

Research Proposal

Development of High-Performance Manganese Based Electrode For Lithium-ion Battery, using Sustainable Materials

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Abstract

The development of high-performance lithium-ion batteries (LIBs) relies heavily on electrode materials with high capacity, excellent cycling stability, and good rate capability. Manganese oxide-based electrodes, such as MnO_2 and LiMn_2O_4 , are attractive due to their low cost, environmental benignity, and high theoretical capacity. However, their practical application is hindered by poor electronic conductivity, structural degradation during cycling, and capacity fading. In this work, agro-derived carbon nanotubes (CNTag) were synthesized and investigated as conductive coating and reinforcing agents for MnO_2 and LiMn_2O_4 electrodes to overcome these limitations. Structural and morphological characterization using X-ray diffraction (XRD) and scanning electron microscopy (SEM) revealed that CNTag incorporation preserved the crystalline framework of the manganese oxides while forming a uniform, interconnected conductive network around the active particles. Energy-dispersive X-ray spectroscopy (EDX) confirmed the high carbon content and chemical purity of the CNTag. Cyclic voltammetry (CV) analysis demonstrated that CNTag coating enhanced redox peak currents and increased the electrochemically active surface area, indicating improved charge transfer kinetics and lithium-ion diffusion. Preliminary galvanostatic charge-discharge (GCD) measurements showed that CNTag-modified electrodes exhibited higher specific capacities, superior rate performance, and improved cycling stability compared to pristine MnO_2 and LiMn_2O_4 . These enhancements were attributed to the conductive framework and structural buffering effect provided by CNTag, which mitigated particle agglomeration, reduced polarization, and maintained electrode integrity during prolonged cycling. The findings highlight the potential of agro-derived CNTs as sustainable, low-cost conductive modifiers for improving the electrochemical performance of manganese oxide-based LIB electrodes.

1. Introduction

As the global population continues to grow, energy consumption is expected to rise dramatically in the near future. This underscores the importance of developing more efficient methods, and sustainable materials for energy generation and storage. Energy storage systems (ESS) store energy generated from other forms of energy resources, such as: solar, wind, and thermal energy. The charged energy storage system can then provide electricity as needed, at the desired level and quality as shown in Figure 1 [1-4]. Energy storage systems can potentially replace or supplement nearly every part of a

power system, including generation, transmission, and distribution [5, 6]. Currently, the world is lacking a safe and affordable large-scale energy infrastructure, and the prevalence of fossil fuels for energy generation means contributes to climate change and various health issues. Hence, it is critical that researchers focus on the development of more efficient materials and methods for energy generation and storage to meet the increasing demand for energy [7-9].

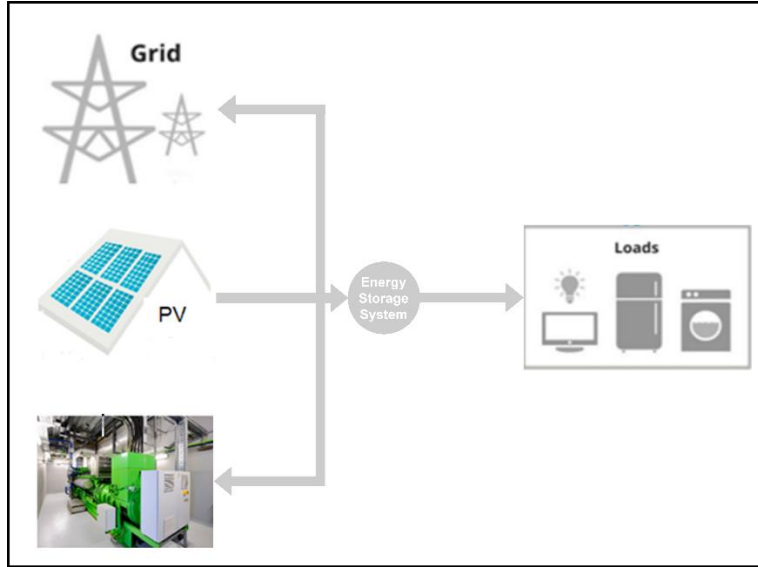


Figure 1: Schematic diagram of Energy Storage System: Generation – Storage – Consumption.

Among various electrochemical energy storage system, lithium-ion batteries (LIBs) have made a profound impact across various sectors, acting as the main power source for handheld electronic devices and playing a pivotal role in energy storage systems [10]. In terms of energy storage, LIBs provide high energy efficiency, extended cycle life, and comparatively high energy density, making them ideal for grid-level energy storage systems [11]. They can contribute to the stability of the grid system, balance power generation, and aid in the integration of renewable energy sources, such as: solar and wind power. LIBs can facilitate efficient energy management by storing surplus energy during periods of low demand and discharging it during peak hours, thereby reducing dependence on the grid and decreasing costs [12]. They also enable the integration of renewable energy resources, improving overall energy efficiency, and ensuring a consistent power supply. In addition, especially in developing nations,

Lithium-ion batteries (LIBs) operate by reversibly shuttling lithium ions between a graphite anode and a lithium-metal-oxide cathode. During discharge, ions move from the anode to the cathode via an electrolyte, while electrons flow externally, generating power and charging reverses this process [13, 14]. The chemistry of LIB's constituent parts is closely related to its performance. A range of cathode

materials, including layered LiFePO_4 , spinel LiMn_2O_4 , and olivine LiCoO_2 , provide trade-offs between thermal stability, cost, and energy density [14]. The most common anode material is graphite, although in order to increase capacity, substitutes, such as: silicon, tin oxides, or bimetallic oxides made from metal-organic frameworks (MOFs) are being investigated. Key evaluation metrics for designing and optimizing LIBs, include: specific capacity (mAh/g), energy density (Wh/kg), Coulombic efficiency (%), cycle life, rate capability, and thermal stability [15].

The advancements in LIB technology in recent years have led to the growth and adoption of electric vehicles (EVs). These advancements have been focused on improving the performance of their energy storage, safety, and sustainability. The future of lithium-ion batteries looks promising, with ongoing research and development, leading to even more efficient, durable, and sustainable battery technologies [16]. As the demand for renewable energy and sustainable storage solutions continues to rise, LIBs are playing an increasingly important role in powering a more sustainable future [17]. Nevertheless, recent studies indicate that lithium-ion batteries, commonly used in a variety of devices, pose sustainability challenges. For instance, lithium-ion batteries contain harmful metals like cobalt and nickel, which pollute water sources and ecosystems if they seep out. Additionally, the extraction and production of lithium, a limited resource, can ultimately lead to environmental issues. To mitigate these challenges, incorporation of readily available minerals, such as: manganese and agro-waste material into the development of LIBs looks promising and achievable for the sustainability of LIBs. This route can lead to the evolution of more sustainable lithium-ion batteries, vital for a future with lower carbon emissions [18, 19].

Transition metal oxides (TMOs) are widely studied as electrode materials, particularly for anodes in lithium-ion batteries, due to their high theoretical capacities, redox properties, and structural versatility. Unlike traditional intercalation materials like graphite, TMOs often work through conversion reactions, offering higher capacities. Notable TMOs researched for LIB electrodes include iron oxides (Fe_2O_3 , Fe_3O_4), cobalt oxide (Co_3O_4), nickel oxide (NiO), vanadium oxides (V_2O_5), and manganese oxides (MnO , Mn_3O_4 , Mn_2O_3 , MnO_2) [20-22].

Manganese-based electrode materials (MBE) are attracting interest for their potential application in LIBs due to their availability, affordability, and safety [23]. The materials have been used as cathode material in lithium-ion manganese oxide batteries (LMO), which operate through the same intercalation/de-intercalation mechanism as other commercialized cathode materials, such as LiCoO_2 [24]. In addition, MBE has been engaged as anode material, replacing traditional graphite. Electrodes based on manganese are cheap, non-toxic, and offer superior thermal stability [25]. **Table 1** presents

the main structural, physical, and electrochemical characteristics of MnO, MnO₂ and LiMn₂O₄ that are pertinent to its use in lithium-ion batteries.

Table 1. Electrochemical, physical and structural properties of MnO, MnO₂ and LiMn₂O₄ relevant to LIBs [20-22, 26, 27, 28].

Property	Description		
Chemical formula	MnO	MnO ₂	LiMn ₂ O ₄
Crystal Structure	Rock salt	α -MnO ₂ (Rutile-like structure) and β -MnO ₂ (Tetragonal structure).	Spinel crystal structure with a space group of Fd3m
Molar Mass	70.94 g/mol	86.94 g/mol	180.81 g/mol
Theoretical Current capacity	$\sim 755 \text{ mAh g}^{-1}$	1232 mAh/g	148 – 350 mAh/g
Lithiation Reaction	$\text{MnO} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Mn}^0 + \text{Li}_2\text{O}$	$\text{MnO}_2 + \text{Li}^+ + \text{e}^- \rightarrow \text{LiMnO}_4$	
Electronic Conductivity	Poor (necessitates conductive additives like carbon)	Low	Relatively low
Main Challenges	Large volume expansion ($\sim 200\%$), poor cycle stability, low-rate performance	Structural instability during cycling, capacity fading	Degradation/Mn dissolution, structural instability
Advantages	Abundant, low cost, environmentally benign, high theoretical capacity	Abundant, low cost, environmentally benign, high theoretical capacity	Abundant, low cost, environmentally benign, high operating voltage
Enhancement Strategies	Nanostructuring, carbon composites, hollow structures, doping/coating, hybridizing with other oxides	Nanostructuring, carbon composites, hollow structures, doping/coating, hybridizing with other oxides	Nanostructuring, carbon composites, hollow structures, doping/coating, hybridizing with other oxides

2. Statement of Problem

Manganese oxide-based Electrodes (MoBEs) are favoured over other Transition metal oxide-based Electrodes (ToBEs) in LIBs due to their diverse structures, abundant manganese content, and the potential for affordability and high capacity [29,30]. These electrode materials have the advantage of enhanced safety, but their cycle and calendar life is limited. Research focus is on developing and optimizing advanced materials with superior properties in LIBs technology, offering potential solutions to cathode-related challenges [31-33].

- An obstacle faced in lithium-ion batteries is the phase transition within manganese oxide-based electrodes which is linked to challenges like Jahn-Teller distortion and structural instability, leading to suboptimal electrochemical performance and limitations in practical application. Addressing this problem involves modifying the surface of MoBEs by altering the crystal structure, introducing foreign element through doping/coating and making morphological adjustments. These modifications enhance electrochemical performance and stability, making manganese oxide-based electrodes more suitable for use in lithium-ion batteries [34-35].
- Manganese dissolution within MoBEs in LIBs is a significant challenge, leading to capacity fading and diminished cycling performance. The release of manganese ions from the electrode material into the electrolyte during cycling results in the depletion of active material and the formation of Solid-Electrolyte Interphase (SEI) layers, ultimately impacting battery performance [36].

All these challenges lead to structural instability, thermal instability and poor electrochemical performances. The incorporation of carbon nanotubes derived from agricultural waste, as dopants/surface modifiers in/on the manganese oxide-based electrode represents a promising approach to overcome these challenges and advance energy storage technology sustainably and economically. This aligns with the increasing interest in utilizing agricultural waste for advanced material synthesis, as highlighted by Aldroubi et al. 2023 [37]. Hence, integrating carbon nanotubes from agricultural waste into the manganese oxide electrode has the potential to improve structural integrity and electrochemical performances of electrode (cathode and anode) materials LIBs.

3. Aim and Objectives

The aim of this project is to develop high energy density - Manganese oxide-based electrode with high thermal and cycling stabilities, and better environmental friendliness using sustainable materials. This will be achieved by the following objectives;

- Synthesizing carbon nanotubes (CNTag) from agro waste corn husk
- Characterization of CNTag
- Development of MnOx and LixMnOy on conducting substrates (Stainless steel and FTO glass by electrodeposition method
- Coating of CNTag at different proportions on MnOx and LixMnOy as electrode materials using doctor blade method
- Investigation of the structural and morphological characteristics of the electrode materials.
- Investigate the electrochemical properties (CV, GCD) of developed electrodes materials for LIBs.
- Investigation of optical parameters of developed electrode materials for LIBs

4. Significance of the project

The development of electrode materials using sustainable materials for use in lithium-ion battery is of significant importance in addressing the urgent need for sustainable and high-performing energy storage solutions. This aligns with the increasing focus on environmentally friendly and renewable materials in energy technologies and offers an opportunity to enhance the electrochemical properties of lithium-ion batteries, potentially leading to improved energy storage capacity and cycling stability. The research contributes to the progress of nanomaterial synthesis, particularly in relation to use of environmentally friendly non-catalytic method of synthesis for energy storage materials. By investigating the electrochemical properties of CNTag – coated manganese oxide-based electrode materials, the study offers valuable insights into the design and optimization of electrode materials for lithium-ion batteries.

Furthermore, the research is also significant in addressing challenges related to the dissolution of manganese ions and the formation of solid electrolyte interphase (SEI) films, which are critical factors influencing the stability and capacity retention of lithium-ion battery electrodes.

The potential impact of the research extends to the development of high-energy lithium-ion batteries, advancing sustainable energy storage technologies, improving electrode materials, and providing fundamental insights into the electrochemical behaviour of manganese oxide-based electrodes [38]. Environmental concerns associated with conventional LIBs, especially the use of materials like cobalt, have raised ethical mining issues and environmental degradation concerns. The extraction and processing of these materials can have adverse effects on the environment and human health. Therefore, by utilizing abundant and economically viable resources, this study can stabilize the supply chain, decrease overall manufacturing costs and reduce environmental challenges of lithium-ion batteries (LIBs). This, in turn, can expedite the global adoption of clean energy solutions. Additionally, the creation of LIBs featuring electrodes made from sustainable materials aligns with regulatory trends endorsing eco-friendly technologies. This ensures that energy storage technologies comply with eco-friendly standards and regulatory frameworks, contributing to the broader objective of establishing a more sustainable and responsible energy storage infrastructure [39,40].

5. The expected outcome

- Development of promising electrodes for batteries and supercapacitors
- Establishment of nanocomposites parameters effects on their energy storage capability
- Fabrication of a prototype of the electrode.
- A complete package battery and or supercapacitor energy storage electrode which shall be tested on high power consuming devices, shall be manufactured.
- Local market collaboration for sustainable energy research.
- International collaboration between Nigeria and other countries.

6. Budget.

The budget for the research proposal, is as follows.

- a. Project Duration: 12 months

Total Budget Requested: #12,600,000

- b. Personnel

- Principal Investigator – #600,000
- Co Investigators/Research Assistants (full-time, 6 months) – #2,000,000
- Laboratory Technicians (part-time, 6 months) – #400,000

- Subtotal: #3,000,000
 - c. Equipment & Supplies
 - Access to advanced characterization and electrochemical testing facilities, #2,500,000
 - Procurement of laboratory materials and chemicals - #1,500,000
 - Collaboration with external experts and institutions. #1,000,000
 - Fabrication of prototype - #1,500,000
 - Subtotal: #6,500,000
 - d. Travel
 - Conference attendance (registration, transportation, accommodation) – #1,500,000
 - Subtotal: #1,500,000
 - e. Other Direct Costs
 - Data processing/analysis /software licenses and publication support - #800,000
 - Printing, communication, and report preparation – #200,000
 - Subtotal: 1,000,000
 - f. Indirect Costs (Overhead)
 - (5% of direct costs: $12,000,000 \times 0.050$) – #600,000
- Total Budget Requested
- #12,600,000

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