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Research Article

Keywords: galvanometric, crystalline nature, nanoparticles, stoichiometric ratio

Posted Date: December 4th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-113681/v1>

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Rapid Microwave Synthesis of β -SnWO₄ Nanoparticles: An Efficient Anode Material for Lithium-ion Batteries

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Abstract

Here, we report a facile synthesis of β -SnWO₄ nanoparticles via microwave heat treatment using SnCl₂ and H₂WO₄, in the presence of tamarind seed powder. X-ray diffraction analysis confirmed the crystalline nature, revealing a cubic structure of β -SnWO₄ nanoparticles. Morphological features were visualized using a scanning electron microscope which exhibited homogeneously distributed clusters of nanoparticles which were further confirmed using transmission electron microscope. The micrographs also displayed some porosity. Energy dispersive X-ray spectroscopy confirmed the elemental contents such as tin, oxygen and tungsten in the same stoichiometric ratio as expected by the respective empirical formula. High-resolution transmission electron microscope was used to find the d-spacing which was ultimately used to analyze the structural parameters. The spectrum obtained using Fourier transform infrared spectroscopy illuminates different stretching vibrations. Additionally, Barrett-Joyner-Halenda analysis was carried out to investigate N₂ adsorption-desorption isotherm as well as to govern the pore size distribution. Cyclic voltammetry measurements were implemented to analyze the ongoing electrode reactions throughout the charge/discharge for β -SnWO₄ nanostructures. The galvanometric charge/discharge curves for β -SnWO₄ have also been discussed. A high specific capacitance (600 mAhg⁻¹ at 0.1 C) and excellent columbic efficiency (~100%) was achieved.

1. Introduction

The demand of energy storage devices with enhanced capabilities has increased manifold in the 21st century. In this context, the researchers world-wide are looking for such devices and materials that might lead the scientific community to cope up with the energy storage needs by

designing and developing innovative resources. In the current era, energy renovation is the forefront of research [1]. Lithium ion batteries (LIBs) are considered as promising because of their high power density, life cycle, gravimetric and volumetric energy along with long self-discharge properties. Therefore, the LIBs are still unbeaten in energy storage industry [2]. Meanwhile, the earth's crust has limited availability of lithium resources and their use is beyond the limits, consequently, they are becoming costly [3, 4]. Alternatively, batteries are facing various problems including storage capacity and chemical stability [5]. Additionally, its specific capacity is extremely low i.e., 372 mAhg^{-1} . To resolve such issues, there is a need to investigate some favorable electrode materials exhibiting promising specific capacities and chemical stabilities. In the realm of rechargeable LIBs, various nanomaterials are under discussion as a potential electrode material.

Historically, the LIBs have shown a massive intensification through the two decades in specific energy values ranging from 90 to 250 mAhg^{-1} [6]. In this regime, there are a lot of breakthroughs in energy storage devices due to the advancement in the field of nanomaterials [7-9]. The nanomaterials have exceptionally attractive physical and chemical properties; hence they are reflected suitable for energy storage devices. The use of single metal oxides including TiO_2 [10], SnO_2 [11] and Ta_2O_5 [12] has led to the loss in capacity with cycling. Whereas, the literature survey reveals good electrochemical performance of $\beta\text{-SnWO}_4$ nanoparticles. Various routes have been adopted for the synthesis of SnWO_4 including hydrothermal synthesis [13], combustion method and microwave method [14]. Initially, the gas sensing properties as well as the phase-structure of α - and $\beta\text{-SnWO}_4$ was reported by Solis and Lantoo by employing different spectroscopic techniques [15, 16]. Ede *et al.* adopted microwave synthesis to prepare SnWO_4 [16]. Warmuth *et al.*, employed microwave assisted method to synthesize $\beta\text{-SnWO}_4$ nanoparticles [17].

Furthermore, the photoelectrochemical properties of β -SnWO₄ nanomaterials were analyzed by Cho *et al.* [18]. ZnWO₄ nanocrystals/reduced graphene oxide hybrids were prepared by Wang Xiao *et al.* via facile hydrothermal route which revealed a performance of 477 mAhg⁻¹ after 40 cycles [19]. Whereas, α -SnWO₄/reduced graphene oxide nanoparticles were synthesized by Renkun Huang *et al.* through facile single step hydrothermal reaction exhibiting a capacity of 500 mAhg⁻¹ after 20 cycles [20].

The search of the finest electrode material for LIBs having high capacity and that can easily be diffused into Li⁺ ions along with increased life cycle is still under investigation. Owing to the promising features associated with β -SnWO₄ nanoparticles, here we report a facile synthesis of this material and present a detailed analysis of its electrochemical performance for its potential use as an electrode material in LIBs.

2. Experimental

2.1 Synthesis of β -SnWO₄ nanoparticles

β -SnWO₄ nanoparticles were prepared through rapid microwave heat treatment by the reaction of SnCl₂ and H₂WO₄ in the presence of tamarind seed powder. A typical procedure involves the addition of 220 mg of SnCl₂, 249 mg of H₂WO₄ in a clean and dried crucible. In the meantime, 220 mg of tamarind seed powder was also added followed by the addition of 10 mL of distilled water. The obtained blend was stirred for about 10 min. At that time, the crucible was kept in a microwave oven at 900 W for 5 min. The resultant product was taken out from the oven and allows it to cool to room temperature naturally. Later, it was grinded in a clean dried mortar and calcined at 700 °C for 4 h under static air. The schematic of sample synthesis is presented in Figure 1.

2.2 Characterization

A Rigaku's Smart Lab, X-ray diffractometer (XRD) with Cu- K_{α} radiations ($\lambda = 1.5406 \text{ \AA}$) was used to determine the crystalline nature and confirmation of phase. Molecular vibrations and structures of the materials were analyzed from $350 - 4000 \text{ cm}^{-1}$ using Bruker Alpha-P Fourier transforms infrared (FTIR) spectrometer by KBr pellet method. JEOL- JCM-6000 Plus scanning electron microscopy (SEM) and a JEOL, JEM-2100 transmission electron microscopy (TEM) were utilized to observe the morphological features, particle size and structural parameters of β -SnWO₄ nanoparticles, respectively. Using Quanta chrome Nova 2200E – BET (surface area analyzer), the pore size and surface area was determined.

2.3 Electrode fabrication for Lithium ion battery

A coin cell was made to examine the electrochemical performance of β -SnWO₄ nanomaterials by fabricating it on a copper foil. The slurry was prepared by mixing the active materials (β -SnWO₄ nanoparticles), PVDF (polyvinylidene fluoride) and acetylene black using a weight ratio of 80:5:15, respectively using few drops of N-Methyl pyrrolidine as a solvent. The prepared slurry was uniformly coated on a Cu foil and subsequently dried at 100°C for 12 h, in a vacuum oven. During the coil cell fabrication, polypropylene membrane (Celgard-2400) was utilized as a separator. LiPF₆ (1M) dissolved in ethylene carbonate, dimethyl carbonate and diethyl carbonate (2: 2: 1) was used as an electrolyte. Cyclic voltametry (CV) and galvanostatic charge-discharge (GCD) studies were recorded using a Bio-logic BCS 805 battery system. The CV measurements were performed in the voltage window from 0.01 to 3 V at 50 mV/s scan rate. The voltage range of 0.01-3 V was also applied during the GCD analysis.

Results and discussion

The XRD pattern of the sample was recorded in the 2θ range of $15\text{--}70^{\circ}$, as shown in Figure 2(a). The existence of intensity peaks corresponding to the (200), (020), (001), (100, (-112), (202),

(411), (222), (112), (212), (211), (322), (820) and (811) planes was perfectly matched with JCPDS (Joint Committee on Powder Diffraction Standards) reference no. 01-070-1497 [16], a characteristic reference pattern of β -SnWO₄. It confirmed the wolframite type cubic crystal structure of the sample, having space group no. 198 and a space group category P-213 [21]. There was not any extra peak signifying the phase purity of sample [16]. Further, the magnified image of some peaks is illustrated in Figure 2(b) to differentiate between these peaks. The lattice parameter (a) was calculated from following equation;

$$a = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \theta_B} \quad (1)$$

The lattice parameter was measured to be $a = b = c = 7.298 \text{ \AA}$, resulting into a unit cell volume of $388.697 \text{ \AA}^3$. The average crystallite size (D_{hkl}) was determined using Scherrer's formula as described by Eq. 2 [22];

$$D = \frac{k\lambda}{\beta \cos \theta_B} \quad (2)$$

Where, β is line broadening termed as full width at half maximum (FWHM), θ_B represents the Bragg's angle, λ is wavelength with a value of $1.54 \text{ \AA}$ and $k = 0.9$, the shape factor. The crystallite size as evaluated by this formula was 28.63 nm .

The crystallite size of as-synthesized samples was also calculated using Williamson-Hall (W-H) method as given by Eq. 3 [23];

$$\beta \cos \theta = k\lambda/D + 4\varepsilon \sin \theta \quad (3)$$

Where, ε is representing the lattice strain. Figure 3 indicates the W-H plot of β -SnWO₄ plotted between $4\sin\theta$ at x -axis and $\beta\cos\theta$ along the y -axis. The D is measured from the y -intercept and depicted to be 24.32 nm while ε measures slope of the linear fit and is measured to be 7.2×10^{-2} . The linear fit of W-H plot is expected to be a straight line parallel to x -axis but in the manifestation

of ε it gives a non-zero slope [26]. The measured crystallite size (24.32 nm) from W-H plot was in close agreement with Scherrer's formula (28.63 nm).

The accurate phase analysis and quantitative phase measurement of β -SnWO₄ was determined through Rietveld refinement analysis via X'pert HighScore Plus software. Figure shows the well fitted XRD pattern of β -SnWO₄ at the same positions as prescribed in Figure 4. No significant phase transformation was perceived attributing pure phase formation of the specimen. The structural reliability was evaluated by measuring R-factors such as R-profile (R_p), R-expected (R_{exp}), R-profile (R_{wp}) and R-Bragg (R_B) as well through the following Eqs. 4-7 [25].

$$R_{wp} = \left[\frac{\sum_i w_i (I_c - I_o)}{\sum_i w_i I_o^2} \right]^{1/2} \quad (4)$$

$$R_{exp} = \left[\frac{N - P}{\sum_i w_i I_o^2} \right]^{1/2} \quad (5)$$

$$R_{Bragg} = \frac{\sum |I(0) - I(c)|}{\sum |I(0)|} \quad (6)$$

$$R_p = \frac{\sum |I(0_i) - I(c_i)|}{\sum |I(0_i)|} \quad (7)$$

Here, P and N represent number of refined parameters and number of experimentally observed points and I_o and I_c present the observed and calculated integrated intensities, respectively. Accordingly, w_i is illustrating weight factor at i point of diffraction profile and goodness of fit (χ^2) was measured using Eq. 8, given as [25];

$$\chi^2 = \frac{R_{wp}}{R_{exp}} \quad (8)$$

The measured parameters from Rietveld refinement analysis are summarized in Table 1. The obtained smaller value of χ^2 is depicting the pure phase development of β -SnWO₄.

The SEM images for β -SnWO₄ are illustrated in Figure 5(a-c). The micrographs are obtained at diverse magnifications revealing the formation of β -SnWO₄ nanoclusters along with

some sorts of layered and rough structure as well. Stone like arbitrary and amalgamated particles of various sizes and shapes could be perceived in the micrographs. Figure 5(b-c) is illustrating some rock like structures along with very small particles. Furthermore, the images also reveal the porosity present in the sample.

The EDX spectrum of β -SnWO₄ has been profiled in Figure 5(d). It confirmed the existence of all the constituent elements such as tin, oxygen and tungsten in the sample. The table shown in an inset of Figure 5(d) is demonstrating the mass percentages of all the elements.

The morphology of β -SnWO₄ was also examined using TEM and HR-TEM to get detailed breakdown about structure and to determine the interlayer *d*-spacing. Figure 6(a-b) is illustrating TEM images obtained at different magnifications. The micrographs are profiling almost spherical shaped particles accompanied by some amalgamation. Further, some pores could also be professed in the micrographs. The interlayer *d*-spacing was examined through HR-TEM and found to be 0.33 nm [26] that could be perceived in Figure 6(c). The lattice fringes of (001) lattice plane of wolframite type cubic crystal structure β -SnWO₄ could be perceived in Figure 5(d) as sketched by selected area electron diffraction (SEAD) pattern. The occurrences of bright rings in the concerning pattern is illustrating the company of highly crystallite particles. The existence of lattice plane is in good agreement with XRD pattern.

The FTIR spectrum for β -SnWO₄ was recorded in the range of 350-4000 and cm⁻¹ is shown in Figure 7. The peak appearing around 609 cm⁻¹ is demonstrating asymmetric stretching vibration of WO₆⁻⁶ group [26, 27]. In the same way, the peaks emerging at 768 and 851 cm⁻¹ are illuminating stretching vibrations of W–W and W–O–W bridging bonds [27]. The structural vibrations of C–C or C–O–C bonds are in well agreement with the peak occurring at 1443 cm⁻¹. Further, the existence

of a strong peak at 1640 cm^{-1} and a broad peak at 3421 corresponds to stretching and bending vibrations of hydroxyl ($-\text{OH}$) group. The symmetric stretching vibration of $\text{C}-\text{H}$ bond can be observed from peak befalling at 2921 cm^{-1} . The co-existence of all the stretching and vibrational peaks confirmed the formation of $\beta\text{-SnWO}_4$ structure [28].

Barrett-Joyner-Halenda (BJH) analysis was carried out to investigate N_2 adsorption-desorption isotherm as well as to determine the pore size distribution. The curve sketched in Figure 8(a) is clearly offering desorption hysteresis of type-IV isotherm curve [29, 30] obtained under a relative pressure (P/P_0) of 0.1-1.0. The characteristics of mesostructured materials can be well explained on the basis of sharp capillary condensation steps occurring between relative pressure intervals of 0.40-0.95. It also perceives mesopores irregularity in the product. The BJH pore size distribution is profiled in Figure 8(b). A sharp peak could be depicted in the beginning of distribution curve demonstrating an average pore diameter of 3.35 nm. The pore volume and surface area of the particles in the sample was determined using Brunauer-Emmett-Teller (BET) analysis. Accordingly, owe to its plentiful range of pore diameter (2–80 nm), it can accumulate higher number of charge carriers, thus improving the electrolyte performance of the current specimen. Hence, it can offer its utilization in a wide collection of potential applications.

CV measurements were implemented to analyze the ongoing electrode reactions throughout the charge/discharge for $\beta\text{-SnWO}_4$ nanostructures. The CV profile was mapped under various current cycles and a potential window of 0.01 to 3.0 V and is demonstrated in Figure 9(a). The composition is clearly describing the actuality of anodic/cathodic peaks. Similar current humps can be perceived from all the current cycles. During lithiation, three peaks can be depicted specifying multi-lithiation progression [21]. The reduction of $\beta\text{-SnWO}_4$ to Sn and W was noticed from 1st reduction peak appeared around 2.31 V as prescribed in Eq. 9. Another reduction peak

occurred at 1.59 V justifying the Sn-metal reaction in excess vicinity of Li⁺ ions (alloying reaction) [31]. The following reaction can be perceived in Eq. 10. In addition, the W-metal reaction with LiSn and excessive Li⁺ ions can be observed in Eq. 11 that is resulted from the existence of 3rd reduction peak around 0.77 V. The reverse of reduction known as oxidation also occurred. The anodic peak appeared around 0.53 V is attributed to the de-alloying of Li_xSn while the peak appeared at 2.40 V is identifying the oxidation of Sn and W to β-SnWO₄. The probable electrochemical reactions are as follows [21];

The galvanometric charge/discharge (GCD) curves for β-SnWO₄ at a scan rate of 0.1 C and in the voltage range of 0.01–3.0 V and is sketched in Figure 9(b). The 1st cycle exhibited a discharge capacity of 1180 mAhg⁻¹ and 2nd cycle displayed charge and discharge capacities of 608 mAhg⁻¹ and 638 mAhg⁻¹, respectively. Theoretically, β-SnWO₄ demonstrates a capacity of 850 mAhg⁻¹ [32]. The excessive discharge capacity is mainly due to interfacial storage [33]. As the curves depict higher discharge capacity than charge capacity that can be attributable to the factors such as; electrolyte decomposition, unavoidable SEI formation and generation of Li₂O, owing to irreversible Li-ions interactions [34]. A decrease in charge/discharge capacities with an increase in current rate is representing an excellent ionic and electrical conductivity, and an exceptional rate capability.

The rate capability of β-SnWO₄ was examined at numerous current rates (0.1–3 C) and has been shown in Figure 9(c). A specific capacity of 54 mAhg⁻¹ was attained at a current rate of 3 C. Further, an excessive specific capacitance of 600 mAhg⁻¹ was noticeable when reverse current was

brought at 0.1 C. The contemporary extreme electrochemical performance of β -SnWO₄ is indicating highly stable electrode material towards energy storage applications.

The specific charge-discharge capacities and coulombic efficiency of β -SnWO₄ were performed at C/10 rate and is profiled in Figure 9(d). From graph, it is evident that almost constant and stabilized charge-discharge capacities of 105 and 58 mAhg⁻¹ were obtained. In addition, a coulombic efficiency of nearly 100% was professed.

Conclusion

β -SnWO₄ nanoparticles were synthesized by microwave heat treatment method, facilitated by the reaction of SnCl₂ and H₂WO₄, in the presence of tamarind seed powder. XRD analysis confirmed the crystalline nature of β -SnWO₄ nanoparticles which was found to be cubic in nature. SEM analysis revealed the formation of β -SnWO₄ stone like arbitrary and amalgamated nanoclusters with some traces of porosity. EDX analysis confirmed the existence of all constituent elements i.e., tin, oxygen and tungsten in the desired stoichiometric ratio. Spherical shaped particles were perceived by TEM analysis and an interlayer *d*-spacing was examined through HR-TEM which was found to be 0.33 nm, corresponding to (001) plane. The occurrences of bright rings in the pattern illustrated the highly crystallite nature of the sample. The peaks emerging in FTIR spectrum at about 609, 768, 851 and 1443 cm⁻¹ illuminated the stretching vibrations of WO₆⁻⁶ group, W–W and W–O–W bridging bonds, C–C or C–O–C bonds, respectively. The mesopores irregularity in the product was perceived by BJH analysis. A sharp peak as evident in the beginning of distribution curve, demonstrated an average pore diameter of 3.35 nm. The CV profile was mapped under various current cycles which confirmed the composition by describing the actuality of anodic/cathodic peaks (multi-lithiation and de-lithiation process). The reduction peak appearing around 2.31, 1.59 and 0.77 V, demonstrated the reduction of β -SnWO₄ to Sn and W, Sn-metal

reaction and W-metal reaction, respectively. In GCD analysis, 1st cycle exhibited a discharge capacity of 1180 mAhg⁻¹ and the 2nd cycle displayed charge and discharge capacities of 608 and 638 mAhg⁻¹, respectively. Moreover, a decrease in charge/discharge capacities was observed with an increase in current rate which represented an excellent ionic and electrical conductivity and exceptional rate capability of about 600 mAhg⁻¹ at 0.1 C (reverse current). In addition, it also exhibited ~100% columbic efficiency, thus β -SnWO₄ is highly favorable to be utilized as an electrode material for energy storage devices.

Acknowledgement

Authors thank the financial support from Kingdom of Saudi Arabia, Ministry of Education, Najran University, Promising Centre for Sensors and Electronic Devices (PCSED) sanction on 2019 (Ref. No: PCSED-021-18). Researchers Supporting Project number (RSP-2020/160), King Saud University, Saudi Arabia. Nagaraju Ganganagappa thank DST Nanomission (Project No. SR/NM/NS-1262/2013 (G), New Delhi, Govt. of India for financial support to carry out the research work.

Author Contributions: Conceptualization, Fahad A. Alharthi, Sumedha H N; Nagaraju Ganganagappa; Data curation, Mabkhoot A. Alsaiari; Shashank M; Formal analysis, Mohammed S. Jalalah; Funding acquisition, Fahad A. Alharthi Resources, Naushad Ahmad; Visualization, Jari S. Algethami, Vishwanth; Writing – original draft, Naushad Ahmad; Writing – review & editing, Fahad A. Alharthi, Nagaraju Ganganagappa, Mabkhoot A. Alsaiari, Mohammed S. Jalalah, and Jari S. Algethami.

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Figure captions

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Figure 3 Williamson-Hall (W-H) plot of β -SnWO₄ nanoparticles

Figure 4 Rietveld refined XRD pattern of β -SnWO₄ nanostructures

Figure 5 (a-c) SEM images and (d) EDAX spectrum (inset: elemental composition) of β -SnWO₄ nanoparticles

Figure 6 (a-b) TEM, (c) HR-TEM and (d) SEAD pattern of β -SnWO₄ nanoparticles

Figure 7 FTIR spectrum of β -SnWO₄ nanoparticles

Figure 8 (a) BJH adsorption-desorption isotherm and (b) pore size distribution of β -SnWO₄ nanostructures

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