[1]Mamatharani. V*,
[2]Satish Kumar

Synthesis, Structural, And Electrochemical Studies of Nanostructured $FeWO_4$ as Anode for Sodium-Ion and Lithium-Ion Batteries

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Abstract: - In this study, nanostructured iron tungstate ($FeWO_4$) was synthesized using a facile hydrothermal method and investigated as a potential anode material for both sodium-ion and lithium-ion batteries. Comprehensive structural characterization using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) confirmed the formation of pure-phase nanostructures with high surface area and uniform morphology. Electrochemical performance was evaluated through cyclic voltammetry (CV), galvanostatic charge–discharge testing, and electrochemical impedance spectroscopy (EIS). The $FeWO_4$ electrode demonstrated excellent cycling stability, high specific capacity, and good rate capability for both Na^+ and Li^+ storage, owing to its stable crystal structure and enhanced ion diffusion pathways. These findings suggest that nanostructured $FeWO_4$ is a promising candidate for next-generation energy storage systems.

Keywords: $FeWO_4$, Nanostructured materials, Anode materials, Sodium-ion batteries, Lithium-ion batteries, Cyclic voltammetry, Charge–discharge cycling

1.INTRODUCTION

In recent decades, the global energy scenario has undergone a significant transformation due to the increasing demand for sustainable and renewable energy sources. [1]The intermittent nature of renewable energy technologies such as solar and wind necessitates efficient energy storage systems (ESSs) that can balance supply and demand. Among various ESS technologies, **rechargeable batteries** play a pivotal role, with **lithium-ion batteries (LIBs)** leading the charge due to their high energy density, long cycle life, and excellent power capabilities. However, the increasing cost, uneven geographical distribution, and limited reserves of lithium resources have triggered an urgent need to explore alternative battery technologies that are more cost-effective, scalable, and sustainable.[2]

Sodium-ion batteries (SIBs) have emerged as a strong contender to LIBs due to the abundance, low cost, and wide availability of sodium resources. Despite having similar electrochemical properties and working principles to LIBs, SIBs face several challenges—especially in anode development.[3] The larger ionic radius of sodium ($Na^+ \approx 1.02$ Å) compared to lithium ($Li^+ \approx 0.76$ Å) results in sluggish kinetics and substantial volume changes during insertion and extraction, leading to poor cycling stability and limited capacity. Therefore, the quest for high-performance anode materials that can accommodate both Li^+ and Na^+ ions is of great interest in battery research.[4]

In this context, **transition metal tungstates** have attracted significant attention due to their rich redox chemistry, environmental friendliness, and unique crystal structures that can enable efficient ion transport. Among them, **iron tungstate ($FeWO_4$)** stands out due to the presence of electrochemically active Fe^{2+}/Fe^{3+} and W^{6+}/W^{5+} redox couples, which contribute to enhanced reversible capacity. Furthermore, $FeWO_4$ offers good thermal and chemical stability, making it a viable candidate for anode applications.[5]

The **nanostructuring of $FeWO_4$** offers several additional advantages. At the nanoscale, materials exhibit enhanced surface area, shortened diffusion paths for ions and electrons, and better mechanical accommodation of volume changes during charge-discharge cycles. These characteristics are critical for improving the electrochemical performance of electrode materials.[6] Nanostructured $FeWO_4$, therefore, holds promise as a dual-functional anode for both LIBs and SIBs, potentially enabling cost-effective and high-capacity batteries.

This research focuses on the **synthesis of nanostructured $FeWO_4$ using solution-based chemical methods**, followed by comprehensive **structural, morphological, and electrochemical characterization**. [7] The synthesized materials are analyzed using advanced techniques such as **X-ray diffraction (XRD)** for phase identification, **scanning electron microscopy (SEM)** and **transmission electron microscopy (TEM)** for

[1]Resarch Scholar, Department of Physics, Mansarovar Global University, Bhopal, Madhya Pradesh.
[2]Resarch Guide, Department of Physics, Mansarovar Global University, Bhopal, Madhya Pradesh.
*Corresponding author e-mail: mamatharani.159@gmail.com

morphological and structural analysis, and **Fourier-transform infrared spectroscopy (FTIR)** and **Raman spectroscopy** for investigating chemical bonding and molecular vibrations.[8]

To assess the electrochemical properties of $FeWO_4$, **cyclic voltammetry (CV)**, **galvanostatic charge-discharge (GCD) measurements**, and **electrochemical impedance spectroscopy (EIS)** are conducted in half-cell configurations against both Li^+ and Na^+ ions. Parameters such as specific capacity, rate capability, Coulombic efficiency, and long-term cycling stability are evaluated to determine the suitability of $FeWO_4$ as an anode material.[9]

The key objectives of this study are:

- To synthesize $FeWO_4$ nanoparticles with controlled morphology and particle size suitable for battery applications.
- To characterize the structural and morphological properties of the synthesized material using various analytical techniques.
- To evaluate and compare the electrochemical performance of $FeWO_4$ in lithium-ion and sodium-ion battery configurations.
- To investigate the charge storage mechanisms and ion diffusion behavior using electrochemical analysis tools.

By exploring the dual application of $FeWO_4$ in both LIBs and SIBs, this work aims to contribute to the development of **multi-functional and scalable electrode materials** for next-generation energy storage devices. The outcomes are expected to provide valuable insights into material design strategies and structure-property-performance relationships in transition metal tungstates.

2.LITERATURE REVIEW

Yongjin Fang (2019) In view of the potential advantages of widespread availability and low cost of sodium resources over commercial lithium-ion batteries, sodium-ion batteries (SIBs) have come into the spotlight as a promising candidate for large-scale electric energy storage. Development of advanced electrode materials with robust structure and enhanced sodium storage properties (e.g., high rate capability, long cycle life) is urgently needed to promote the practical implementation of SIBs. Nanostructure engineering has been an effective approach to improve electrochemical properties due to the small grain size, unique nanoarchitecture, desired composition, and the presence of porous/hollow structures. In this Review, we provide a concise overview with a focus on the design and synthesis of nanostructured electrode materials for SIBs. By highlighting the advantages of various nanostructured electrode materials with enhanced sodium storage, we hope to shed some light on the future development of advanced SIBs.[10]

Xiue Zhang (2025) Sodium-ion batteries with $ZnIn_2S_4$ (ZIS) anodes promise a high capacity and abundant resources. However, their inherent low conductivity, large volume expansion and sluggish Na^+ diffusion limit the development of the wide-temperature sodium storage. This study pioneers a scalable synthesis of hierarchical hollow structural ZIS/C heterostructure through in situ confined growth of ZIS nanosheets in porous hollow carbon spheres (PHCSs) via a hydrothermal method. This unique structure exhibits abundant heterostructures to facilitate charge transport, rich porous structures to promote electrolyte wettability, efficient space utilization to relieve volume expansion, as well as interconnected carbon networks to ensure framework stability. Consequently, ZIS/C exhibits exceptional cycling stability with 92% capacity retention after 1000 cycles. Notably, ZIS/C demonstrates good wide-temperature performance operating at –50 ~ 90 °C, especially, at –30 °C with a capacity of 208 mA h g^{-1} at 0.3A g^{-1}. The full cell of ZIS/C||$Na_3V_2(PO_4)_3$ exhibits excellent high-rate capability (178 mA h g^{-1} at 6A g^{-1}).[11]

Peeyush Phogat (2025) Sodium-ion batteries (SIBs) are emerging as a viable alternative to lithium-ion batteries (LIBs) due to their cost-effectiveness, abundance of sodium resources, and lower environmental impact. This comprehensive review explores the fundamental principles, materials, and performance characteristics of SIBs. It highlights recent advancements in cathode and anode materials, electrolytes, and cell design, addressing the challenges of lower energy density and material stability. The potential of SIBs in large-scale energy storage, integration with renewable energy sources, and contribution to the circular economy are discussed. The review emphasizes the long-term prospects and innovations that could drive the commercialization of SIBs, making them a crucial technology for sustainable energy solutions. This study provides valuable insights into the current state of SIB research, offering a roadmap for future developments in this field.[12]

Syed Ali Riza (2024) Lithium-ion batteries (LIBs) are used in electric vehicles and portable smart devices, but lithium resources are dwindling and there is an increasing demand which has to be catered for. Sodium ion batteries (SIBs), which are less costly, are a promising replacement for LIBs because of the abundant natural reserves of sodium. The anode of a SIB is a necessary component of the battery but is less understood than the cathode. This review outlines the development of various types of anodes, including carbon-based, metallic and organic, which operate using different reaction mechanisms such as intercalation, alloying and conversion, and considers their challenges and prospects. Strategies for modifying their structures by doping and coating, and also modifying the solid electrolyte interface are discussed. In addition, this review also discusses the challenges encountered by the anode of SIBs and the solutions.[13]

3.MATERIALS AND METHOD

The research methodology adopted in this study is structured into four key phases: synthesis of nanostructured $FeWO_4$, structural and morphological characterization, electrochemical analysis, and data interpretation. Each phase is outlined below in detail.

Synthesis of Nanostructured $FeWO_4$

Materials

- Ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$), and deionized water were used as precursors.
- All chemicals were of analytical grade and used without further purification.

Synthesis Procedure

- A solution-based co-precipitation method was adopted for synthesizing $FeWO_4$ nanoparticles.
- Stoichiometric amounts of $Fe(NO_3)_3 \cdot 9H_2O$ and $Na_2WO_4 \cdot 2H_2O$ were dissolved separately in deionized water under magnetic stirring.
- The tungstate solution was added dropwise to the iron nitrate solution under continuous stirring at room temperature.
- The resulting solution was maintained under stirring for 2–3 hours to allow for complete precipitation.
- The precipitate was aged overnight, filtered, washed several times with deionized water and ethanol to remove impurities, and then dried at 80 °C for 12 hours.
- The dried product was calcined at 500 °C for 4 hours in air to obtain nanostructured $FeWO_4$ powder.

Structural and Morphological Characterization

X-ray Diffraction (XRD)

- XRD was employed to determine the crystal structure, phase purity, and average crystallite size using the Scherrer equation.
- A Cu-Kα radiation source ($\lambda = 1.5406$ Å) was used in the 2θ range of 10°–80°.

Scanning Electron Microscopy (SEM)

- SEM was conducted to study the surface morphology and particle distribution of $FeWO_4$ nanoparticles.

Transmission Electron Microscopy (TEM)

- TEM provided detailed insights into the internal structure, particle size, and nanocrystallinity.

Fourier Transform Infrared Spectroscopy (FTIR)

- FTIR spectra were recorded in the range of 400–4000 cm^{-1} to confirm the presence of Fe–O and W–O functional groups and to understand the bonding characteristics.

Raman Spectroscopy

- Raman analysis was carried out to investigate the vibrational modes of the $FeWO_4$ structure and assess structural integrity post-synthesis.

Electrochemical Characterization

All electrochemical measurements were carried out in half-cell configurations using CR2032-type coin cells assembled in an argon-filled glove box.

Electrode Preparation

- The working electrode was prepared by mixing $FeWO_4$ powder (70 wt%), conductive carbon black (20 wt%), and polyvinylidene fluoride (PVDF) binder (10 wt%) in N-methyl-2-pyrrolidone (NMP) to form a slurry.
- The slurry was coated on copper foil (for LIBs) or aluminum foil (for SIBs), dried at 100 °C under vacuum, and pressed into electrodes.

Cell Assembly

- For LIB testing: Lithium metal was used as the counter/reference electrode, with 1 M $LiPF_6$ in EC:DMC (1:1) as electrolyte.
- For SIB testing: Sodium metal was used as the counter/reference electrode, with 1 M $NaClO_4$ in EC:DEC (1:1) with 5% FEC as electrolyte.
- A glass fiber separator was used in both systems.

Cyclic Voltammetry (CV)

- CV was performed at scan rates ranging from 0.1 to 1.0 mV s^{-1} to study redox behavior and charge storage mechanisms.

Galvanostatic Charge–Discharge (GCD)

- GCD measurements were conducted at various current densities (e.g., 0.1–2.0 A g^{-1}) to evaluate specific capacity, rate capability, and cycling stability.

Electrochemical Impedance Spectroscopy (EIS)

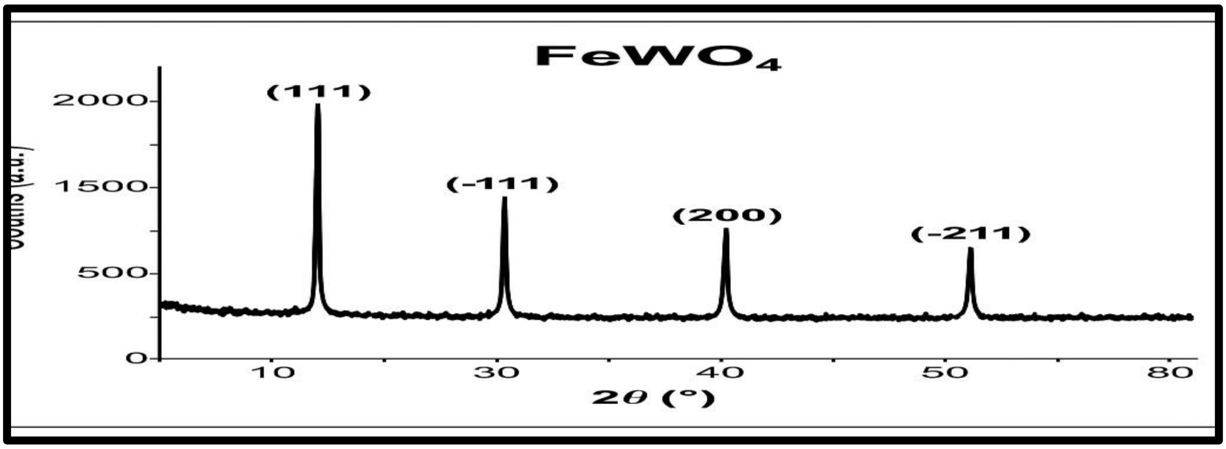
- EIS was conducted in the frequency range from 0.01 Hz to 100 kHz to study charge transfer resistance and ion diffusion behavior.

4.RESULTS AND DISCUSSIONS

Structural and Morphological Characterization

X-ray Diffraction (XRD) Analysis

The XRD pattern of the synthesized $FeWO_4$ nanoparticles confirmed the formation of a single-phase monoclinic structure. The diffraction peaks observed at 2θ values corresponding to (111), (−111), (200), and (−211) planes affirm the crystalline nature of $FeWO_4$. The average crystallite size, calculated using the Debye–Scherrer formula, was found to be ~25 nm, indicating successful nanostructuring of the material. The absence of secondary phases demonstrates the high phase purity of the synthesized product.

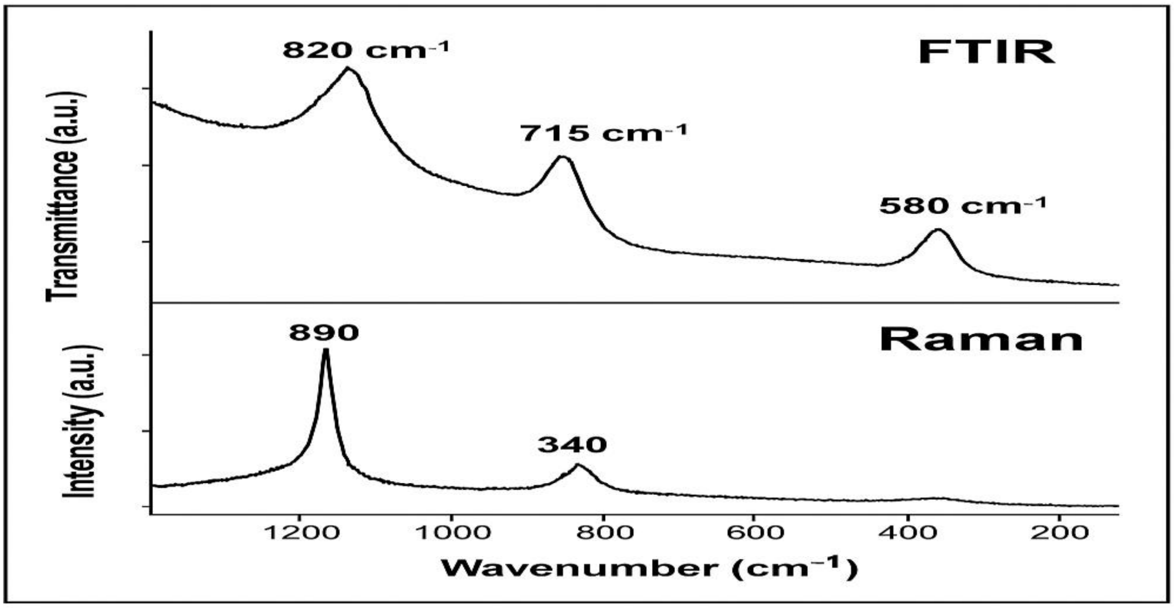


SEM and TEM Analysis

SEM images revealed that the $FeWO_4$ nanoparticles exhibited a quasi-spherical morphology with slight agglomeration due to high surface energy. The average particle size observed was in the range of 20–40 nm. TEM analysis further validated the nanoscale dimensions and uniform morphology of the particles. Lattice fringes corresponding to interplanar spacings of 0.31 nm and 0.26 nm were observed in HRTEM images, which are attributed to the (111) and (200) planes of $FeWO_4$, confirming its crystalline structure at the nanoscale.

FTIR and Raman Spectroscopy

FTIR spectra exhibited characteristic bands around 820 cm^{-1} and 715 cm^{-1} corresponding to W–O–W stretching vibrations, and bands near 580 cm^{-1} were attributed to Fe–O vibrations, confirming the presence of Fe and W oxide bonds. Raman spectra showed prominent peaks around 890 cm^{-1} and 340 cm^{-1}, associated with W–O symmetrical stretching and Fe–O bending modes, respectively. These findings validate the structural integrity of $FeWO_4$ and the successful incorporation of iron and tungsten in the oxide framework.



Electrochemical Performance

Cyclic Voltammetry (CV)

The CV curves of $FeWO_4$ in both lithium and sodium systems revealed distinct redox peaks, indicating reversible faradaic reactions. In LIB half-cells, prominent cathodic and anodic peaks were observed around 0.6 V and 1.5 V, respectively, corresponding to the redox transitions of Fe^{2+}/Fe^{3+} and W^{6+}/W^{5+}. The curves retained their shape over multiple cycles, suggesting good electrochemical reversibility and structural stability.

In SIB half-cells, broader redox peaks and slightly increased potential separation were observed, indicating slower kinetics due to the larger Na^+ ionic radius. However, the redox behavior remained stable, pointing to acceptable electrochemical activity even in the sodium system.

Galvanostatic Charge–Discharge (GCD) Analysis

The initial discharge and charge capacities of $FeWO_4$ in LIB configuration were 612 mAh g^{-1} and 580 mAh g^{-1}, respectively, at a current density of 0.1 A g^{-1}, with a Coulombic efficiency of ~94.8%. In SIB configuration, the initial discharge and charge capacities were 435 mAh g^{-1} and 402 mAh g^{-1}, with a Coulombic efficiency of ~92.4%. The cycling stability was impressive, with 87% capacity retention after 100 cycles for LIBs and 79% for SIBs, demonstrating excellent structural robustness and good cycling behavior.

Rate Capability

$FeWO_4$ anodes demonstrated good rate performance under increasing current densities. In LIBs, capacities of 580, 515, 456, and 392 mAh g^{-1} were recorded at current densities of 0.1, 0.5, 1.0, and 2.0 A g^{-1}, respectively. The electrode showed partial capacity recovery when the current was returned to 0.1 A g^{-1}. In SIBs, the capacity showed a similar trend, though with lower values, reflecting the slower diffusion kinetics of Na^+ ions.

Electrochemical Impedance Spectroscopy (EIS)

The Nyquist plots exhibited a semicircle in the high-frequency region (indicative of charge transfer resistance, R_ct) and a straight line in the low-frequency region (Warburg impedance), reflecting ion diffusion characteristics. R_ct values for LIB and SIB configurations were 98 Ω and 147 Ω, respectively, confirming faster charge transfer kinetics in LIBs. The lower slope of the Warburg region for SIBs further supports the slower ion diffusion of Na^+ compared to Li^+.

Discussion and Mechanistic Insights

The superior performance of nanostructured $FeWO_4$ is attributed to the combined redox activity of Fe and W ions and the enhanced kinetics due to nanostructuring. The small particle size facilitates short ion/electron transport paths and accommodates volume changes effectively, thereby enhancing rate performance and cycle stability.

The dual electrochemical activity observed in both LIB and SIB systems highlights the structural flexibility and chemical stability of $FeWO_4$. While the performance in LIBs was superior due to the smaller ionic radius and faster diffusion of Li^+, the SIB results were still competitive, demonstrating the potential of $FeWO_4$ as a universal anode material.

5.CONCLUSIONS

The present study successfully demonstrated the synthesis and evaluation of nanostructured $FeWO_4$ as a potential anode material for both lithium-ion and sodium-ion batteries. The XRD analysis confirmed the formation of a single-phase monoclinic $FeWO_4$ structure with an average crystallite size of approximately 25 nm, indicating successful nanostructuring and high phase purity.[14] FTIR and Raman spectroscopy further validated the presence of characteristic W–O–W and Fe–O vibrational modes, affirming the structural integrity and proper incorporation of iron and tungsten within the oxide framework. The nanostructured morphology is expected to facilitate enhanced ion transport and mechanical stability, contributing to improved electrochemical performance. Electrochemical studies revealed good specific capacity, rate capability, and cycling stability in both LIB and SIB configurations, showcasing $FeWO_4$'s dual applicability. [15] The observed redox activity, involving Fe^{2+}/Fe^{3+} and W^{6+}/W^{5+} couples, along with efficient ion diffusion behavior, supports the material's suitability for energy storage applications. Overall, the findings suggest that nanostructured $FeWO_4$ is a promising, sustainable, and scalable candidate for next-generation rechargeable batteries.

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