



## Investigation of transition metal oxides (TMOs) nanomaterials as electrodes for sodium-ion batteries (SIBs)

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### Abstract

Sodium-ion batteries (SIBs) have emerged as a promising alternative to Lithium-ion batteries due to the abundance and low cost of sodium resources. Transition metal oxides (TMOs) have shown great potential as electrode materials for SIBs owing to their high theoretical capacities, diverse redox chemistry and structural stability. This review comprehensively explores the recent advances in TMOs nanomaterials as electrodes for SIBs, focusing on their synthesis methods, electrochemical performance and structure property relationships. The challenges and future perspectives for the development of high performance TMOs electrodes for SIBs are also discussed.

**Keywords:** Sodium-ion batteries, Transition metal oxide, Nanomaterial electrodes, Energy storage

### Introduction

The increasing demand for sustainable and affordable energy storage systems has driven the search for alternatives to lithium-ion batteries (LIBs). Sodium-ion batteries (SIBs) have attracted significant attention due to the abundance and low cost of sodium resources, as well as their similar working principles to LIBs [1]. However, the larger ionic radius of Na<sup>+</sup> (1.02 Å) compared to Li<sup>+</sup> (0.76 Å) poses challenges in finding suitable electrode materials that can accommodate the larger ions and maintain structural stability during the charging and discharging processes [2]. Transition metal oxides (TMOs) have emerged as promising electrode materials for SIBs due to their high theoretical capacities, diverse redox chemistry and structural stability [3]. TMOs encompass a wide range of compounds, including simple oxides (e.g., TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and MnO<sub>2</sub>), complex oxides (e.g., Na<sub>x</sub>MnO<sub>2</sub> and Na<sub>x</sub>CoO<sub>2</sub>), and mixed metal oxides (e.g., Na<sub>x</sub>NiyMnzO<sub>2</sub>) [6]. These materials exhibit various crystal structures, such as layered, spinel and tunnel structures, which can facilitate Na<sup>+</sup> insertion/extraction and provide distinct electrochemical properties [4].

Nanostructuring of TMOs has proven to be an effective strategy to enhance their electrochemical performance in SIBs. Nanomaterials offer several advantages, such as increased surface area, shortened diffusion paths for Na<sup>+</sup> ions and improved structural stability [5]. Various nanostructures, including nanoparticles, nanowires, nanosheets and hollow structures have been synthesized and investigated as electrodes for SIBs. This manuscript aims to provide a comprehensive overview of the recent advances in TMOs nanomaterials as electrodes for SIBs. The synthesis methods, electrochemical performance and structure property relationships of different TMOs nanomaterials will be discussed in detail. The challenges and future perspectives for the development of high performance TMOs electrodes for SIBs will also be highlighted.

### Materials and Methods

Various synthesis methods have been employed to prepare TMOs nanomaterials with controlled morphologies, sizes and compositions. Top down approaches like mechanical milling and exfoliation, as well as bottom up approaches like hydrothermal/solvothermal synthesis, co-precipitation, and sol-gel synthesis, are discussed in details [6].

**Top down approaches:** Top down approaches involve the breaking down of bulk materials into smaller nanostructures. Mechanical milling is a commonly used top down method for the synthesis of TMOs nanomaterials [7]. In this method, bulk TMOs powders are subjected to high energy ball milling, which reduces the particle size and introduces defects and strain into the material. The milling process can be carried out in dry or wet conditions and the milling parameters, such as the ball-to-powder ratio, milling speed and milling time can be adjusted to control the particle size and morphology [8].

Another top down approach is the exfoliation of layered TMOs into two dimensional (2D) nanosheets [9]. This method exploits the weak vander Waals interactions between the layers of certain TMOs such as MoO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> allowing them to be easily exfoliated into thin nanosheets. The exfoliation can be achieved through various techniques, such as liquid-phase exfoliation ion intercalation and mechanical cleavage [10].

**Bottom-up approaches:** Bottom up approaches involve the assembly of atoms, molecules or clusters into nanostructures. Solution based methods, such as hydrothermal/solvothermal synthesis, co-precipitation and sol-gel synthesis are widely used bottom up approaches for the synthesis of TMOs nanomaterials [11]. Hydrothermal/solvothermal synthesis involves the reaction of precursors in an aqueous or organic solvent under high

temperature and pressure conditions in a sealed autoclave. This method allows for the formation of various nanostructures, such as nanoparticles, nanowires and hollow structures by tuning the reaction parameters, such as temperature, time, pH and precursor concentration [12]. For example, synthesized Fe<sub>2</sub>O<sub>3</sub> nanoparticles with a uniform size distribution by a hydrothermal method using FeCl<sub>3</sub> as the precursor and ethylene glycol as the solvent.

Co-precipitation is a simple and scalable method for the synthesis of TMOs nanomaterials [13]. In this method, metal salts are dissolved in an aqueous solution and a precipitating agent, such as NaOH or NH<sub>4</sub>OH, is added to form a precipitate of the metal hydroxide or oxide. The precipitate is then collected, washed and calcined to obtain the desired TMOs nanomaterial. Prepared NiO nanoparticles by a co precipitation method using Ni(NO<sub>3</sub>)<sub>2</sub> as the precursor and NaOH as the precipitating agent [14]. Sol gel synthesis involves the formation of a colloidal suspension (sol) from a solution of metal precursors, followed by the gelation of the sol to form a three-dimensional network (gel) [15]. The gel is then dried and calcined to obtain the TMOs nanomaterial. This method allows for the control of the particle size, morphology and composition by adjusting the solgel parameters, such as the type of precursors, pH and aging conditions [16]. For instance, synthesized TiO<sub>2</sub> nanoparticles by a sol-gel method using titanium isopropoxide as the precursor and acetic acid as the catalyst. Other bottom up approaches, such as template-assisted synthesis, electrospinning and spray pyrolysis [17] have also been employed for the synthesis of TMOs nanomaterials with specific morphologies and structures.

## Results and Discussion

The electrochemical performance of TMOs nanomaterials as electrodes for SIBs has been extensively investigated. The key performance metrics include specific capacity, rate

capability and cycling stability. This section discusses the electrochemical performance of various TMOs nanomaterials, including simple oxides, complex oxides and mixed metal oxides.

**Simple Oxides:** Simple TMOs, such as TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and MnO<sub>2</sub>, have been studied as electrode materials for SIBs due to their high theoretical capacities and low cost. However, these materials often suffer from poor electrical conductivity and structural instability during cycling. TiO<sub>2</sub> has a theoretical capacity of 335 mAh g<sup>-1</sup> based on the Ti<sup>4+</sup>/Ti<sup>3+</sup> redox couple. Nanostructured TiO<sub>2</sub>, such as nanoparticles [18], nanowires and nanotubes [19], have shown improved rate capability and cycling stability compared to bulk TiO<sub>2</sub>. For example reported, TiO<sub>2</sub> nanoparticles with a specific capacity of 200 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> and a capacity retention of 92% after 100 cycles [20].

Fe<sub>2</sub>O<sub>3</sub> has a high theoretical capacity of 1007 mAh g<sup>-1</sup> based on the conversion reaction between Fe<sub>2</sub>O<sub>3</sub> and Na [35]. However, the poor electrical conductivity and large volume changes during cycling limit its practical application. Nanostructuring of Fe<sub>2</sub>O<sub>3</sub>, such as the synthesis of nanoparticles, nanorods, and hollow structures, has been shown to mitigate these issues. Synthesized hollow Fe<sub>2</sub>O<sub>3</sub> nanospheres with a specific capacity of 600 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> and a capacity retention of 80% after 200 cycles [21].

MnO<sub>2</sub> exists in various polymorphs, such as α-, β-, γ-, and δ-MnO<sub>2</sub>, which exhibit different electrochemical properties. α-MnO<sub>2</sub> with a tunnel structure has been widely studied as an electrode material for SIBs due to its high theoretical capacity (1230 mAh g<sup>-1</sup>) and fast Na<sup>+</sup> diffusion and prepared α-MnO<sub>2</sub> nanowires with a specific capacity of 350 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> and a capacity retention of 85% after 100 cycles [22]. Summarizes the advantages and disadvantages of different synthesis methods for TMOs nanomaterials. Are shown in Table-1

**Table 1:** Comparison of synthesis methods for TMOs nanomaterials

Synthesis Method	Advantages	Disadvantages
Mechanical milling	- Simple and scalable - Applicable to a wide range of materials	- Limited control over particle size and morphology - Potential contamination from milling media
Exfoliation	- Produces 2D nanosheets - High surface area	- Limited to layered TMOs - Low yield and scalability
Hydrothermal/Solvothermal	- Controllable morphology and size - High crystallinity	- High temperature and pressure required - Long reaction times
Co-precipitation	- Simple and scalable - Mild reaction conditions	- Limited control over particle size and morphology - Potential impurities from precursors
Sol-gel	- Controllable particle size and morphology - High purity	- Long processing times - Potential shrinkage and cracking during drying

Summarizes the electrochemical performance of selected simple TMOs nanomaterials [22] as electrodes for SIBs are given in Table-2.

**Table 2:** Electrochemical performance of selected simple TMOs nanomaterials in SIBs

TMOs Nanomaterial	Specific Capacity (mAh g <sup>-1</sup> )	Rate Capability (A g <sup>-1</sup> )	Cycling Stability (%)
TiO <sub>2</sub> nanoparticles	200	0.1	92% after 100 cycles
Hollow Fe <sub>2</sub> O <sub>3</sub> nanospheres	600	0.1	80% after 200 cycles
α-MnO <sub>2</sub> nanowires	350	0.1	85% after 100 cycles

**Complex Oxides:** Complex TMOs, such as Na<sub>x</sub>MnO<sub>2</sub> and Na<sub>x</sub>CoO<sub>2</sub>, have attracted attention as electrode materials for SIBs due to their layered structures, which facilitate Na<sup>+</sup> insertion/extraction. The electrochemical performance of these materials can be further enhanced through

nanostructuring. Na<sub>x</sub>MnO<sub>2</sub> exists in various polymorphs, including O<sub>3</sub>-type, P<sub>2</sub>-type, and P<sub>3</sub>-type, depending on the stacking arrangement of the MnO<sub>2</sub> layers and the Na<sup>+</sup> coordination. P<sub>2</sub>-type Na<sub>x</sub>MnO<sub>2</sub> has been extensively studied as a cathode material for SIBs due to its high

theoretical capacity (243 mAh g<sup>-1</sup>) and good Na<sup>+</sup> mobility. Zhu *et al.* synthesized P<sub>2</sub>-Na<sub>0.7</sub>MnO<sub>2</sub> nanoflakes with a specific capacity of 190 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> and a capacity retention of 90% after 100 cycles [23].

Na<sub>x</sub>CoO<sub>2</sub> is another layered oxide that has shown promise as a cathode material for SIBs. P<sub>2</sub>-type Na<sub>x</sub>CoO<sub>2</sub> exhibits a high theoretical capacity (250 mAh g<sup>-1</sup>) and good structural stability [24]. However, its practical application is hindered

by the high cost of cobalt. Nanostructuring of Na<sub>x</sub>CoO<sub>2</sub>, such as the synthesis of nanoparticles and nanosheets has been shown to improve its electrochemical performance, reported P<sub>2</sub>-Na<sub>0.7</sub>CoO<sub>2</sub> nanoparticles with a specific capacity of 120 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> and a capacity retention of 80% after 50 cycles [25]. Presents the electrochemical performance of selected complex TMOs nanomaterials as electrodes for SIBs [25] are given in Table-3.

**Table 3:** Electrochemical performance of selected complex TMOs nanomaterials in SIBs

TMOs Nanomaterial	Specific Capacity (mAh g <sup>-1</sup> )	Rate Capability (A g <sup>-1</sup> )	Cycling Stability (%)
P <sub>2</sub> -Na <sub>0.7</sub> MnO <sub>2</sub> nanoflakes	190	0.1	90% after 100 cycles
P <sub>2</sub> -Na <sub>0.7</sub> CoO <sub>2</sub> nanoparticles	120	0.1	80% after 50 cycles

**Mixed Metal Oxides:** Mixed metal oxides, such as Na<sub>x</sub>NiyMnzO<sub>2</sub>, have been developed to combine the advantages of different transition metals and achieve superior electrochemical performance. The incorporation of multiple transition metals allows for the tuning of the redox potentials, electronic conductivity, and structural stability of the material [26].

Na<sub>x</sub>NiyMnzO<sub>2</sub> has been extensively studied as a cathode material for SIBs due to its high theoretical capacity (>200 mAh g<sup>-1</sup>) and good cycling stability. The composition of Na<sub>x</sub>NiyMnzO<sub>2</sub> can be adjusted to optimize its electrochemical properties. For example, increasing the Ni

content can improve the electronic conductivity, while increasing the Mn content can enhance the structural stability. Synthesized Na<sub>0.6</sub>Ni<sub>0.2</sub>Mn<sub>0.8</sub>O<sub>2</sub> nanosheets with a specific capacity of 180 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> and a capacity retention of 85% after 100 cycles [27]. Other mixed metal oxides, such as Na<sub>x</sub>FeyMnzO<sub>2</sub> and Na<sub>x</sub>CoyMnzO<sub>2</sub>, have also been investigated as electrode materials for SIBs. These materials exhibit similar electrochemical properties to Na<sub>x</sub>NiyMnzO<sub>2</sub>, with the composition being adjusted to optimize the performance. Summarizes the electrochemical performance of selected mixed metal oxide nanomaterials as electrodes for SIBs [27] are given in Table-4.

**Table 4:** Electrochemical performance of selected mixed metal oxide nanomaterials in SIBs

TMOs Nanomaterials	Specific Capacity (mAh g <sup>-1</sup> )	Rate Capability (A g <sup>-1</sup> )	Cycling Stability (%)
Na <sub>0.6</sub> Ni <sub>0.2</sub> Mn <sub>0.8</sub> O <sub>2</sub> nanosheets	180	0.1	85% after 100 cycles

### Structure-Property Relationships of TMOs Nanomaterials

The electrochemical performance of TMOs nanomaterials as electrodes for SIBs is closely related to their structural properties, such as crystal structure, particle size, and morphology. Understanding the structure-property relationships is crucial for the rational design and optimization of TMOs nanomaterials for SIBs.

**Crystal Structure:** The crystal structure of TMOs nanomaterials plays a significant role in their electrochemical performance. TMOs with layered structures, such as Na<sub>x</sub>MnO<sub>2</sub> and Na<sub>x</sub>CoO<sub>2</sub>, generally exhibit better Na<sup>+</sup> insertion/extraction kinetics and higher specific capacities compared to those with tunnel or spinel structures. The interlayer spacing and the coordination of Na<sup>+</sup> ions in the layered structure influence the Na<sup>+</sup> diffusion and storage properties [28]. The phase transitions of TMOs nanomaterials during cycling can also affect their electrochemical performance. For example, the phase transition from the O<sub>3</sub> to P<sub>3</sub> structure in Na<sub>x</sub>MnO<sub>2</sub> during Na<sup>+</sup> extraction can cause structural instability and capacity fading. Strategies such as ion doping and surface coating have been employed to stabilize the crystal structure and mitigate the phase transitions [29].

**Particle Size and Morphology:** The particle size and morphology of TMOs nanomaterials significantly influence their electrochemical performance. Nanostructuring of TMOs increases the surface area, shortens the Na<sup>+</sup> diffusion paths and accommodates the volume changes during cycling, leading to improved rate capability and cycling

stability [30]. Various nanostructures, such as nanoparticles, nanowires, nanosheets, and hollow structures, have been synthesized and investigated as electrodes for SIBs. Nanoparticles offer high surface area and fast Na<sup>+</sup> diffusion, but they may suffer from poor electrical conductivity and side reactions with the electrolyte. One-dimensional (1D) nanostructures, such as nanowires and nanotubes, provide efficient electron transport and accommodate the volume changes during cycling, but their synthesis can be complex and costly [31]. Two-dimensional (2D) nanosheets exhibit high surface area and fast Na<sup>+</sup> diffusion, but they may suffer from restacking and structural instability. Hollow structures, such as hollow spheres and nanoboxes, offer high surface area, short Na<sup>+</sup> diffusion paths and accommodated volume changes, but their synthesis can be challenging [32]. The optimal particle size and morphology of TMOs nanomaterials depend on the specific TMOs and the desired electrochemical properties. In general, a balance between the surface area, electrical conductivity, and structural stability is required to achieve high-performance TMOs electrodes for SIBs.

**Surface Properties:** The surface properties of TMOs nanomaterials, such as surface area, porosity, and surface chemistry, also play a crucial role in their electrochemical performance. A high surface area and porosity can increase the contact area between the electrode and the electrolyte, facilitating Na<sup>+</sup> insertion/extraction and improving the rate capability. However, excessive surface area may lead to side reactions with the electrolyte and capacity fading [33]. Surface modification of TMOs nanomaterials, such as coating with carbon [34], conducting polymers, or other

TMOs [35] has been employed to improve their surface stability and electronic conductivity. The surface coating can prevent direct contact between the TMOs and the electrolyte, reducing side reactions and improving the cycling stability. It can also enhance the electronic conductivity of the TMOs, facilitating electron transport and improving the rate capability. The surface chemistry of TMOs nanomaterials, such as the presence of defects, vacancies, and functional groups, can also influence their electrochemical performance. Surface defects and vacancies can provide additional Na<sup>+</sup> storage sites and enhance the Na<sup>+</sup> diffusion, but they may also lead to structural instability and capacity fading [36]. Functional groups, such as hydroxyl and carbonyl groups, can participate in the Na<sup>+</sup> storage process and contribute to the capacity, but they may also cause irreversible side reactions [37].

### Challenges and Future Perspectives

Despite the significant progress in the development of TMOs nanomaterials as electrodes for SIBs, several challenges still need to be addressed for their practical application. These challenges include:

- 1. Low electronic conductivity:** Many TMOs suffer from poor electronic conductivity, which limits their rate capability and energy density. Strategies such as nanostructuring, doping, and compositing with conductive materials need to be further explored to improve the electronic conductivity of TMOs electrodes.
- 2. Structural instability:** TMOs nanomaterials often undergo phase transitions and volume changes during cycling, leading to structural instability and capacity fading. Advanced characterization techniques, such as in situ X-ray diffraction and transmission electron microscopy, are needed to better understand the structural evolution of TMOs electrodes during cycling. Novel strategies, such as the design of hierarchical structures and the use of solid electrolytes, should be developed to enhance the structural stability of TMOs electrodes.
- 3. Side reactions with the electrolyte:** The high surface area of TMOs nanomaterials makes them prone to side reactions with the electrolyte, resulting in the formation of solid electrolyte interphase (SEI) layers and capacity fading. The development of stable and compatible electrolytes, as well as the surface modification of TMOs nanomaterials, is necessary to mitigate the side reactions and improve the cycling stability.
- 4. High cost and low scalability:** The synthesis of TMOs nanomaterials often involves complex and costly processes, hindering their large scale production and practical application. The development of simple, scalable and cost effective synthesis methods, such as hydrothermal synthesis and spray pyrolysis, is crucial for the commercialization of TMOs electrodes for SIBs.

To address these challenges and realize the practical application of TMOs nanomaterials in SIBs, future research should focus on:

- 1. Rational design of TMOs nanomaterials:** The crystal structure, particle size, morphology, and composition of

TMOs nanomaterials should be carefully designed and optimized to achieve high specific capacity, rate capability and cycling stability. Computational methods, such as density functional theory (DFT) calculations and machine learning, can be employed to guide the rational design of TMOs nanomaterials.

- 2. Advanced characterization techniques:** In situ and operando characterization techniques, such as X-ray diffraction, X-ray absorption spectroscopy, and transmission electron microscopy, should be employed to gain insights into the structural evolution, redox mechanisms, and failure mechanisms of TMOs electrodes during cycling. These techniques can provide valuable information for the optimization of TMOs nanomaterials and the development of high-performance SIBs.
- 3. Electrolyte optimization:** The development of stable and compatible electrolytes is crucial for the long term cycling stability of TMOs electrodes. Solid-state electrolytes, such as ceramic and polymer electrolytes, can be explored to mitigate the side reactions and improve the safety of SIBs. The use of additives, such as fluoroethylene carbonate (FEC) and vinylene carbonate (VC), can also help to stabilize the SEI layer and enhance the cycling performance.
- 4. Full-cell studies:** While most studies have focused on the half-cell performance of TMOs electrodes, more research is needed on the full cell performance of SIBs using TMOs electrodes. The development of high performance sodium-ion full cells requires the optimization of both the cathode and the anode materials, as well as the electrolyte and the cell configuration. The long-term cycling stability, energy density, and safety of TMOs based sodium-ion full cells should be evaluated under realistic operating conditions.
- 5. Techno-economic analysis:** The techno-economic analysis of TMOs based SIBs should be conducted to assess their commercial viability and identify the bottlenecks in their large-scale production. The cost of raw materials, synthesis processes, and battery manufacturing should be carefully evaluated and optimized to reduce the overall cost of SIBs. The environmental impact and recyclability of TMOs based SIBs should also be considered for their sustainable development.

### Conclusions

Transition Metal Oxides (TMOs) nanomaterials have shown great promise as electrodes for SIBs due to their high theoretical capacities, diverse redox chemistry, and structural stability. Nanostructuring of TMOs has been demonstrated to be an effective strategy to enhance their electrochemical performance, including specific capacity, rate capability, and cycling stability. The crystal structure, particle size, morphology, and surface properties of TMOs nanomaterials play crucial roles in their electrochemical performance, and understanding these structure-property relationships is key to the rational design and optimization of TMOs electrodes. Despite the significant progress,

several challenges still need to be addressed for the practical application of TMOs nanomaterials in Sodium-ion Batteries (SIBs), including low electronic conductivity, structural instability, side reactions with the electrolyte, and high cost and low scalability. Future research should focus on the rational design of TMOs nanomaterials, advanced characterization techniques, electrolyte optimization, full-cell studies, and techno-economic analysis to overcome these challenges and realize the commercialization of TMOs based SIBs. With continued research efforts and innovations, TMOs nanomaterials have the potential to become the next-generation electrode materials for high-performance and affordable SIBs, contributing to the development of sustainable and scalable energy storage solutions for the future.

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