Synthesis and Characterization of MnO_2 by Hydrothermal Method for Supercapacitor

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Abstract

In this study, manganese dioxide (MnO_2) nanowires were successfully synthesized via a hydrothermal method and evaluated for their electrochemical performance as pseudocapacitor materials. The synthesis was carried out under varying temperature conditions (80 °C, 100 °C, and 120 °C), and the resulting structures were characterized using X-ray diffraction (XRD). XRD analysis confirmed a body-centred tetragonal phase with sharp diffraction peaks, indicating high crystallinity and phase purity. Electrochemical characterization, including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS), demonstrated excellent capacitive behaviour. The optimized MnO_2 nanowire electrode exhibited a high specific capacitance of 1066 F/g at low scan rates, with good reversibility and minimal internal resistance. GCD curves showed symmetrical charge-discharge profiles, while EIS indicated low charge-transfer resistance and fast ion diffusion.

Keywords: MnO_2 nanowires, hydrothermal synthesis, supercapacitor, specific capacitance, electrochemical performance

1. Introduction

The growing demand for efficient and sustainable energy storage systems has intensified interest in supercapacitors, also known as electrochemical capacitors, due to their superior power density, rapid charge-discharge capabilities, and long cycle life [1]. These characteristics make them particularly attractive for next-generation applications, including electric vehicles, portable electronics, hybrid energy systems, and aerospace technologies [2]. Compared to conventional batteries, supercapacitors bridge the gap between batteries and dielectric capacitors by offering faster dynamics and better durability, although their energy density remains relatively lower [3]. Supercapacitors are typically classified into two major categories based on their charge storage mechanisms: (i) electric double-layer capacitors (EDLCs), which rely on electrostatic charge accumulation at the electrode-electrolyte interface, and (ii) pseudocapacitors, where a charge is stored through fast and reversible faradaic redox reactions [4]. While EDLCs commonly employ carbon-based materials, pseudocapacitive electrodes are often composed of transition metal oxides or conducting polymers, which provide higher specific capacitance due to their redox activity [5].

Among various pseudocapacitive materials, manganese dioxide (MnO_2) has emerged as a particularly promising candidate due to its natural abundance, environmental benignity, low cost, and high theoretical specific capacitance (~1370 F/g [6, 7]. MnO_2 also exhibits multiple polymorphic forms (α-, β-, γ-, δ-, λ-, and ε-), with β-MnO_2 being thermodynamically the most stable. These polymorphs differ in their tunnel structures, which significantly affect ion diffusion and electrochemical performance [8, 9]. Furthermore, MnO_2-based materials possess excellent electrochemical reversibility and high oxidation states, enabling multiple electron-transfer processes during redox reactions [10].

Despite these advantages, bulk MnO_2 suffers from low electrical conductivity (~10^{-5} to 10^{-6} S/cm) and limited active site accessibility, leading to poor rate capability and low practical capacitance [11]. To overcome these challenges, nanostructured MnO_2 has been explored as a strategy to enhance surface area, improve ion transport kinetics, and optimize electron pathways [12]. Synthesis methods such as sol-gel processing, hydrothermal and solvothermal techniques, chemical precipitation, electrochemical deposition, and microwave-assisted methods have

been widely employed to control the morphology and crystallinity of MnO_2 nanostructures [13]. Among these, hydrothermal synthesis has gained particular attention due to its cost-effectiveness, environmental friendliness, and ability to produce one-dimensional architectures such as nanorods and nanowires that are favorable for fast charge transport [14]. In addition to its use in supercapacitors, MnO_2 has also demonstrated potential in other technological applications, including lithium-ion batteries, zinc-ion batteries, fuel cell catalysts, biosensors, and environmental remediation [15]. However, achieving an optimal balance between conductivity, structural stability, and electrochemical performance remains a major research challenge. The electrochemical behavior of MnO_2 is strongly influenced by its morphology, phase composition, and particle size, highlighting the need for precise control over synthesis parameters [16].

In this study, we report the synthesis of [insert synthesis strategy: e.g., hydrothermally derived α-MnO_2 nanorods] and evaluate their electrochemical performance as electrode materials for pseudocapacitor applications. The relationship between morphology, structure, and capacitive behavior is systematically investigated to provide insights into the design of high-performance MnO_2-based energy storage devices.

2. Experimental

2.1 Material

Potassium Permagnate ($KMnO_4$) and hydrochloric acid (HCL) were obtained from molychem chemical reagent co. All solvents and chemicals were used without further purification.

2.2 Synthesis of MnO_2 via hydrothermal method

In a typical synthesis, 5.53 g of potassium permanganate ($KMnO_4$) and 1.27 mL of hydrochloric acid (HCl) were each dissolved separately in 70 mL of distilled water under continuous magnetic stirring to ensure homogeneity. The resulting solutions were combined and stirred thoroughly to form a uniform precursor mixture. The homogeneous solution was then transferred into a Teflon-lined stainless-steel autoclave. To prevent contamination from the top interface of the autoclave, the upper edge of the Teflon liner was sealed using polytetrafluoroethylene (PTFE) tape. The sealed autoclave was subjected to a stepwise hydrothermal treatment at 80 °C, 100 °C, and 120 °C, each for 1 h, sequentially. After the thermal treatment, the autoclave was allowed to cool naturally to room temperature. Following the reaction, the solid product (precipitated MnO_2) was carefully collected, thoroughly washed several times with deionized water to remove any residual ions or unreacted precursors, and then dried under vacuum at 40 °C for 12 h.

3. Result and discussion

3.1 XRD

The XRD patterns for the prepared MnO_2 are shown in **Fig. 1** above The XRD of MnO_2 shows the sharp & polycrystalline sample. The broad peaks are not observed. The peaks in the XRD pattern are indexed to cubic body-centred tetragonal MnO_2 structure with lattice constants of a= 1.20nm, b= 1.204nm, and C= 1.532nm. The Full Width Half Maximum (FWHM) of the sample is 0.94192°. Crystalline size using Scherrer's equation ($D = 0.9\lambda/ \beta\cos\theta$) of sample about 4.6673°. This indicates that the synthesized material is purely an individual phase without any additional second phase.

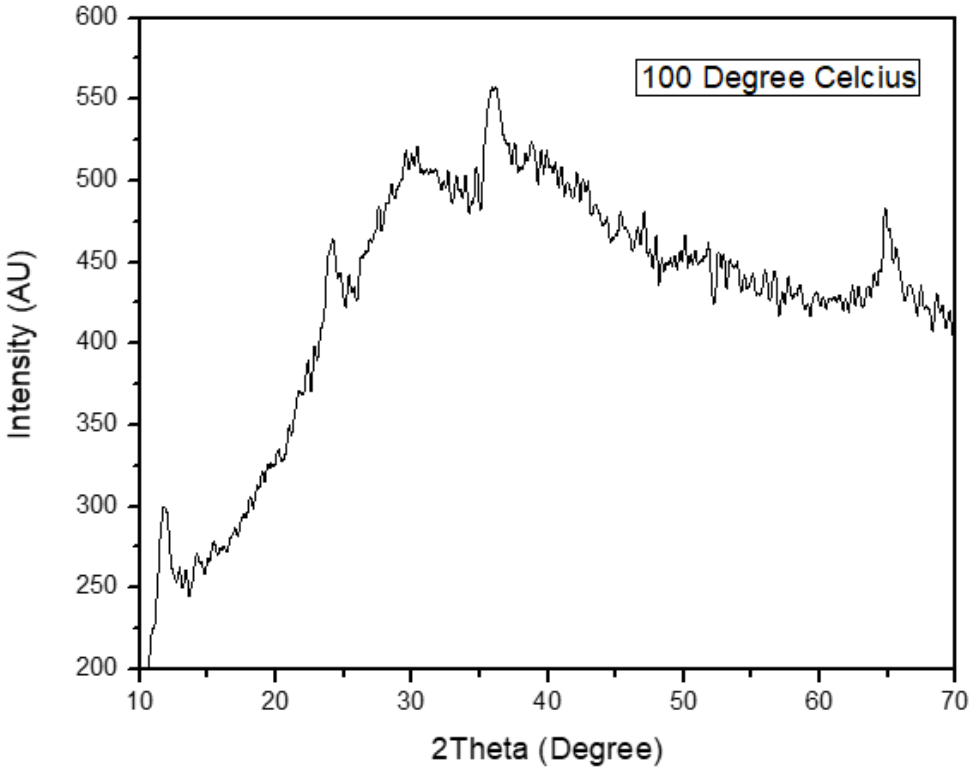

Fig. 1: X-ray diffraction pattern of nanostructured MnO_2 synthesized hydrothermally at 100° C for 1 h.

3.2 Cyclic voltammetry

The cyclic voltammetry (CV) analysis of the synthesized MnO_2 electrode is shown in **Fig. 2**. Among the samples, the MnO_2 prepared with a hydrothermal duration of 10 h exhibited the most favorable electrochemical performance, which can be attributed to its higher surface area and enhanced K^+ ion content within the structure. These characteristics contribute significantly to improved ion transport and charge storage capability. The CV curves display a quasi-rectangular shape, which is indicative of ideal capacitive behavior and excellent electrochemical reversibility. This shape reflects the electric double-layer capacitance and suggests rapid charge propagation within the MnO_2 nanowire network. However, with increasing scan rates, the CV curves begin to deviate from the ideal rectangular shape. This deviation is attributed to a reduced effective interaction between electrolyte ions and the active electrode surface at higher scan rates. As a result, the specific capacitance decreases with increasing scan rate due to limited ion diffusion and slower faradaic reaction kinetics.

The electrode composed of MnO_2 nanowires showed superior electrochemical response, suggesting that the nanowire morphology facilitates efficient ion diffusion and electron transport. This morphology enhances the utilization of the active material and supports improved capacitive performance. The specific capacitance of the MnO_2 nanowire electrode was found to be dependent on the scan rate, with higher values observed at lower scan rates. At the lowest scan rate investigated (0.01 V s^{-1}, assumed), the specific capacitance reached 1066 F g^{-1}, highlighting the excellent energy storage capability of the material.

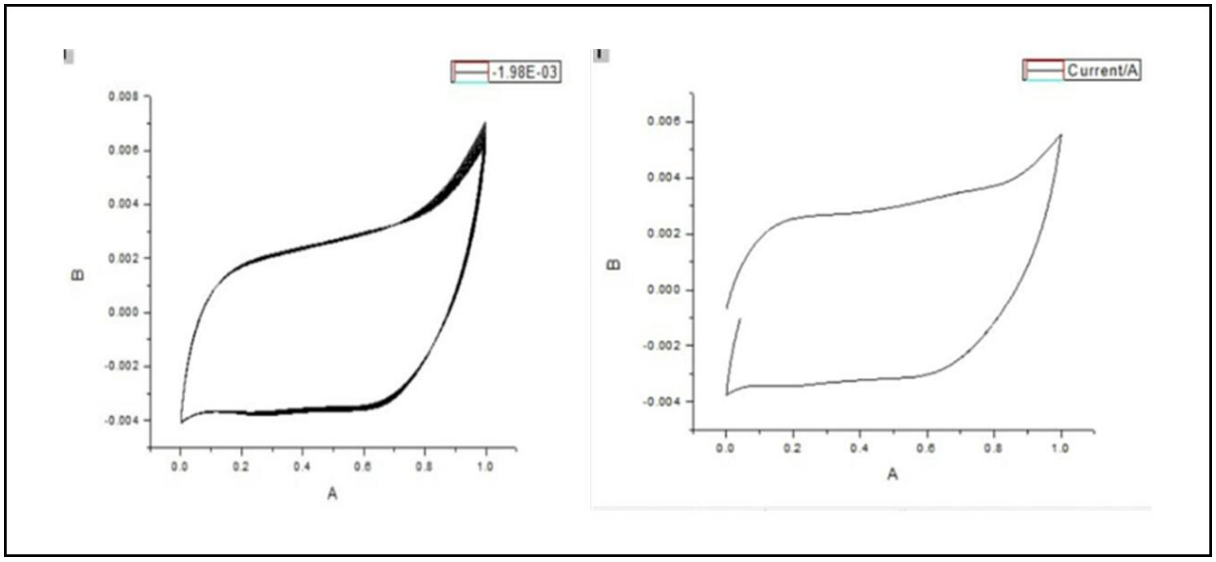

Fig. 2: Cyclic voltammetric at different scan rates form 0.01-0.09mVs^{-1}(100°c for 1hr).

3.3 Charge-discharge

The galvanostatic charge-discharge (GCD) profile of the MnO_2 nanowire electrode is presented in **Fig. 3 (a).** The GCD curves exhibit a linear and nearly symmetrical shape during both the charge and discharge processes, indicating excellent capacitive behavior and electrochemical reversibility of the electrode material. The minimal iR drop observed further supports the presence of low internal resistance and efficient charge transport within the MnO_2 nanowire structure. The applied constant current during both the charging and discharging phases was 0.001 A, and the charge/discharge times were identical at 999 seconds, suggesting good symmetry and stability of the electrode during the electrochemical process.

The charge storage mechanism is primarily governed by the intercalation and de-intercalation of cations (Na^+ and K^+) into the MnO_2 matrix. This mechanism is characteristic of pseudocapacitive behavior and contributes to the efficient storage of charge. The specific areal capacitance of the MnO_2 nanowire electrode, calculated from the discharge slope of the GCD curve, was found to be approximately 0.02724 F/cm², demonstrating its potential applicability in supercapacitor devices.

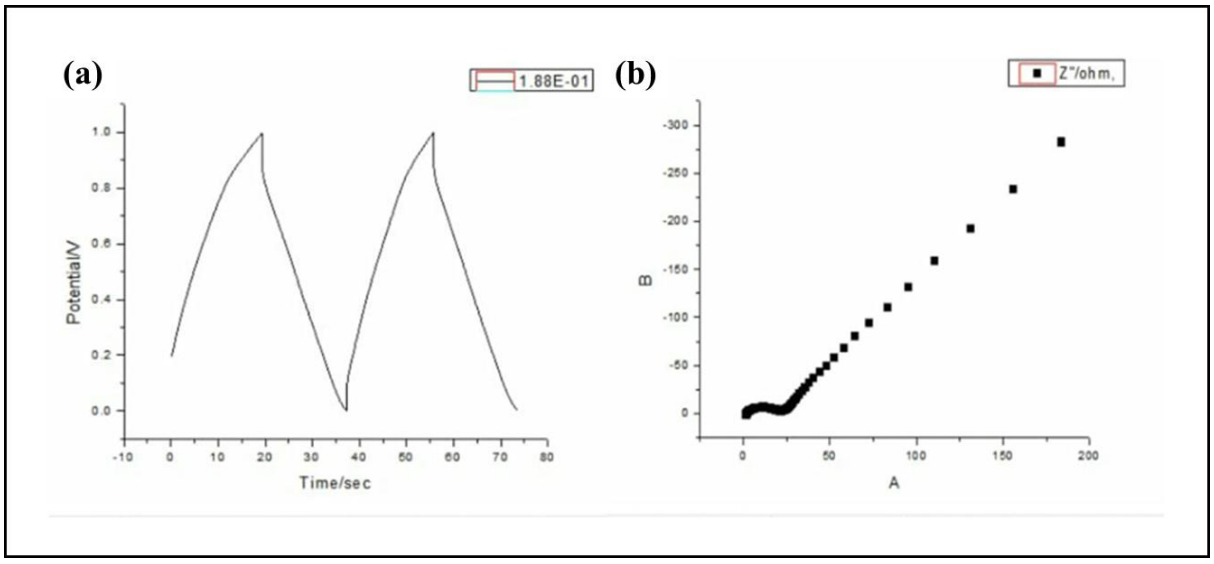

Fig. 3: (a) the galvanostatic charge-discharge curve of MnO_2 nanowires and (b) Nyquist plot for MnO_2 nanowire electrode

3.4 EIS

The electrochemical impedance spectroscopy (EIS) analysis of the MnO_2 nanowire electrode is presented in **Fig. 3 (b)**. The Nyquist plot displays a small semicircle in the high-frequency region, corresponding to a low charge transfer resistance (R_ct), followed by a straight, sloped line in the low-frequency region, which is indicative of ideal capacitive behavior. The steepness of the line in the low-frequency domain confirms efficient ion diffusion and rapid charge transport at the electrode-electrolyte interface. The low time constant, derived from the EIS data, further suggests that the MnO_2 nanowire electrode facilitates fast charge-discharge kinetics, making it a promising material for high-power supercapacitor applications. These results affirm the excellent electrochemical performance, including low internal resistance and high reversibility, of the MnO_2 nanowires as an efficient pseudocapacitive electrode material.

4. Conclusion

MnO_2 nanowires were successfully synthesized via a hydrothermal method, and their pseudocapacitive properties were studied for the first time. XRD analysis confirmed a cubic body-centered crystal structure, indicated by equal lattice parameters (a = b = c). The MnO_2 nanostructures were synthesized under varying temperatures (80 °C, 100 °C, and 120 °C) and durations, with the optimal electrochemical performance observed under specific conditions. CV analysis at a scan rate of 0.1 V/s demonstrated enhanced specific capacitance and excellent power capability, attributed to the rapid current-voltage response and good electrochemical reversibility of the MnO_2 nanowire electrode. Galvanostatic charge–discharge measurements showed symmetrical profiles with equal cathodic and anodic currents (0.001 A) and times (999 s), indicating stable capacitive behavior. EIS results further confirmed low charge transfer resistance and favorable electrochemical characteristics.

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