
Research article

Sustainable production of MnO₂/activated carbon hybrid electrodes from pomegranate peels for efficient energy storage

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Abstract: To meet the enhanced demand for renewable energy sources, high-performance and sustainable energy storage devices are needed. In this study, KOH activation and the controlled redox deposition of MnO₂ at different mass loadings (10, 25, and 40 wt.%) were used to synthesize biomass-based activated carbon (AC) and hybrid AC/MnO₂ electrodes from pomegranate peel biomass. The porous structure of the uniformly distributed MnO₂ nanoparticles was confirmed by detailed structural analysis using field emission scanning electron microscopy (FESEM), Brunauer-Emmett-Teller (BET) analysis, and X-ray diffraction (XRD) techniques. Electrochemical analysis was performed using a three-electrode system with 1M Na₂SO₄ as the electrolyte. The results showed that the AC/MnO₂-25 electrode possessed the highest electrochemical response with a specific capacitance of 394 Fg⁻¹ at 1 Ag⁻¹, along with good rate capability and low internal resistance. Even after 5000 cycles, the capacitance retention was 94.5%. The results confirmed a good electrochemical response with a Coulombic efficiency of approximately 98%. The enhanced electrochemical response was due to the combination of high-surface-area activated carbon with MnO₂ nanoparticles, which contributes to electric double-layer capacitance and pseudocapacitance. The results confirmed the suitability of pomegranate peel biomass as a sustainable source of biomass to produce high-performance electrode materials for the fabrication of high-performance supercapacitor devices.

Keywords: activated carbon; pomegranate peel; MnO₂ hybrid electrodes; supercapacitors; sustainable energy storage

1. Introduction

Owing to the rapid integration of renewable energy sources and the pressing need to mitigate the effects of climate change, supercapacitor technologies have advanced significantly in response to the growing global demand for efficient and sustainable energy storage systems. Despite their continued widespread use, traditional batteries are limited by their low energy density, short cycle life, slow charge-discharge kinetics, disposal, and toxicity issues [1]. Supercapacitors have emerged as a highly promising solution owing to their high power density, rapid charge-discharge capability, extended operational lifespan, and improved safety profile [2]. These limitations have accelerated the search for alternative energy storage devices with higher energy densities. They are essential components for many applications, such as electric and hybrid cars, grid stabilization, portable electronics, and smart energy systems, owing to their capacity to fill the gap between traditional capacitors and batteries.

The type and structure of the electrode materials significantly affect the supercapacitor performance. Owing to its low cost, wide availability, environmental friendliness, and adjustable surface and pore structures, biomass-derived activated carbon has attracted considerable attention as a potential alternative [3]. Biomass-based carbon materials offer a sustainable and profitable substitute for synthetic carbon sources, which frequently involve high-energy procedures and nonrenewable raw materials [4]. Pomegranate peels and other agricultural wastes have been identified as outstanding precursors for the production of activated carbon because of their high carbon content, natural porosity, and surface functional groups, which promote improved ion accessibility and charge-storage behavior [5].

Pomegranate peels have two benefits when used to produce activated carbon: They reduce agricultural waste, which promotes environmental sustainability, and they enable the creation of high-performance, reasonably priced, carbon-based electrodes [6]. Additionally, the abundance of oxygen-containing functional groups in pomegranate-derived carbons enhances charge transfer during electrochemical processes by improving wettability and interaction with electrolytes [7]. Notwithstanding these inherent benefits, activated carbon derived from biomass frequently exhibits low specific capacitance and energy density when used as a standalone electrode material, which limits its use in high-performance supercapacitors [8]. Several investigations have shown that biomass-derived carbons offer potential advantages as electrode materials based on their sustainability, inexpensiveness, porosity, and surface chemistry. Furthermore, the presence of functional groups that contain oxygen and nitrogen in their chemical structures increases the electrolyte wettability, thus enhancing the charge-transfer process. These properties make biomass-derived carbons highly attractive candidates as supercapacitors [9,10]. The hierarchical pores, functionalized surfaces, and renewable nature of biomass-based activated carbons prepared from various types of agricultural waste products have proved very promising for energy storage applications by virtue of their structural, chemical, and electrical properties [4,5]. Research has been conducted to use agricultural waste such as coconut shells, rice husks, sugarcane bagasse, walnut shells, and fruits as carbon precursors for supercapacitors with significant electrochemical performance and minimized environmental impacts due to the disposal of agricultural waste [5,8]. However, the electrochemical behavior of biomass-based carbons relies greatly on their aforementioned physical properties [7,8].

To overcome these constraints, researchers have focused on hybrid electrode systems that combine transition metal oxides, particularly manganese dioxide (MnO_2), with activated carbon derived from biomass [11]. MnO_2 (manganese dioxide) is well known for its high theoretical

capacitance (~ 1370 F/g), cost-effectiveness, environmental safety, and natural abundance [12]. The electric double-layer capacitance (EDLC) of activated carbon and the pseudocapacitance of MnO_2 work together to improve the overall specific capacitance, energy density, and rate capability of hybrid electrodes [13,14]. The porous and high-surface-area structure of activated carbon makes it a perfect scaffold for uniform MnO_2 deposition, enabling effective electron and ion transport pathways that are necessary for quick and stable charge storage [15]. Although carbon/ MnO_2 electrode structures show a good level of performance, the electrochemical properties of such materials depend greatly on the amount and distribution of MnO_2 incorporated into the carbon matrix. Several researchers have confirmed that a low MnO_2 content contributes little to pseudocapacitance, while high amounts can lead to pore blocking, lower accessible surface area, less penetration of the electrolyte, and higher charge-transfer resistance [16–18]. Hence, finding the optimum point for the combination of EDLC and pseudocapacitance is difficult [18].

The development of synthesis and activation methods has accelerated the development of these hybrid systems. Techniques such as hydrothermal synthesis, controlled pyrolysis, and thermal and chemical activation (using KOH or ZnCl_2) have been extensively investigated to customize the pore size distribution, surface area, and conductivity of activated carbon [16,17]. Researchers have demonstrated notable improvements in the specific capacitance, energy density, and cycle stability by adjusting these parameters [18]. Furthermore, advanced electrochemical characterization methods, such as galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV), have elucidated the resistance properties, ion diffusion behavior, and charge storage mechanisms [19,20].

Despite rapid advancements in this field, several research gaps restrict the full utilization of activated carbon/ MnO_2 hybrid electrodes derived from biomass. Most researchers have focused on assessing the initial electrochemical performance in controlled laboratory environments and improving the synthesis conditions. Nevertheless, there is insufficient research on their long-term stability, cycling durability, and performance in actual operating environments [21]. Designing materials with consistent and repeatable performance is difficult because of the incomplete understanding of the basic mechanisms controlling interfacial charge transfer and storage at the carbon– MnO_2 interface [22]. The scalability and reproducibility of synthetic processes present another significant obstacle. Despite producing encouraging results, laboratory-scale techniques face practical implementation challenges in industrial applications owing to their high energy consumption, hazardous chemical use, and non-scalable processes.

The novelty of this research can be traced to the use of pomegranate peel waste as a source of sustainable carbon precursors along with in situ redox deposition of MnO_2 through a process that does not adversely impact the environment. This contrasts with other researchers who have concentrated mainly on synthesis or electrochemical analysis, and not both. In this investigation, however, we examined the effect of the addition of MnO_2 at different concentrations on the performance of biomass-based hybrid electrodes in terms of structural, morphological, and electrochemical properties.

By thoroughly examining the impact of synthesis parameters, including activation temperature, chemical activation agents, and MnO_2 loading levels, on the microstructure, pore distribution, surface chemistry, and electrochemical response, this study fills a knowledge gap regarding the synergistic interactions between activated carbon and MnO_2 . To provide a more thorough understanding of the suitability of hybrid electrodes for real-world applications, we assessed the rate capability, cycling stability, and real-world performance metrics of the electrodes. Furthermore, we aimed to fill an

important research gap regarding the optimization of the loading of MnO_2 in the biomass hybrid electrode system. This was achieved by analyzing various loading amounts and how they affect performance parameters such as capacitance and resistance.

To provide a foundation for logical design and performance optimization, we aimed to strengthen our basic knowledge of the mechanisms governing hybrid electrode systems derived from biomass. By converting inexpensive agricultural waste into valuable materials for high-performance energy storage devices, this study practically supports global sustainability goals. Our results of this study aim to bridge the gap between laboratory-scale research and industrial implementation by encouraging scalable and ecologically friendly fabrication processes, thereby paving the way for next-generation sustainable supercapacitor technologies.

In summary, we aimed to improve the specific capacitance, energy density, power density, and cycling durability by synthesizing and refining hybrid electrodes made of MnO_2 and activated carbon derived from pomegranate peel. We addressed the limitations in the literature and suggest novel approaches for enhancing the electrochemical performance of biomass-derived materials by methodically analyzing the structure–performance relationship. Pomegranate-based AC/ MnO_2 hybrids could be effective, cost-friendly, and eco-friendly electrodes for advanced supercapacitors by connecting theoretical ideas with real-world applications.

2. Methodology and materials

2.1. Materials

After collection from nearby agricultural waste sources, pomegranate peels were carefully cleaned with distilled water to remove any surface contaminants and oven-dried for 24 h at 100 °C. To ensure consistent particle size, the dried peels were ground into a fine powder using a mechanical grinder. The following chemicals were purchased from Sigma-Aldrich and were of analytical grade: conductive carbon black, potassium hydroxide (KOH , $\geq 85\%$), potassium permanganate (KMnO_4 , $\geq 99\%$), polyvinylidene fluoride (PVDF), N-methyl-2-pyrrolidone (NMP), and hydrochloric acid (HCl , 37%). No further purification was performed. Nickel foam was used as the current collector during electrode fabrication, and deionized (DI) water was used for all cleaning and synthesis processes.

2.2. Activated carbon (AC) synthesis

Pomegranate peels were carbonized and chemically activated to produce AC. The prepared pomegranate peel powder was subjected to carbonization inside a tubular reactor in a flow of pure nitrogen gas (100 mL min^{-1}). The carbonization temperature was gradually increased from ambient temperature up to 400 °C by applying heating rates of 5 °C min^{-1} followed by stabilization at this temperature for 2 h to achieve the formation of carbonaceous char. The low temperature used in the carbonization process was chosen to retain a considerable number of oxygen-containing functionalities on the surface since they have been reported to increase the efficiency of further chemical activation and MnO_2 nucleation/deposition during redox synthesis [23]. Deionized water was added in small quantities to aid the mixing process; this produced a charcoal sample that was mixed with KOH in a ratio of 1:3 (char: KOH), giving a homogenous slurry. The drying process involved heating to 80 °C

for 12 h, followed by activation at 800 °C for 1 h with a nitrogen flow rate of 100 mL min⁻¹ and a heating rate of 5 °C min⁻¹. The high-temperature KOH activation step enabled the formation of pores, and thus, the development of a high specific surface area of the activated carbon [24]. It is worth mentioning that the large specific surface area achieved in this investigation was mostly obtained through the KOH activation process carried out at 800 °C and not through the initial carbonization carried out at 400 °C. The function of the initial carbonization process is mostly to create a stable carbon structure while retaining functional groups with reactive oxygen atoms [23,24].

2.3. AC/MnO₂ hybrid composite synthesis

In this regard, three distinct theoretical loadings of MnO₂ (10%, 25%, and 40% by weight) derived from stoichiometric KMnO₄ addition were chosen to study the effect of MnO₂ loading in the structure and electrochemistry of composites. The following formula was used to determine the theoretical MnO₂ mass for each loading level:

$$m(\text{MnO}_2) = [w/(1 - w)] \times m(\text{AC}) \quad (1)$$

The stoichiometry of the redox reaction ($3\text{C} + 2\text{KMnO}_4 + \text{H}_2\text{O} \rightarrow 2\text{MnO}_2 + 2\text{KOH} + \text{CO}_2$) was used to calculate the necessary KMnO₄ mass as follows:

$$m(\text{KMnO}_4) = m(\text{MnO}_2) \times (M(\text{KMnO}_4) / M(\text{MnO}_2)) \approx m(\text{MnO}_2) \times 1.818 \quad (2)$$

where $M(\text{MnO}_2) = 86.94$ g/mol, $M(\text{KMnO}_4) = 158.04$ g/mol, and w is the desired weight fraction of MnO₂.

Table 1. The calculated masses of MnO₂ and KMnO₄ required for every 100 mg of AC.

Sample	w (MnO ₂ wt%)	m (MnO ₂) (mg)	m (KMnO ₄) (mg)
AC/MnO ₂ -10	0.10	11.1	20.2
AC/MnO ₂ -25	0.25	33.3	60.6
AC/MnO ₂ -40	0.40	66.7	121.2

To achieve uniform dispersion, 100 mg of AC was dissolved in 100 mL of DI water and sonicated for 30 min during the synthesis process. To enable the in situ redox deposition of MnO₂ onto the AC surface, a calculated volume of KMnO₄ solution (0.05 M) was added dropwise while continuously stirring at room temperature. This process was continued for six hours. After filtering and repeated washing with DI water until the pH was neutral, the resulting composite was dried at 80 °C. AC/MnO₂-10, AC/MnO₂-25, and AC/MnO₂-40 were assigned to the samples.

2.4. Fabrication of electrodes

To prepare a homogeneous slurry, 80 wt% active material (either AC or AC/MnO₂), 10 wt% conductive carbon black, and 10 wt% PVDF were mixed in NMP. The slurry was uniformly coated onto nickel foam (1 cm²) using the doctor's blade technique. To enhance the mechanical integrity and electrical contact, the electrodes were vacuum-dried at 80 °C for 12 h and subsequently compressed at 10 MPa. The typical active material mass loading for each electrode was 2–3 mg/cm².

2.5. Characterization of materials

- Morphological and Structural Analysis: The surface morphology and nanostructure were investigated using FESEM.
- Surface Area and Porosity: The BET method was used to measure nitrogen adsorption–desorption isotherms to ascertain the surface area and pore size distribution.
- Crystallographic Analysis using XRD.

2.6. Electrochemistry measurements

Electrochemical testing was conducted using a three-electrode setup with a 1 M Na₂SO₄ aqueous electrolyte. Ag/AgCl was used as the reference electrode, a platinum wire as the counter electrode, and the prepared AC or AC/MnO₂ electrodes as the working electrode.

- To assess the capacitive behavior, CV was used at scan rates ranging from 5 to 100 mV/s, and GCD was performed to evaluate the rate capability at current densities ranging from 0.5 to 10 A/g.
- Electrochemical Impedance Spectroscopy (EIS): Measured with a perturbation amplitude of 5 mV over a frequency range of 0.01 Hz to 100 kHz.

Using the formula below, the specific capacitance (C, F/g) was computed from the discharge profile of the GCD curves as follows:

$$C = (I \times \Delta t) / (m \times \Delta V) \quad (3)$$

where m is the mass of the active material (g), ΔV is the potential window (V), Δt is the discharge time (s), and I is the discharge current (A).

The synthesis and electrochemical performance assessments of the AC and AC/MnO₂ hybrid electrodes for high-performance supercapacitor applications are guaranteed to be accurate, repeatable, and reliable owing to this standardized methodology.

3. Results

3.1. Microstructural analysis and surface morphology

The FESEM results for pristine AC (Figure 1a) show a highly porous structure with interconnected pores. The macropore channels ranged from 300 to 310 nm. BET measurements (Table 2) show a surface area of $1850 \pm 25 \text{ m}^2 \text{ g}^{-1}$, a pore volume of $1.05 \pm 0.02 \text{ cm}^3 \text{ g}^{-1}$, and an average pore diameter of $2.8 \pm 0.1 \text{ nm}$. Incorporation of 10 wt.% MnO₂ shows a reduced macropore size of 180–200 nm. BET measurements show a reduced surface area of $1620 \pm 20 \text{ m}^2 \text{ g}^{-1}$, and the pore diameter is slightly increased to $3.0 \pm 0.1 \text{ nm}$. Adding 25 wt.% MnO₂ makes the surface structure thicker and reduces the size of the larger pores to 150–170 nm, as seen in the FESEM images (Figure 1c). BET measurements show a reduced surface area of $1380 \pm 18 \text{ m}^2 \text{ g}^{-1}$, a pore volume of $0.92 \pm 0.02 \text{ cm}^3 \text{ g}^{-1}$, and an increased pore diameter of $3.1 \pm 0.2 \text{ nm}$. The EDS mapping is shown in Figure 2. Incorporation of 40 wt.% MnO₂ shows reduced macropore sizes of 130 nm, as confirmed by FESEM images (Figure 1d). BET measurements show a reduced surface area of $1100 \pm 15 \text{ m}^2 \text{ g}^{-1}$, a reduced pore volume of $0.81 \pm 0.02 \text{ cm}^3 \text{ g}^{-1}$, and an increased pore diameter of $3.3 \pm 0.2 \text{ nm}$. Figures 3(a) and (b) illustrate the N₂ adsorption-desorption isotherms and pore size distribution curves of the pristine AC and

AC/MnO₂ composites, respectively. All the samples possess the typical Type IV N₂ adsorption pattern accompanied by a hysteresis loop, demonstrating the mesoporous nature of the composites. The adsorption capacity of nitrogen monotonically drops with an increase in the content of MnO₂, demonstrating the filling of the porous structure of AC by MnO₂. This conclusion correlates with the data on the reduction in the BET surface area and pore volume provided in Table 2. Additionally, the analysis of the pore size distribution curves demonstrates a tendency toward an increase in the average pore diameter due to MnO₂ modification. Despite the decrease in surface area and volume, the mesoporosity of the samples persist, making them suitable for electrolyte ion mobility. These results imply that the deposition of MnO₂ results in the filling of some pores and changes their sizes; however, the porous network is not fully destroyed.

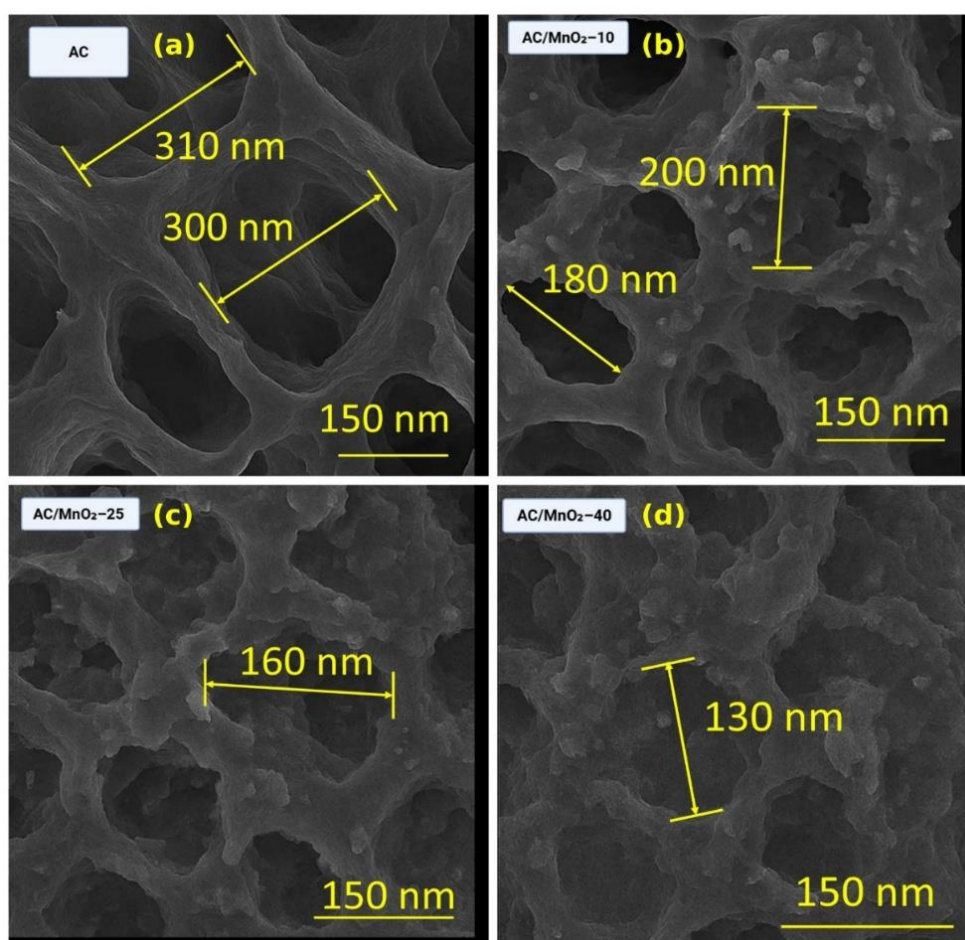


Figure 1. FESEM images of AC and AC/MnO₂ composites with different amounts of MnO₂, indicating that the pore size decreased from approximately 310 nm (AC) to approximately 130 nm (AC/MnO₂-40).

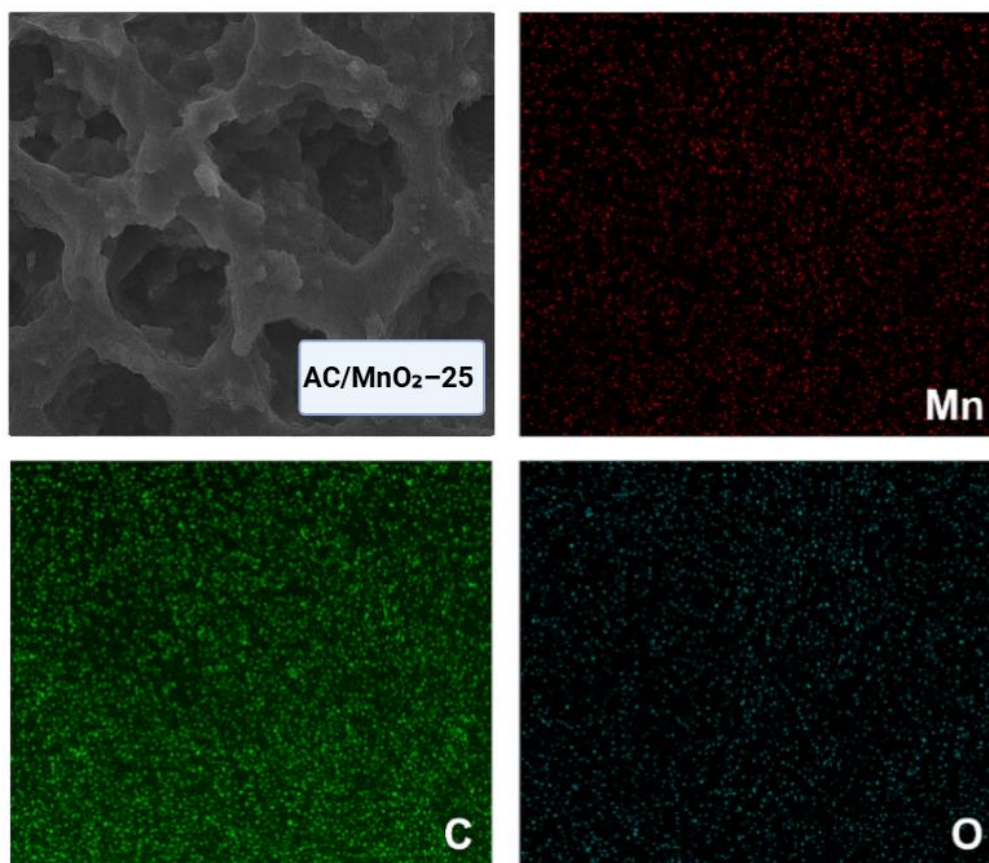


Figure 2. FESEM image and corresponding EDS elemental mapping of the AC/MnO₂-25 composite showing a uniform distribution of Mn, C, and O.

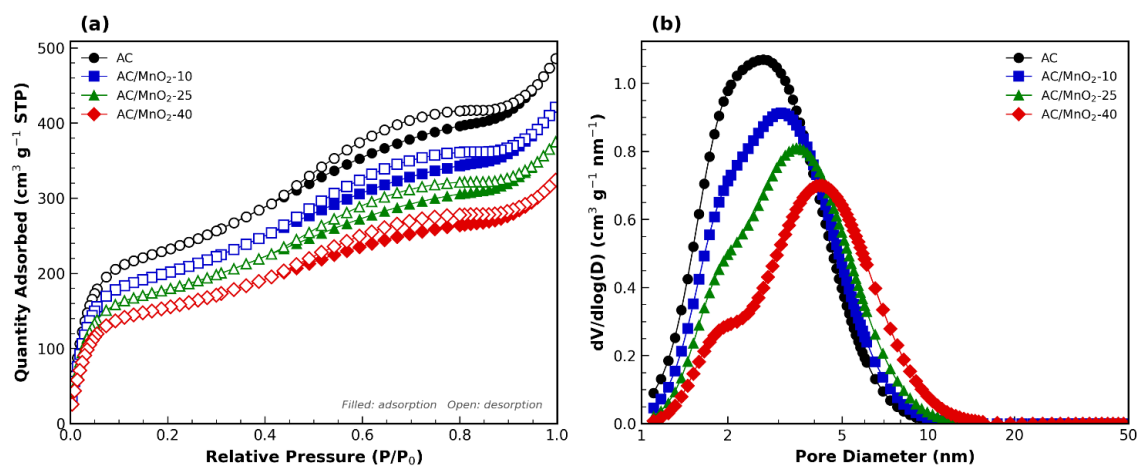


Figure 3. (a) Adsorption-desorption isotherms and (b) pore-size distribution plots for pristine AC electrode and AC/MnO₂ composite electrode. The filled symbols indicate the adsorption part, while the open symbols indicate the desorption part.

Table 2. BET surface area and porosity parameters.

Sample	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Mesopore Diameter (nm, BET)	Macropore Size (nm, FESEM)
AC	1850 ± 25	1.05 ± 0.02	2.8 ± 0.1	300–310
AC/MnO ₂ -10	1620 ± 20	0.98 ± 0.03	3.0 ± 0.1	180–200
AC/MnO ₂ -25	1380 ± 18	0.92 ± 0.02	3.1 ± 0.2	~160
AC/MnO ₂ -40	1100 ± 15	0.81 ± 0.02	3.3 ± 0.2	~130

3.2. Properties of crystals and structures (XRD)

The XRD patterns of the pristine AC and AC/MnO₂ electrode samples with various MnO₂ amounts are presented in Figure 4. It can be seen that there is a wide band of diffraction at about $2\theta = 24^\circ$, which corresponds to (002) plane of amorphous carbon. In the case of AC/MnO₂, diffraction bands at approximately 37° , 42° , 56° , and 66° correspond to the reflection planes of the γ -MnO₂ phase (orthorhombic ramsdellite-type, PDF No. 00-014-0644), indicating that MnO₂ is deposited on the carbon substrate.

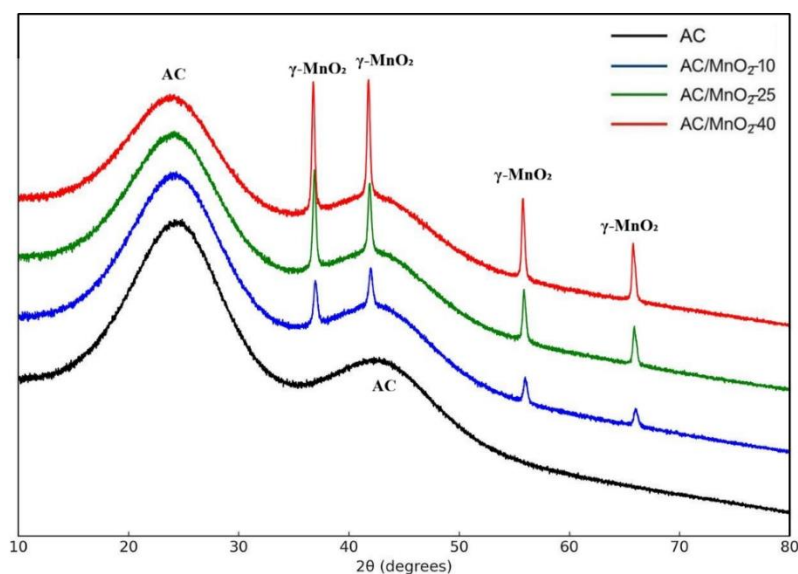


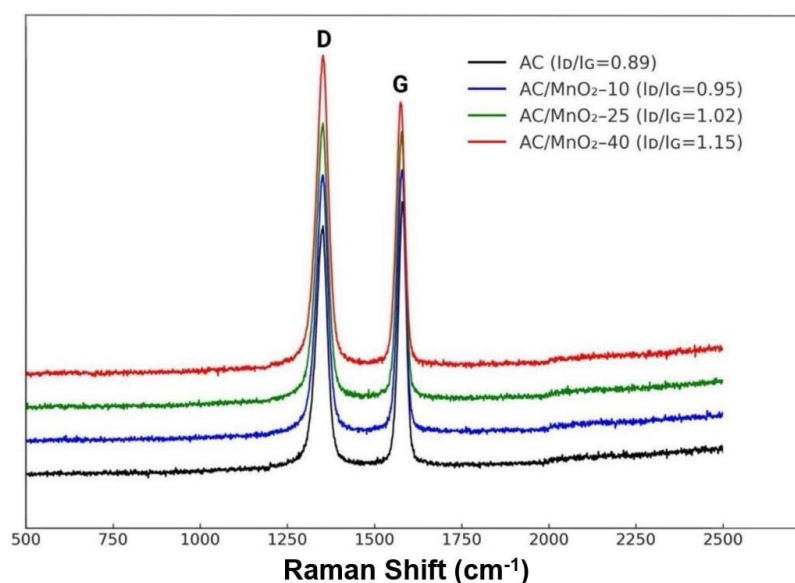
Figure 4. XRD patterns of AC and AC/MnO₂ composites with varying MnO₂ content, showing characteristic peaks of amorphous carbon (AC) and crystalline γ -MnO₂.

3.3. Raman spectroscopy

Raman spectroscopy was used to examine the structure of the pure AC and AC/MnO₂ hybrid electrodes. In the Raman spectra (Figure 5), two peaks are observed at 1351 cm^{-1} (D band) and 1581 cm^{-1} (G band). The intensity ratio (I_D/I_G), as presented in Table 3, was used to study the level of disorder in the carbon structure. A moderate intensity ratio (I_D/I_G) is observed in the Raman spectrum of the pristine AC sample. With an increase in the MnO₂ loading level, the value of the (I_D/I_G) ratio increases. The highest value of the (I_D/I_G) ratio is observed in AC/MnO₂-40.

Table 3. Raman analysis (I_D/I_G ratio) of pristine AC and the AC/MnO₂ composites.

Sample	D band (cm ⁻¹)	G band (cm ⁻¹)	I_D/I_G ratio
AC	1351	1581	0.89
AC/MnO ₂ -10	1352	1579	0.96
AC/MnO ₂ -25	1352	1578	1.02
AC/MnO ₂ -40	1353	1576	1.15

**Figure 5.** Displays the Raman spectra of AC and the AC/MnO₂ composites, showing the common D and G bands of carbon with varying amounts of MnO₂.

3.4. Performance of electrochemistry

The electrochemical performance of the electrodes was investigated through cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy. Figure 6 shows the cyclic voltammetry curves for the AC and AC/MnO₂ composites. Information about charge storage capabilities can be gathered from the results of the CV curves. It can be seen that the improved redox performance of the AC/MnO₂ composites can be supported by the specific capacitance values acquired through GCD, which are listed on Table 4. Redox peaks are observed in the cyclic voltammetry curves of the AC/MnO₂ composites, whereas a rectangular curve is observed for the AC electrode. The GCD curves of the AC and AC/MnO₂ composites are shown in Figure 7. The AC electrode presents a triangular curve, whereas the AC/MnO₂ composites exhibit nonlinear curves. The specific capacitance values obtained from the GCD curves are listed in Table 4. As shown in Table 4, the specific capacitance increases from 242 F g⁻¹ to 325 F g⁻¹, 394 F g⁻¹, and 365 F g⁻¹ for the AC/MnO₂-10, AC/MnO₂-25, and AC/MnO₂-40 composites, respectively, at a current density of 1 A g⁻¹.

Figure 8 shows the electrochemical impedance spectroscopy curves of the AC and AC/MnO₂ composites. The electrochemical impedance spectroscopy response of the studied electrodes can be described using the equivalent circuit presented in the inset of Figure 8, including R_s (solution resistance), R_{ct} (charge-transfer resistance), CPE (constant phase element), and Z_w (Warburg diffusion

element). R_s is an indicator of the electrolyte and contact resistance. R_{ct} indicates the charge transfer reaction occurring at the electrode-electrolyte interface. The CPE considers the non-ideality of the capacitive response of the porous electrode surface. The impedance behavior differs between the AC and AC/MnO₂ composites. The electrochemical impedance spectroscopy parameters are listed in Table 5: The R_s and R_{ct} values for the AC, AC/MnO₂-10, AC/MnO₂-25, and AC/MnO₂-40 composites are 0.88 Ω , 1.54 Ω ; 0.72 Ω , 1.11 Ω ; 0.57 Ω , 0.90 Ω ; and 0.62 Ω , 1.23 Ω , respectively. The cycling performances of the AC and AC/MnO₂ composites are listed in Table 6. As can be seen from Table 6, the capacitance retentions after 5000 cycles are 85%, 88%, 94.5%, and 86% for AC, AC/MnO₂-10, AC/MnO₂-25, and AC/MnO₂, respectively.

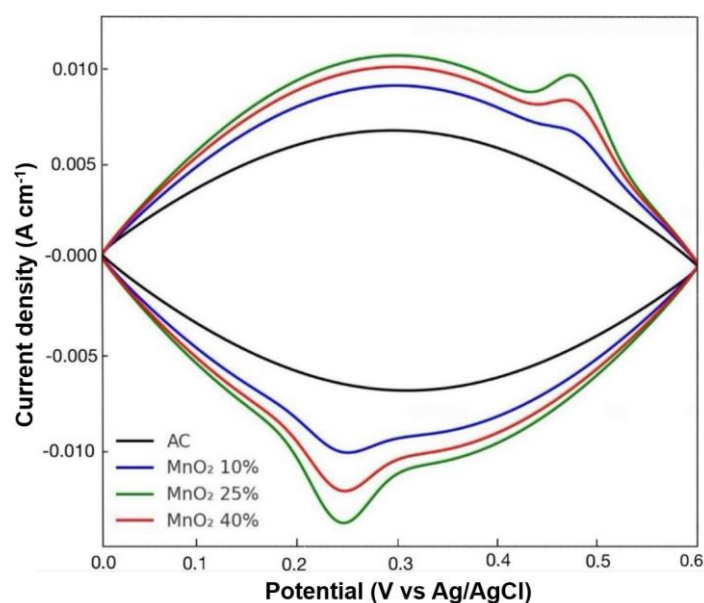


Figure 6. CV profile.

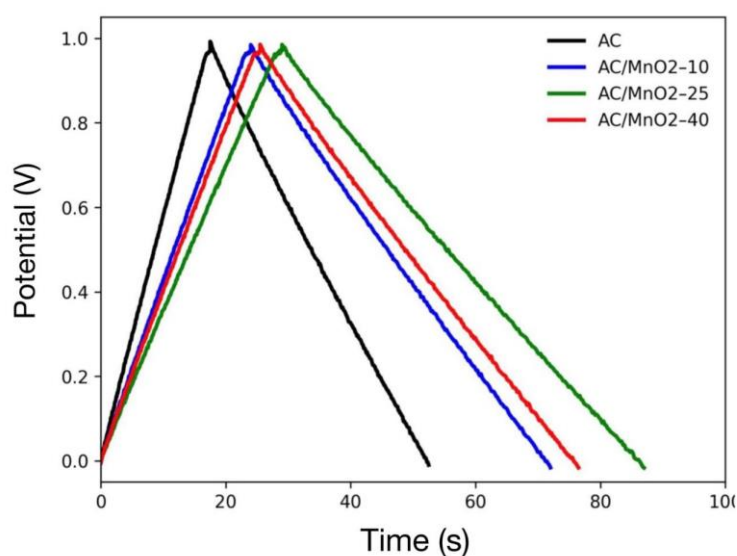


Figure 7. Galvanostatic charge-discharge curves of AC and AC/MnO₂ electrodes at 1 A g⁻¹.

Table 4. Specific capacitance values from GCD analysis.

Sample	0.5 A/g (F/g)	1.0 A/g (F/g)	2.0 A/g (F/g)	5.0 A/g (F/g)	10 A/g (F/g)
AC	272	242	212	180	156
AC/MnO ₂ -10	366	325	293	255	218
AC/MnO ₂ -25	429	394	354	304	261
AC/MnO ₂ -40	405	365	322	273	229

Table 5. EIS Parameters for Pristine AC and AC/MnO₂ composite.

Sample	Rs (Ω)	Rct (Ω)	Slope at Low Frequency
AC	0.88	1.54	1.85
AC/MnO ₂ -10	0.72	1.11	2.10
AC/MnO ₂ -25	0.57	0.90	2.35
AC/MnO ₂ -40	0.62	1.23	2.00

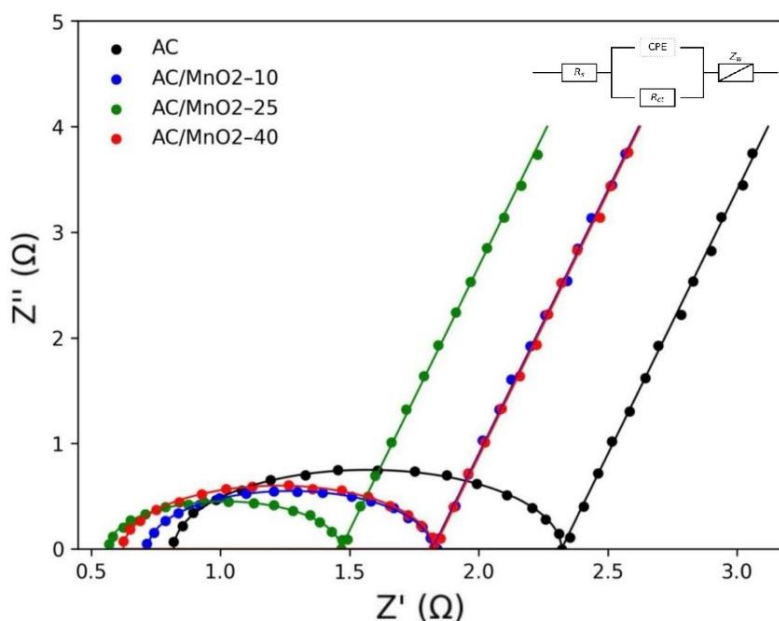


Figure 8. Nyquist plots for the AC and AC/MnO₂ electrode systems indicate the values of Rs and Rct. Insert: Equivalent circuit model depicting the solution resistance (Rs), charge transfer resistance (Rct), constant phase element (CPE), and diffusion Warburg impedance (Zw).

Table 6. Cycling stability performance.

Sample	Cycles	Capacitance retention (%)	Coulombic efficiency (%)
AC	5000	85 $\pm$ 0.6	96.0 $\pm$ 0.4
AC/MnO ₂ -10	5000	88 $\pm$ 0.5	97.2 $\pm$ 0.3
AC/MnO ₂ -25	5000	94.5 $\pm$ 0.2	98.0 $\pm$ 0.3
AC/MnO ₂ -40	5000	86.0 $\pm$ 0.5	96.8 $\pm$ 0.4

4. Discussion

4.1. Microstructural analysis and surface morphology

The microstructural properties of the synthesized materials also significantly influence their electrochemical properties. FESEM and BET studies have confirmed that pristine AC exhibits a highly porous structure with a large surface area, which can favorably accommodate ions and form an electric double layer [12–14]. The microstructure of the AC changes with MnO₂ loading. At a low loading (10 wt.%), a highly porous structure with MnO₂ particles on the pore walls can be observed. Figure 2 confirms the uniform distribution of Mn, C, and O on the surface of the AC via EDS mapping. This uniform distribution of active materials on the surface of AC can significantly improve its electrochemical properties [3,18]. At moderate loading (25 wt.%), a well-balanced structure can be achieved. Figures 4 and 5 show that a uniform layer of MnO₂ covers the AC. In this case, EDS confirms a uniform distribution of all elements on the surface of the AC without any signs of agglomeration. This structure can accommodate ions favorably and provide numerous active sites for electrochemical reactions. This phenomenon has been widely reported to improve the electrochemical properties of composite materials consisting of AC and metal oxides [4,22]. However, excessive amounts of MnO₂ in the AC (40 wt.%) result in a highly disordered structure. Figures 4 and 5 show that excessive amounts of MnO₂ result in pore blockage and agglomeration. In this case, although EDS confirms the presence of MnO₂ on AC, their distribution is less uniform owing to agglomeration effects. This disordered structure can negatively impact ion movement and the utilization of active sites on the electrode surface [6,18]. Thus, it can be concluded that a well-balanced structure can favorably impact the electrochemical properties of composite materials consisting of AC and metal oxides. From the FESEM images, it can be deduced that MnO₂ deposition occurs via the deposition of finely dispersed nanosized MnO₂ particles onto the activated carbon surface. From the EDS elemental mapping of AC/MnO₂-25, it can be seen that there is an even distribution of elements in AC/MnO₂-25, which is conducive to the effective transfer of charge and better access by electrolyte molecules. In addition, the presence of γ -MnO₂ diffraction peaks in the XRD spectra confirms the formation of crystalline MnO₂ in the composite material. Finally, it can be concluded that MnO₂ addition leads to an increase in the Raman ID/IG ratio, indicating the creation of new defects and good interfacial interaction between MnO₂ and the carbon matrix. However, based on the characterization results obtained, the exact shape of MnO₂ (i.e., nanospheres, nanorods, or nanosheets) and the type of chemical bonds formed between MnO₂ and the carbon matrix remain unknown.

4.2. Structural and crystallographic properties (XRD)

The XRD results provide helpful knowledge regarding the structural changes in the AC and AC/MnO₂ composites with different MnO₂ loadings. The broad peak observed at $2\theta \approx 24^\circ$ corresponds to the (002) plane of amorphous carbon. This indicates the amorphous nature of the carbon matrix. Such amorphous materials have been proven to offer a high density of active sites, thus enabling efficient charge storage in electric double-layer capacitors [12,13]. In addition, with the incorporation of MnO₂, other peaks appear, which correspond to the crystalline phases of γ -MnO₂. With an increase in MnO₂ loading, the intensity of the peaks also increase, indicating the successful growth and crystallization of MnO₂ in the carbon matrix. With moderate amounts of MnO₂ (25 wt.%), the XRD

pattern shows a stable structure that includes carbon and MnO_2 phases. This indicates the presence of a carbon framework with sufficient MnO_2 loading to enable additional electrochemical activity. This configuration enhances the synergistic effect between the electric double-layer capacitance and pseudocapacitance [6,11].

In the presence of a high MnO_2 loading (40 wt.%), the XRD peaks corresponding to MnO_2 become more prominent, while the peak corresponding to carbon is suppressed. This indicates the presence of excess MnO_2 , which disrupts the structural configuration and suppresses the role of the carbon matrix. Such effects have been observed in carbon-based metal oxide composites, where excessive metal oxide loading disrupts the structural configuration and leads to reduced device efficiency [4,22]. Thus, the XRD results confirm the formation of a hybrid structure consisting of amorphous carbon and crystalline MnO_2 , with an intermediate MnO_2 loading of 25 wt.% being the most favorable configuration.

4.3. Raman spectroscopy discussion

Further insight can be gained on the level of structural disorder and defect density within the AC and AC/ MnO_2 composite materials via Raman spectroscopy. The D and G peaks at 1350 and 1580 cm^{-1} , respectively, indicate the coexistence of disordered and graphitic structures within the composite. The increase in I_D/I_G ratio with increasing MnO_2 indicates an increase in structural defects within the composite. The formation of defects within the composite can be linked to the interaction between the metal oxide and carbon matrices. The deposition of MnO_2 on AC disrupts the sp^2 network of carbon and creates more active sites within the composite. At low MnO_2 loading (10 wt.%), a moderate increase in the I_D/I_G ratio is observed. This indicates a low level of disorder within the composite structure. At intermediate MnO_2 loading (25 wt.%), a higher increase in the I_D/I_G ratio is observed. This indicates an optimal level of disorder within the composite structure.

The disorder within the composite structure enables ions to access more active sites within the AC while maintaining conductivity within the composite structure. At a higher MnO_2 loading (40 wt.%), a further increase in the I_D/I_G ratio is observed. This indicates excessive disorder within the composite structure. This excessive disorder may disrupt the conductivity within the composite structure and reduce the efficiency of electron transport. The Raman results are consistent with the XRD and BET results and further confirm that an intermediate level of MnO_2 loading provides an optimal level of disorder within the AC structure and hence improves the electrochemical performance. This can be attributed to the enhanced electrochemical performance of the AC/ MnO_2 -25 composite materials. This enhanced performance can be attributed to an optimized level of disorder within the AC structure.

In addition to the D and G bands related to activated carbon, the Raman spectra were also analyzed for the vibration bands specific to Mn-O bonds that can be expected in MnO_2 compounds. The spectra does not show any Mn-O bands. This is most probably caused by the small MnO_2 content, superposition of the carbon bands, and strong contribution of the carbon phase to the total Raman spectrum. As observed in the case of carbon-based MnO_2 compounds, carbon contributes too much to the spectrum, and hence, Mn-O bands cannot be detected.

4.4. Performance of electrochemistry

4.4.1. Cyclic voltammetry (CV)

The cyclic voltammetry curves help us understand how well the AC and AC/MnO₂ composite materials can store charge. The cyclic voltammogram of pristine AC demonstrates a rectangular and symmetric curve, which indicates electric double-layer capacitance characteristics [12,13]. When MnO₂ is added to AC, a slightly distorted rectangular curve with moderate redox peaks can be observed, indicating capacitive behavior with a degree of pseudocapacitance resulting from MnO₂ [6,22]. Redox peaks are observed in the anodic and cathodic sweeps. The current density of AC and AC/MnO₂ composite materials also increase compared to that of pristine AC, indicating an enhanced charge storage ability. Among all the composite materials studied, AC/MnO₂-25 demonstrates a higher current density than AC/MnO₂-40 and AC/MnO₂-10. The cyclic voltammogram curve has a balanced shape, indicating that the electrochemical response is reversible and stable. The results show that incorporating MnO₂ into AC changes the charge storage behavior from electric double-layer capacitance to a mixed electric double-layer capacitance and pseudocapacitance behavior.

4.4.2. Galvanostatic charge–discharge (GCD)

GCD curves can provide direct information about the charge storage properties of electrodes and their capacitive behavior. The GCD curve of pristine AC shows a linear and almost symmetrical curve with a sharp triangle shape, which is characteristic of ideal EDLC behavior with little or no contribution from Faradaic reactions [12,13]. On the other hand, the GCD curves of the AC/MnO₂ composites show slight deviations from the linear curve with a sharp triangular shape, which is characteristic of the pseudocapacitive behavior of MnO₂-based electrodes due to the reversible redox reaction of MnO₂ [6,22]. The charge/discharge curves of the AC/MnO₂ composites are almost symmetrical, indicating good reversibility.

The SC values of the different electrodes calculated from the GCD curves are listed in Table 4. At a current density of 1 A g⁻¹, the SC increases from 242 F g⁻¹ to 325 F g⁻¹, 394 F g⁻¹, and 365 F g⁻¹ for the AC/MnO₂-10, AC/MnO₂-25, and AC/MnO₂-40 composite electrodes, respectively. These results indicate enhanced capacitance behavior with the incorporation of MnO₂ into the AC matrix, with the highest value observed with the AC/MnO₂-25 composite. Although the AC/MnO₂-40 composite shows enhanced capacitance behavior compared to pristine AC, the value is slightly lower than that observed with the AC/MnO₂-25 composite. This is evident from the longer discharge time observed for the 25 wt.% composite. From the GCD results, the incorporation of MnO₂ into the AC matrix enhances the charge storage behavior with the contribution of the pseudocapacitive effect while maintaining good reversibility, with the AC/MnO₂-25 composite showing the most favorable behavior compared to the other composite electrodes.

4.4.3. Electrochemical impedance spectroscopy (EIS)

EIS analysis provides information about the charge transfer characteristics of the electrodes. In the Nyquist plots (Figure 8), a semicircle in the high-frequency region followed by a straight line in the low-frequency region is observed. This is typical of the EIS plots of the electrodes. In the EIS

plots, the intercept of the semicircle on the real axis in the high-frequency region gives the solution resistance (R_s), whereas the diameter of the semicircle gives the charge-transfer resistance (R_{ct}). Table 5 lists the obtained EIS parameters.

As indicated in Table 5, the pristine AC electrode shows a solution resistance of $0.88\ \Omega$ and a high R_{ct} value. However, the resistance of the solution (R_s) and the charge transfer resistance (R_{ct}) of the AC/MnO₂ electrodes decrease when MnO₂ is added. For the AC/MnO₂-10 electrode, the R_s value is $0.72\ \Omega$, whereas the R_{ct} value is $1.11\ \Omega$. For the AC/MnO₂-25 electrode, the R_s value is $0.57\ \Omega$, whereas the R_{ct} value is $0.90\ \Omega$. From Table 5, it is also observed that the AC/MnO₂-25 electrode exhibits the lowest R_{ct} value among the AC/MnO₂ electrodes. For the AC/MnO₂-40 electrode, the value of the solution resistance (R_s) decreases, whereas the value of R_{ct} increases. In the AC/MnO₂-40 electrode, the value of the solution resistance (R_s) is $0.62\ \Omega$, whereas the value of R_{ct} is $1.23\ \Omega$. In the EIS plots of the AC/MnO₂ electrodes, the slope of the straight line in the low-frequency region also varies.

4.4.4. Stability when cycling

The cycling stability of the electrodes was tested over 5000 cycles, and the results are shown in Table 6. The cycling stability of the pristine AC electrode indicates 85% capacitance retention. The AC/MnO₂ composites exhibit improved cycling stability compared to pristine AC. The capacitance retention values increase to 88% for AC/MnO₂-10, and a maximum value of 94.5% is obtained for AC/MnO₂-25. The CE values for all the composites remain high, with values greater than 96%. The maximum value, 98.0%, is obtained for AC/MnO₂-25.

The cycling stability of the AC/MnO₂-40 composite retains 86% capacitance, which is slightly lower than that obtained for the 25 wt.% composite. The cycling stability of the composites show better capacitance retention and CE values, with the highest value found in AC/MnO₂-25. The stable cycling performance of the composites indicates that their structural integrity is maintained, and the reversibility of the charge storage process is possible.

4.5. Discussion and comparative analysis

A connection can be drawn between the properties of the obtained compounds and their electrochemical activities. As shown in Table 2, one can observe that the specific surface area gradually decreases from $1850\ \text{m}^2/\text{g}$ for AC to 1620, 1380, and $1100\ \text{m}^2/\text{g}$ for the AC/MnO₂-10, AC/MnO₂-25, and AC/MnO₂-40 samples, respectively. A similar tendency is also observed for the pore volume (1.05 , 0.91 , 0.81 , and $0.70\ \text{cm}^3/\text{g}$ for pristine AC, AC/MnO₂-10, AC/MnO₂-25, and AC/MnO₂-40 samples, respectively). This decrease can be explained by the gradual pore occupancy by the MnO₂ particles. However, despite the observed decrease, the specific capacitance increases from $242\ \text{F/g}$ for pristine AC to $325\ \text{F/g}$ and then reaches its maximum value of $394\ \text{F/g}$ for AC/MnO₂-25, after which it decreases again to $365\ \text{F/g}$ for the AC/MnO₂-40 sample. Therefore, it can be concluded that the electrochemical performance depends on the accessible surface area and pseudocapacitive contribution of MnO₂.

This trend can be confirmed by Raman measurements. Indeed, the ratio of defects, I_D/I_G , increase from 0.89 in the case of pristine AC to 0.96 , 1.02 , and 1.15 for the AC/MnO₂-10, AC/MnO₂-25, and AC/MnO₂-40 samples, respectively. This indicates that the number of active sites increase during this

process. In the AC/MnO₂-25 sample, the optimum defect density ($I_D/I_G = 1.02$) is achieved, which promotes charge accumulation while preserving the electron conductivity. Nevertheless, in the AC/MnO₂-40 sample ($I_D/I_G = 1.15$), the presence of too many defects likely leads to decreased conductivity and low electrochemical activity.

Impedance measurements revealed the same trend. Thus, for example, for the pristine AC sample, the charge-transfer resistance amounts to 1.54 Ω , whereas for the AC/MnO₂-10 and AC/MnO₂-25 samples, it is equal to 1.11 Ω and 0.90 Ω , respectively. However, the same value, $R_{ct} = 1.23 \Omega$, is observed for AC/MnO₂-40, which is likely due to partial blocking of the channels of ion movement. As a result, the highest capacitance retention (94.5%) and Coulombic efficiency (98%) are recorded for AC/MnO₂-25.

For a low MnO₂ content (10 wt.%), the AC backbone possesses an impressive surface area and porous structure that enables easy accessibility; however, the deposited amount of MnO₂ is not enough to make any considerable pseudocapacitive contribution. As a result, while there is an improvement in the electrochemical characteristics of AC when compared to unmodified AC, the boost in specific capacitance is quite minimal because the mechanism of storing the electrical charge is dominated by the electric double-layer effect. At 25 wt.% MnO₂, there is sufficient availability of the redox sites and ions can freely move through the pores.

The results obtained from the combined analysis of the structural, morphological, and electrochemical properties of the AC/MnO₂ composites show the influence of the incorporation of MnO₂ particles on the performance of the AC-based electrodes. The evidence of the transition from purely electric double-layer capacitance of pristine AC electrodes to a hybrid capacitance of AC/MnO₂ composites, including a pseudocapacitive component, is confirmed by all electrochemical techniques: CV, GCD, and EIS.

The AC/MnO₂-25 composite exhibits the highest performance because of the balance of its structural and electrochemical properties. The preserved porosity seen in the FESEM images helps the ions move easily, which is supported by the BET analysis results. The presence of defect sites, confirmed by Raman spectroscopy, as well as the presence of crystalline MnO₂ particles, confirmed by XRD analysis, result in the highest specific capacitance (394 Fg⁻¹ at 1 A g⁻¹) and lowest charge-transfer resistance (0.90 Ω).

In contrast, the AC/MnO₂-40 composite exhibits decreased performance despite the higher content of the active material. Such a trend is associated with pore blockage, reduced surface area, and disorder in the structure of the AC/MnO₂ composites, all of which negatively influence the efficiency of ion transport and charge transfer during electrochemical processes. Such effects of metal oxide particles on the performance of carbon-metal oxide composites are commonly reported in the literature [4,22]. In comparison with reported results on the capacitance of carbon-based electrodes derived from biomass precursors, it is evident that the capacitance values obtained in this study are competitive or higher than those reported previously, especially considering the relatively low content of MnO₂ particles in the AC/MnO₂ composites.

To analyze the performance of the AC/MnO₂ electrode fabricated in this study, the results are compared with those from the literature on biomass-based carbonaceous supercapacitor electrodes in Table 7. It is observed that the performance of the AC/MnO₂ electrode is either comparable to or better than that of most other studies entailing a straightforward method for fabrication with a sustainable precursor material.

Table 7. Electrochemical performance of the pomegranate peel-derived AC/MnO₂ electrode compared to other biomass-based carbon or carbon/MnO₂ supercapacitor electrodes reported in the literature.

Biomass precursor/Electrode material	Activation/Synthesis method	SSA (m ² g ⁻¹)	Electrolyte	Specific capacitance; rate capability; cycling stability	Ref.
Orange peel AC	KOH activation	—	Aqueous	460 F g ⁻¹ ; 98% after 10000 cycles	[25]
Orange peel AC/MnO ₂	MnO ₂ compositing	—	Aqueous	656 F g ⁻¹ at 1 A g ⁻¹	[25]
Birchwood porous AC/MnO ₂ (1D nanorods)	Hydrothermal	643.5	Neutral aqueous	208.8 F g ⁻¹ at 0.5 A g ⁻¹ ; 87.4% retention	[26]
Silkworm-excrement carbon/MnO ₂	ZnCl ₂ /FeCl ₃ + hydrothermal	—	Aqueous	238 F g ⁻¹ at 0.5 A g ⁻¹ ; ~93% after 2000 cycles	[27]
Tea-leaf hierarchical porous carbon/MnO _x	KMnO ₄ redox	—	Aqueous	337 F g ⁻¹ (+70% vs. AC)	[28]
Pomegranate peel AC (PG-2)	Chemical activation (1:2)	1737	Aqueous	190 F g ⁻¹ at 1 A g ⁻¹	[29]
N-doped pomegranate peel AC	NaOH + NH ₃	2085	1 M KCl	338 F g ⁻¹ at 0.4 A g ⁻¹	[30]
Cucumber peel AC	Chemical activation, 800 °C	2333	Aqueous	286 F g ⁻¹ at 1 A g ⁻¹ ; 100% after 2000 cycles	[31]
Pomelo peel N,P co-doped porous carbon nanosheets	NH ₄ H ₂ PO ₄ activation/doping	—	Aqueous (3-electrode)	314 F g ⁻¹ ; 82% rate retention at 20 A g ⁻¹ ; 99% after 10 000 cycles	[32]
Pomegranate peel AC/MnO ₂ -25 (this work)	KOH activation + redox MnO ₂ deposition	1380	1 M Na ₂ SO ₄	394 F g ⁻¹ at 1 A g ⁻¹ ; 94.5% after 5000 cycles, ~98% CE	—

From Table 7, it is evident that the current AC/MnO₂-25 electrode fabricated in this study demonstrates an electrochemical performance that is either equal to or superior to that of many other biomass-based carbonaceous materials that have been reported previously. Such performance is made possible through proper manipulation of the amount of MnO₂ in the material. Additionally, the use of pomegranate peel waste in the process makes this study eco-friendly and economically sustainable.

In conclusion, it is evident that the results obtained in this study confirm the importance of the balance of porosity, conductivity, and defect density of the AC/MnO₂ composites, as reported previously [1]. The AC/MnO₂-25 composite exhibits the best balance of all properties, resulting in the highest capacitance, charge-transfer characteristics, and cycling stability compared to composites with higher or lower MnO₂ loadings. What must be mentioned is that the MnO₂ concentrations (10, 25, and 40 wt.%), presented in the research, are the theoretical values that were calculated considering the stoichiometric amount of KMnO₄ used for MnO₂ deposition by the redox technique. Although the presence of MnO₂ in the activated carbon sample is proven via XRD and EDS investigations, the concentration of manganese oxide is not determined. Thus, for future studies, more accurate methods such as ICP-OES/MS, TGA, or XRF should be considered to determine the MnO₂ concentration.

5. Conclusions

AC/MnO₂ hybrids from pomegranate peel waste were obtained via an eco-friendly in situ redox deposition method, which was used to create sustainable electrode materials for supercapacitor applications. Structural analysis showed the presence of a porous carbon structure and crystalline γ -MnO₂ formed in the carbon matrix. The AC/MnO₂-25 composition possessed the highest electrochemical activity, showing a high specific capacitance value of 394 F g⁻¹ at 1 A g⁻¹, low charge transfer resistance of 0.90 Ω , and outstanding cycling stability, with only 5.5% capacitance loss over 5000 cycles. High performance of the AC/MnO₂-25 composition was achieved owing to the good balance between the electric double-layer capacitance contributed by AC and the pseudocapacitance due to manganese oxide. Sufficient porosity, beneficial defect density, effective ionic transport, and charge transfer characteristics were retained in this sample, whereas an excess amount of MnO₂ reduced the electrochemical efficiency because of pore blockage and high resistance. Thus, the obtained results confirmed that composite electrodes from pomegranate peel AC/MnO₂ are potential low-cost sustainable materials for advanced supercapacitors and can be considered useful for developing biomass-based hybrid supercapacitor materials. While this study was based on three-electrode electrochemical analysis to study the inherent behavior of the fabricated material, it would be beneficial to analyze the functionality of the fabricated electrodes using the two-electrode supercapacitor configuration in subsequent research for practical application in energy storage devices.

6. Future

Building on these encouraging findings, researchers should strive to achieve the following goals.

- The scale of the synthesis method for industrial applications should be increased to assess the process dependability and cost-effectiveness.
- To further improve the energy density and capacitance retention, additional transition metal oxides and/or conductive polymers should be incorporated.
- The actual device performance should be examined by testing it in solid-state, flexible, and two-electrode supercapacitor systems.
- Long-term durability assessments should be conducted under various environmental conditions to gain a better understanding of performance reliability in real-world scenarios.
- Employ sophisticated in situ characterization methods (such as XRD or operando Raman) to learn more about the dynamics of the interface and charge storage mechanisms during cycling.

Use of AI tools declaration

The authors declare that they have not used Artificial Intelligence (AI) tools in the creation of this article.

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Conflict of interest

The authors declare no conflicts of interest.

Author contributions

Conceptualization: M.A.A., A.K.A.-K. and A.M.F.; methodology, A.K.A.-K., T.K.A.-H., A.S.A., T.W.M. and A.M.F.; software, M.A.A. and A.S.A.; validation, A.K.A.-K., T.K.A.-H., A.S.A. and T.W.M.; formal analysis, A.M.F., A.S.A. and T.W.M.; investigation, A.S.A., M.A.A. and T.W.M.; resources, T.K.A.-H.; data curation, M.A.A.; writing—original draft preparation, A.M.F.; writing—review and editing, A.K.A.-K., T.K.A.-H., M.A.A., T.W.M. and A.M.F.; visualization, A.S.A.; supervision, A.M.F. and M.A.A.; project administration, T.K.A.-H.

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