, J., Aguilera, L., Pérez de la Cruz, J. & Leyet, Y. (2019). Novel and simple way to synthesize Na2Ti6O13 nanoparticles by sonochemical method. *Solid State Sciences*, *88*, 63–66. https://doi.org/10.1016/j.solidstatesciences.2018.11.014

Ghosh, S. (2020). Sonochemically synthesized Na2Ti6O13 nanorod: an efficient electrode material for Na-ion battery. *Bulletin of Materials Science*, *43*(1). https://doi.org/10.1007/s12034-020-02215-2

Ji, P., Wan, J., Xi, Y., Guan, Y., Zhang, C., Gu, X., Li, J., Lu, J. & Zhang, D. (2019). In situ growth of MnO@Na2Ti6O13 heterojunction nanowires for high performance supercapacitors. *Nanotechnology*, *30*(33). https://doi.org/10.1088/1361-6528/ab0cd1

Lee, D. H., Shim, H. W., Lee, G. H. & Park, K. S. (2024). Enhanced visible-light photocatalytic activity of N-doped C/Na2Ti6O13/TiO2 hollow spheres for efficient dye degradation. *Heliyon*, *10*(13), e33153. https://doi.org/10.1016/j.heliyon.2024.e33153

Li, J., Zou, W., Li, J. & Deng, Q. (2012). *Na2Ti3O7/C composite as the advanced anode material for sodium-ion battery*. *7*(Scheme 1), 4111.

Li, P., Wang, P., Qian, S., Yu, H., Lin, X., Shui, M., Zheng, X., Long, N. & Shu, J. (2016). Synthesis of Na2Ti6O13 nanorods as possible anode materials for rechargeable lithium ion batteries. *Electrochimica Acta*, *187*(January 2022), 46–54. https://doi.org/10.1016/j.electacta.2015.11.057

Zhu, H., Yang, K., Lan, H., Qian, S., Yu, H., Yan, L., Long, N., Shui, M. & Shu, J. (2017). Electrochemical kinetics of Na2Ti3O7 as anode material for lithium-ion batteries. *Journal of Electroanalytical Chemistry*, *788*, 203–209. https://doi.org/10.1016/j.jelechem.2017.02.013