



Asymmetric supercapacitors based on biomass-derived porous activated carbon (PAC)/1D manganese oxide (MnO₂) electrodes with high power and energy densities

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ARTICLE INFO

Keywords:

Biomass derived hierarchically porous carbon
1D β -MnO₂ nanorods
Pseudo capacitance
Asymmetric capacitors

ABSTRACT

In this study, we present the electrochemical performance of an asymmetric supercapacitor (ASC) composed of one-dimensional manganese oxide (MnO₂) nanorods embedded in porous activated carbon sheets (MnO₂/PAC) as the positive electrode (positrode), and renewable porous activated carbon (PAC) as the negative electrode (negatrode). This configuration facilitates a high rate of charge/discharge while maintaining substantial specific capacity. The MnO₂/PAC composite was successfully synthesized using a hydrothermal technique, while the PAC material was produced through pyrolysis reaction. The MnO₂/PAC composite exhibited a maximum specific capacitance of 208.75F g⁻¹ at 0.5 A/g and demonstrated a cyclic stability of 87.43 % in neutral aqueous electrolytes. This notable electrochemical performance is attributed to the significant contribution of the high pseudo-capacitance offered by dense MnO₂ nanorods, in addition to the expansive surface area of the activated carbon sheets with closely packed structures. The ASC constructed as PAC//MnO₂/PAC displayed a high energy density of 23.3 Wh kg⁻¹ and a power density of 350.4 W kg⁻¹ at a current density of 0.5 A/g. Furthermore, the device showcased exceptional cycling stability, retaining 90.3 % at a current density of 4 A/g. These results underscore the substantial untapped potential of ASC devices for innovative applications in advanced energy storage.

1. Introduction

In the face of changing global climate and environmental degradation, renewable energy sources have become more critical than ever. Adaptive and scalable energy storage systems are essential to efficiently harness these renewable energy sources [1]. Applications like portable electronics and hybrid electric cars can greatly benefit from electrochemical energy storage devices [2,3]. The lithium-ion battery, known for its high energy density and thermal stability, has garnered significant

interest in energy storage systems [4,5]. However, it's important to note that Lithium (Li) is a hazardous substance with the potential to cause significant environmental impact. Supercapacitors (SCs) have captured considerable attention due to their remarkable characteristics, including high power density, specific capacitance, rate capability, rapid charging, and minimal environmental footprint [3–5]. Nevertheless, SCs have lower energy density compared to batteries and fuel cells, limiting their practical applications [2,4].

The primary objective of researchers in both academic and industrial

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contexts within this field is to develop electrode materials and electrolytes with enhanced efficiency [2,6]. This endeavor aims to maintain the power density of supercapacitors while simultaneously increasing their energy density. SCs are broadly categorized into electrical double layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors based on the charge storage mechanisms of electrode materials [7]. EDLCs predominantly employ carbon-based materials as electrodes. In the case of EDLCs, porous carbon materials serve as the electrode material due to their remarkable surface area and commendable conductivity [8]. Biomass stands out as a promising source for high-quality carbon materials, given its high carbon content, wide availability, environmental friendliness, and cost-effectiveness [9,10]. Nonetheless, the capacitance of porous carbon materials is constrained by their limited charge storage capacity (dependent solely on electrostatic forces) on the electrode surface [3,9,11].

Conversely, pseudocapacitors rely on the swift and reversible redox reactions occurring between ions in the electrolyte and the electroactive materials [12,13]. SCs commonly integrate pseudocapacitors, known for their multi-crystal structure and varying oxidation states. Transition metal oxides (TMOs) such as manganese dioxide (MnO_2), RuO_2 , $\text{Ni}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, and V_2O_5 are frequently employed in the construction of these pseudocapacitors [3,14,15]. This indicates that metal oxides exhibit greater electrochemical stability compared to conductive polymers and offer higher energy density than carbon materials [14,16]. Among the valuable TMOs, MnO_2 has emerged as a prominent pseudocapacitive material. This is due to its advantageous attributes, which encompass a high theoretical specific capacitance of 1370 F g^{-1} , cost-effectiveness, robust chemical and thermal stability, abundant presence in the Earth's crust, and environmentally acceptable properties [17–19].

The combination of activated carbon (AC) with MnO_2 proves to be a successful technique for creating high-performance composite electrode materials. This approach enhances the overall conductivity of MnO_2 , increases the specific capacitance of AC, and consequently leads to a higher energy density [20,21]. The hybrid composite electrodes, comprising AC and MnO_2 , demonstrate exceptional energy storage capabilities due to the synergistic effects of several factors. These factors include the high reversible capacitance, structural stability, and rapid cation diffusion at high charge/discharge rates characteristic of MnO_2 . Additionally, the large specific surface area (SSA), micro/mesopore volume, and chemical stability of AC contribute to the enhanced energy storage capacity [22].

In this study, birchwood was employed as the raw material to produce porous carbon sheets, which were subsequently used as a substrate for the growth of 1D MnO_2 nanorods. The current work introduces a homogenous porous activated carbon (PAC)/ MnO_2 hybrid structure fabricated through an initial hydrothermal technique. The resultant MnO_2 /PAC composite showcases a high SSA of $643.5\text{ m}^2/\text{g}$, an impressive pore volume of $0.6\text{ cm}^3\text{ g}^{-1}$, and well-defined crystalline MnO_2 nanorods. Operating at a current density of 0.5 A/g , MnO_2 /PAC achieves an exceptional specific capacitance of 208.75 F g^{-1} , owing to the combined influence of EDLC and pseudocapacitance. Furthermore, an asymmetric supercapacitor (ASC) constructed using PAC/ MnO_2 (positrode) and PAC (negatrode) demonstrates an energy density of 23.3 Wh kg^{-1} at a power density of 350.4 W kg^{-1} .

2. Experimental methods

2.1. Materials

The chemicals utilized in this experiment were procured from Sigma Aldrich, Republic of Korea. No further processing was required as analytical grade chemicals and reagents were directly employed in the experiments. The chemicals included potassium hydroxide (KOH), potassium permanganate (KMnO_4), nitric acid (HNO_3), N, N'-dimethylformamide (DMF), polyvinylidene difluoride (PVDF), acetylene

black, N-methyl-2-pyrrolidone (NMP), ethanol, and acetone. Fresh deionized (DI) water was used for all solution preparations and cleaning procedures.

2.2. Preparation of porous activated carbon (PAC)

The PAC material was synthesized using a chemical activation method, as previously described [23], with slight modifications. Birchwood sourced from the local Korean market was first divided into small fractions and subjected to thorough cleaning with DI water, repeating the process more than five times. The resulting powder underwent pre-carbonization and activation at $400\text{ }^\circ\text{C}$ for 2 h in a nitrogen (N_2) environment, using a quartz tube furnace with a heating rate of $5\text{ }^\circ\text{C}/\text{min}$. The pre-carbonized powder was then accurately weighed, uniformly mixed in an agate mortar, and activated using NaOH salt at a mass ratio of 3:1. The activation treatment was carried out with a heating rate of $5\text{ }^\circ\text{C}/\text{min}$, raising the temperature to $800\text{ }^\circ\text{C}$. The total activation time was 6 h upon a rise time of 3 h and a maintain time of 3 h. Subsequently, the boat containing the material was removed and allowed to cool down to room temperature. To eliminate potential inorganic salts, such as K_2O and/or K_2CO_3 originating from the activation process, the black activated powder was subjected to centrifugation and subsequently washed multiple times in a solution of 1 M HCl and DI water until the pH of the cleaning solution reached neutrality. Ultimately, the centrifuged products were obtained and then dried at $80\text{ }^\circ\text{C}$ overnight, resulting in the formation of PAC.

2.3. Synthesis of MnO_2 nanorods and PAC/ MnO_2 composite

The MnO_2 nanorods were synthesized through a hydrothermal process involving a mixture of 0.5 M KMnO_4 and 0.2 M HNO_3 . This mixture was subjected to a hydrothermal treatment at $160\text{ }^\circ\text{C}$ for 16 h within a Teflon autoclave. The resulting MnO_2 powder was subsequently filtered, washed with ethanol, and DI water, and finally dried at $120\text{ }^\circ\text{C}$ for a duration of 24 h. To prepare the solution, 0.5 g of PAC was subjected to sonication for 10 min, facilitating its dissolution in 30 mL of water, resulting in a stable solution. Subsequently, this solution was combined with a mixture of 0.5 M KMnO_4 and 0.2 M HNO_3 , while employing vigorous stirring for a period of 2 h. The resulting mixture was then transferred to a Teflon autoclave and treated under the same conditions as previously stated. The product of this process, the PAC/ MnO_2 composite, was subsequently filtered and dried at $120\text{ }^\circ\text{C}$ for 24 h.

2.4. Physiochemical characterizations

This study employed high-resolution transmission electron microscopy (HR-TEM) with a JEOL JEM2100F instrument and field emission scanning electron microscopy (FE-SEM) using a Hitachi SU8200 to analyze the morphologies of PAC, PAC/ MnO_2 composite and MnO_2 nanorods. The crystal structures of all samples were investigated through X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation, utilizing a Rigaku TTRAX III instrument. Fourier-transform infrared (FT-IR) spectra were obtained using a Perkin Elmer Spectrum One spectrophotometer with the KBr pellet method. N_2 adsorption and desorption measurements were performed at $-196\text{ }^\circ\text{C}$ using a Micromeritics ASAP 2020 apparatus. Prior to the analysis, the samples were degassed under vacuum at $250\text{ }^\circ\text{C}$ for 24 h. The specific surface area (SSA) was determined using the multi-point Brunauer–Emmett–Teller (BET) method in accordance with the BET consistency criteria presented by the International Standard Organization [ISO 9277:2022]. The specific pore volume (SPV) was estimated using the single-point Gurvich rule at relative pressures of ~ 1 . Surface chemistry analysis of the samples was conducted via X-ray photoelectron spectroscopy (XPS) using an ESCALAB 250Xi instrument with $\text{Al K}\alpha$ radiation at 1486.6 eV and 25 W . Raman spectroscopy was carried out on a Nanobase Raman spectrometer (Korea), using a 532 nm laser.

2.5. Electrochemical characterizations

The working electrodes were coated onto pre-treated carbon cloth using a conventional slurry technique [20,23]. For electrode preparation, active materials, conductive carbon (acetylene black), and PVDF were ground and mixed in an 80:10:10 ratio to create a slurry in NMP. This well-mixed slurry was evenly applied onto a current collector carbon cloth, resulting in a loading mass of 5 mg cm^{-2} . The coated cloth was then dried in an oven at 60°C for a duration of 8 h. The electrochemical performance of all electrode materials was evaluated using a three-electrode configuration, employing an Ag/AgCl reference electrode and a platinum wire counter electrode. The Biologic SP150 instrument was utilized for this assessment. In an aqueous electrolyte of 1 M Na_2SO_4 , the electrochemical characteristics were examined through cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS), both in three-electrode and two-electrode measurements. An ASC device was assembled using PAC/ MnO_2 as the positive electrode and PAC nanosheets as the negative electrode. The resulting device was characterized by a 1 M Na_2SO_4 aqueous electrolyte solution while ensuring mass balance. Comprehensive details for the electrochemical measurements are available in the [Supporting Information \(SI\)](#).

3. Results and discussion

3.1. Physio-chemical characterization

The schematic of the steps required for fabricating for PAC/ MnO_2 nanocomposite are illustrated in Fig. 1. Fig. 1a illustrates the carbonization and activation process for the synthesis PAC sheets under N_2 environment. Fig. 1b displays the schematic of hydrothermal process of PAC/ MnO_2 nanorods composite. The phase structures of PAC, MnO_2 and PAC/ MnO_2 nanocomposite were characterized using XRD and Raman spectra. In Fig. 2a, the XRD pattern of PAC displays distinct diffraction peaks, notably one at approximately 23.44° (002) and another at 43.3° (100). These peaks in amorphous carbon are indicative of the production of graphite layers with partial graphitization [23,24]. In contrast, the XRD peaks of hydrothermally synthesized MnO_2 exhibit characteristic peaks at 28.89° (110), 37.4° (101), 42.71° (111), 56.9° (211), 59.26° (220), and 72.1° (112) [25,26]. These peaks correspond to the tetragonal MnO_2 crystal structure indexed to $\beta\text{-MnO}_2$ (JCPDS Card No: 024-0735). The XRD pattern of the PAC/ MnO_2 composite reveals broad

diffraction peaks around 23.1° (002) and 43.3° (100), indicating the presence of AC phase. Additional diffraction peaks at 28.8° (110), 42.17° (111), and 59.26° (220) directly confirm the formation of composite structures [23,26]. Notably, the XRD patterns of $\beta\text{-MnO}_2$ in both MnO_2 nanorods and PAC/ MnO_2 composites closely resemble each other, suggesting that the addition of PAC does not alter the crystal form and structure of MnO_2 .

Raman spectroscopy was employed to probe the vibrational properties of PAC and composite samples, as depicted in Fig. 2b. The obtained spectra reveal distinct G- and D-bands. The G-band (1580 cm^{-1}) of PAC indicates C–C stretching vibrations (sp^2 hybridization), while the D-band (1350 cm^{-1}) signifies disorder within the material. The higher intensity of the D-band relative to the G-band signifies a higher degree of disorder, indicative of the considerable porosity of PAC. In the Raman spectrum of MnO_2 , a prominent peak at approximately 631 cm^{-1} corresponds to the Mn–O vibrations oriented perpendicular to the MnO_6 octahedral double strands within the MnO_2 structure [27,28]. The Raman spectrum of PAC/ MnO_2 composites exhibits strong carbon peaks for both the D-band and the G-band. Furthermore, a modest peak corresponding to Mn–O vibrations appears around 631 cm^{-1} , providing further evidence of the effective synthesis of the composite containing both PAC and MnO_2 .

The structural characteristics and formation processes of MnO_2 , PAC, and PAC/ MnO_2 are further illuminated through FT-IR spectroscopy within the $4000\text{--}400 \text{ cm}^{-1}$ range. For the PAC material, the broad peak at 3467.7 cm^{-1} is attributed to the O–H stretching of the C–OH bond formed during the oxidation process [29,30]. Additional weak peaks, such as those at $400\text{--}700 \text{ cm}^{-1}$, 1380 cm^{-1} , 1636 cm^{-1} , and 2972.1 cm^{-1} , correspond to various vibrational modes. These include C–C stretching, C–O–C stretching, C=C symmetric stretching, and C–H symmetric stretching, which collectively confirm the formation of activated carbon [29,31]. In the MnO_2 lower frequency region, spanning from 526.86 to 585.04 cm^{-1} (as shown in Fig. 2c), the strong and broad band corresponds to the stretching bonds of Mn–O and O–Mn–O. This confirms the growth of MnO_2 [17,32]. In addition, the wider band observed within the range of 3400 to 3500 cm^{-1} , coupled with a weaker band around 1630 cm^{-1} , signifies the stretching and bending vibrations of O–H molecules present in MnO_2 nanorods [33]. In the FT-IR spectrum of the PAC/ MnO_2 composite, vibrational atom modes of both MnO_2 (around 435 cm^{-1} and 597 cm^{-1}) [17] and AC (1637 cm^{-1} , 2848 cm^{-1} , and 3442 cm^{-1}) [29] can be observed. This observation suggests a significant formation of carbon bonds and Mn atoms on the surface of PAC/

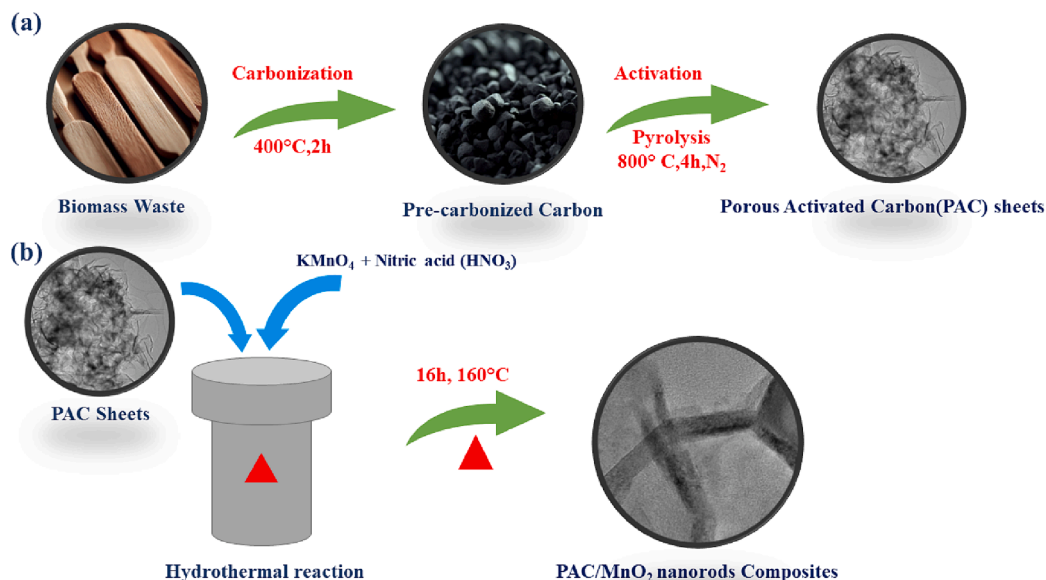


Fig. 1. (a) Schematic illustration of PAC and (b) PAC/ MnO_2 nanocomposite by hydrothermal process.

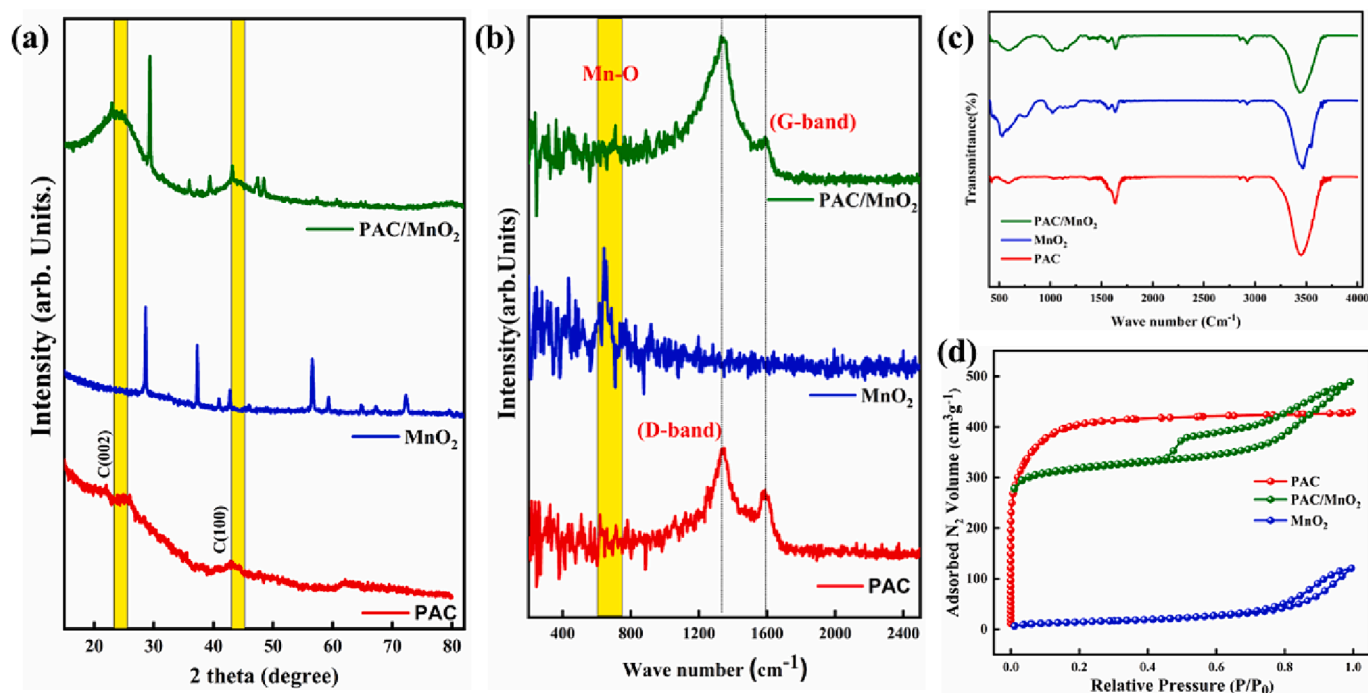


Fig. 2. (a) Powder XRD patterns, (b) Raman spectra and (c) FTIR spectra and (d) N₂ adsorption-desorption isotherm curve of PAC, MnO₂ rods and PAC/MnO₂ composite.

MnO₂, achieved through a straightforward hydrothermal reaction.

The surface area and pore volume of the samples were assessed by analyzing N₂ adsorption-desorption isotherms. Fig. 2d presents the N₂ adsorption and desorption isotherms collected at -196°C for MnO₂ nanorods, PAC, and PAC/MnO₂. After undergoing carbonization procedures, PAC samples exhibit characteristics in line with a Type I adsorption isotherm according to the classification of the International Union of Pure and Applied Chemistry (IUPAC), revealing a lack of hysteresis loop. This signifies the presence of micropores and a limited quantity of mesopores within the material [17,23]. In contrast, the N₂ adsorption and desorption capacity of MnO₂ nanorods is notably low, as evidenced by the Type II isotherm featuring an H3 hysteresis loop [34]. This observation implies a deficient and insufficient pore structure. Specifically, the nanorods present non-rigid aggregates of plate-like particles accompanied by slit-shaped pores, particularly in the region of macropores at high relative pressures ($P/P_0 > 0.9$) [35]. Upon undergoing the hydrothermal process, the MnO₂/PAC composite material exhibits a transition from a Type I to a mixed Type I and Type IV isotherm. Additionally, an H4 hysteresis loop appears within the range of $0.4 < P/P_0 < 0.7$, signifying the presence of a hierarchical pore structure. The SSA of PAC, calculated through the BET method (see Table 1), corresponds to approximately $779\text{ m}^2/\text{g}$, surpassing that of the PAC/MnO₂ composite ($644\text{ m}^2/\text{g}$). The decline in surface area of MnO₂/PAC is primarily attributed to the formation of MnO₂ within the micropore channels of PAC's surface [36]. This phenomenon demonstrates the formation of composite structures. The PAC/MnO₂ composite exhibits substantial surface area and hierarchically porous structures, which can enhance the wetting behavior at the electrolyte-electrode

interface. This enhanced wetting behavior holds the potential for facilitating ion diffusion during electrochemical processes [37].

The chemical environments of components on the material surfaces, including carbon, nitrogen, oxygen, and manganese were analyzed through XPS. As illustrated in Fig. 3a, the XPS survey spectrum of PAC exhibits distinct peaks, particularly C1s (284.5 eV) and O1s (531 eV), unequivocally confirming the presence of carbon and oxygen [17,38]. Also, Fig. 3a for MnO₂ nanorods display binding energies at 641.84 and 531.4 eV corresponding to Mn 2p and O 1s peaks, respectively [20]. In Fig. 3a, the presence of MnO₂ grown on the PAC surface results in the appearance of C 1s, O 1s, and Mn 2p peaks [17,20]. The high-resolution C 1s spectrum of PAC (Fig. 3b) was deconvoluted into several peaks, with the dominant peak intensity centered at 284.4 eV corresponding to hybridized $\text{sp}^3\text{C-C}/\text{sp}^2\text{C=C}$ graphitic carbon, belonging to the carbon skeleton of the electrode [39]. The other three peaks at the binding energies of 284.9, 285.7, 286.8, 288.2 eV and 289.5 eV are ascribed to C-H/C-N bonds, C-O bonds, C=O bonds, O-C=O bonds and chemisorbed oxygen species [17,38]. In the case of PAC/MnO₂ the deconvoluted C 1s spectrum of PAC/MnO₂ (Fig. 3b) also showed major peaks of at $\text{sp}^3\text{C-C}/\text{sp}^2\text{C=C}$ (284.5 eV) and minor peaks of C-H/C-N (284.9 eV), C=O (286.5 eV) and O-C=O bonds (288.4 eV) evidencing there is no such formation of additional functional groups during hydrothermal process. The Mn 2p spectra of PAC/MnO₂ (Fig. 3c) deconvoluted into two peaks 653.2 eV (Mn $2\text{p}_{3/2}$) and 641.6 eV (Mn $2\text{p}_{1/2}$) [22]. The peaks fitted with spin energy separation of 11.2 eV, the peak area ratio ($2\text{p}_{3/2}:2\text{p}_{1/2}$) of 2:1. The Mn $2\text{p}_{3/2}$ of PAC/MnO₂ have major fitted peak at 642.7 eV indicating a predominance of MnO₂ (Mn^{4+}) and other peaks such as 642.53 eV and 644.23 eV exhibit the oxidation states of Mn ($\text{OH})_4$ (Mn^{3+}) and KMnO_2 (Mn^{7+}) respectively [17,32]. The O 1s XPS spectra of PAC (Fig. 3d) was fitted with three peaks located at 530.9 eV, 532.2 eV, and 533.6 eV, which are attributed to C=O-N, C-O-C and C-OH, respectively [17,20]. Also, Fig. 3d shows the O1s spectrum of PAC/MnO₂, having three main peaks attributed to Mn-O-Mn (529.4 eV), Mn-OH (531.5 eV), and C-OH (532.3 eV) respectively [20,22]. In summary, XPS outcomes provide clear evidence of the successful incorporation of MnO₂ onto PAC within the composite electrodes.

The surface morphologies and microstructures of PAC, MnO₂ and

Table 1

The BET-specific surface areas, Isotherm, and pore volumes of PAC, MnO₂, and PAC/MnO₂ composite.

Samples	Isotherm	SSA (m^2/g)	Pore volume ($\text{cm}^3\text{ g}^{-1}$)
MnO ₂	Type II	53	0.1
PAC	Type I	778	0.7
PAC/MnO ₂	Type I and IV	643	0.6

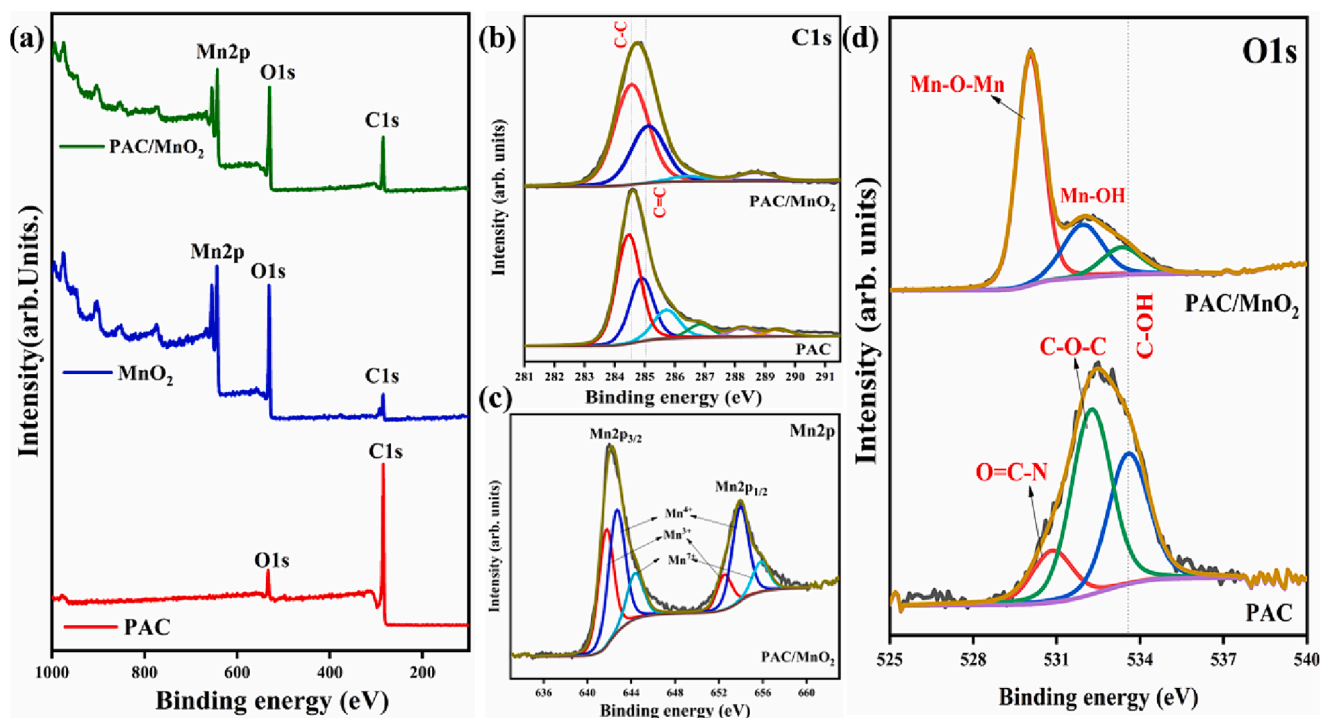


Fig. 3. (a) XPS survey spectra of PAC, MnO_2 rods and PAC/MnO_2 composite electrodes. (b) High resolution XPS spectra of C 1s of PAC, and PAC/MnO_2 , (c) Mn 2p of PAC/MnO_2 and (d) O 1s of PAC & PAC/MnO_2 composite.

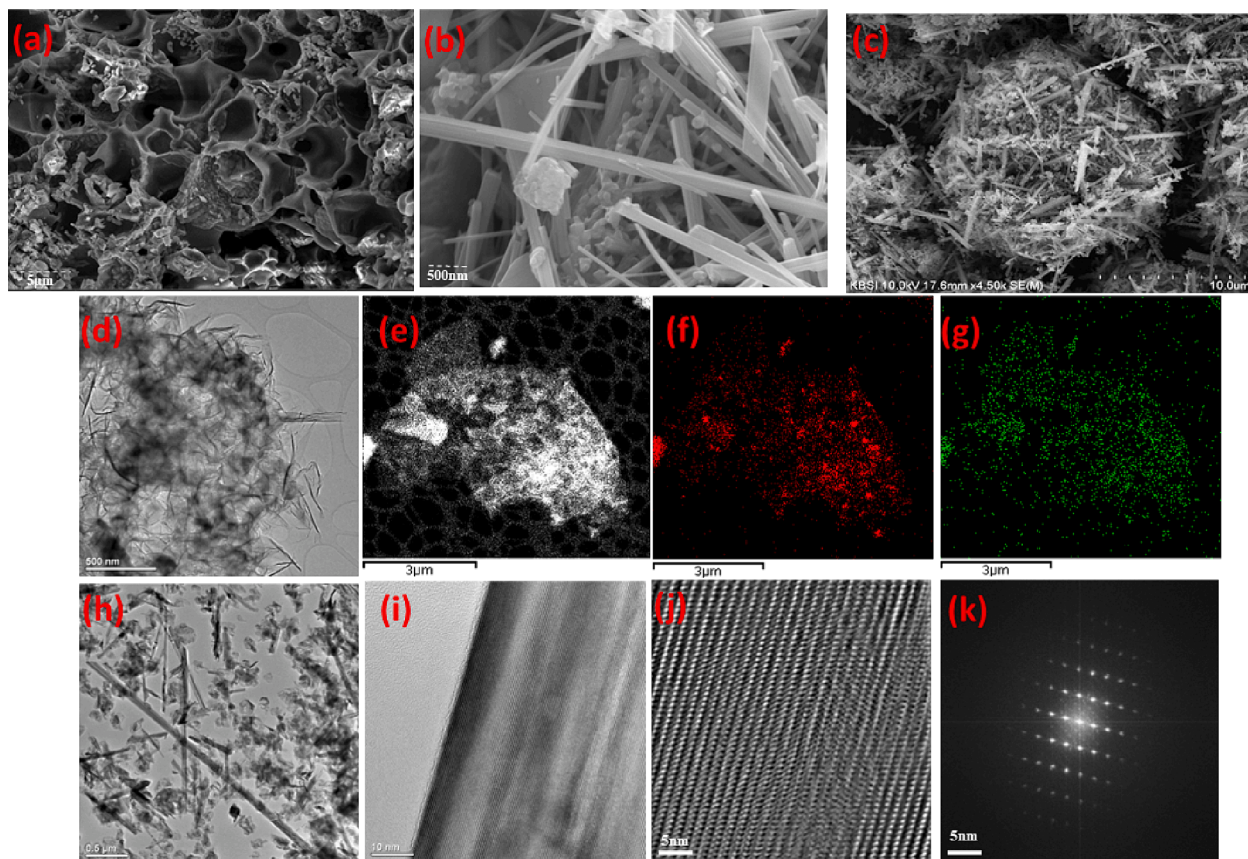


Fig. 4. FESEM images of (a) PAC, (b) MnO_2 nanorods and (c) PAC/MnO_2 composite. HR-TEM images of (d) PAC (e, f, g) elemental mapping of C, O, and N distribution, (h) MnO_2 nanorods and the corresponding (j) lattice fringes and (k) SAED pattern.

PAC/MnO₂ were characterized using FE-SEM and FE-TEM. Fig. 4a presents the surface morphology of PAC, revealing distinct honeycomb sheet-like patterns. These structures are attributed to the interaction between the activating agent and the precursor material [40,41]. The honeycomb-like sheets serve as conducting networks, facilitating rapid electron transfer, and provide a suitable foundation for the attachment of pseudocapacitive materials [42,43]. Further visualized through FE-SEM images (as shown in Fig. 4b), β -MnO₂ exhibits a smooth and aggregated nanorod morphology. Post-hydrothermal processing, MnO₂ becomes uniformly anchored across the surface of activated carbon sheets, as depicted in Fig. 4c. This anchoring effect highlights the successful integration of MnO₂ onto the PAC structure.

Fig. 4d presents TEM image of PAC, revealing a distinct sheet-like morphology. This image provides evidence of the amorphous nature of the carbon sheets, with pronounced porosity observed predominantly in the center of the sheet, while graphitic carbon is more prevalent around the sheet's margins [33]. Moreover, the energy-dispersive X-ray (EDAX) mapping analysis of PAC (shown in Fig. 4(e–g)) demonstrates the uniform distribution of carbon (C), oxygen (O), and nitrogen (N) elements across the surface. The as-prepared MnO₂ (Fig. 4h) exhibits smooth nanorod structures with an average width of 30–50 nm. The lattice fringes observed in Fig. 4j indicate high crystallinity and 1D channels, characteristic of MnO₂ nanorods. The selected area electron diffraction (SAED) pattern (Fig. 4k) taken from a MnO₂ nanorod confirms its single-crystalline nature. The TEM image of PAC/MnO₂ (depicted in Fig. 5a) reveals nanorods uniformly anchored on the carbon surface with a continuous 1D morphology, showcasing the robustness of the PAC structure [34,36]. The MnO₂ nanorods are well aligned with the graphitic layers of carbon, as observed in the high-magnification TEM image (Fig. 5b). Fig. 5(c–f) displays the EDX mapping of PAC/MnO₂, illustrating the distributions of carbon (C), oxygen (O), manganese (Mn), and nitrogen (N) elements. The uniform distribution of Mn elements across the PAC confirms the reliability of the hydrothermal synthesis method [36].

3.2. Electrochemical characterization

The initial electrochemical behaviors of PAC, MnO₂, and PAC/MnO₂ composite electrodes were investigated in an aqueous 1 M Na₂SO₄ electrolyte solution using a standard three-electrode setup. The CV curves of PAC (illustrated in Fig. 6a), scanned from -1 V to 0 V at rates ranging from 2 to 100 mV s⁻¹, exhibit a nearly rectangular shape in both the forward and reverse sweeps. This rectangular shape is indicative of the typical EDLC behavior associated with carbon materials [23,39]. Consistently confirming EDL behavior, the GCD curves (as shown in Fig. 6b) reveal linear charge–discharge behavior across the range of tested current densities (0.5 – 5 A/g) [17,38]. The Nyquist plots of PAC (Fig. 6c) display pure EDLC behavior, without any semicircle at high frequencies and a nearly vertical Warburg tail at low frequencies [23,44]. Specific capacitances were calculated from GCD curves at 0.5 A/g, yielding a value of 178.7 F g⁻¹ for PAC electrodes (Fig. S1). Moreover, PAC exhibits a high-rate capability of 81.6 % at 5 A/g. These superior specific capacitance and rate capability attributes of PAC can be attributed to its high SSA and hierarchical porous volume within the carbon framework [23]. In Fig. 6d, the electrochemical characteristics of β -MnO₂ nanorods and PAC/MnO₂ microstructures were assessed using a three-electrode system within a potential range of 0 – 1 V, and at a scan rate of 20 mV s⁻¹. The CV curves of MnO₂ nanorods and PAC/MnO₂ display pseudo-rectangular shapes. Notably, the area under the CV curve of PAC/MnO₂ is larger than that of MnO₂, indicating a combined effect of PAC's SSA and the MnO₂'s Faradaic reactions [33,34]. The GCD characteristics (Fig. 6e) of MnO₂ nanorods and PAC/MnO₂ nano-composites shows typical capacitive behaviour can be observed from the linear charge–discharge curves, but the composite electrode shows high discharge time than pristine MnO₂ nanorods. The real axis intercept (R_s) values were found to be 2.92 Ω and 3.14 Ω for the PAC/MnO₂ and MnO₂ electrodes, respectively (see Fig. 6f).

Moreover, a superior interfacial charge transfer characteristic is evidenced by the low Charge transfer resistance R_{ct} for PAC/MnO₂. The slopes of the Warburg impedance curves indicate that the electrode process is not fully capacitive but contains electrolyte diffusion in the electrode material [45]. Fig. 6g shows the CV plots at scan rates from 2

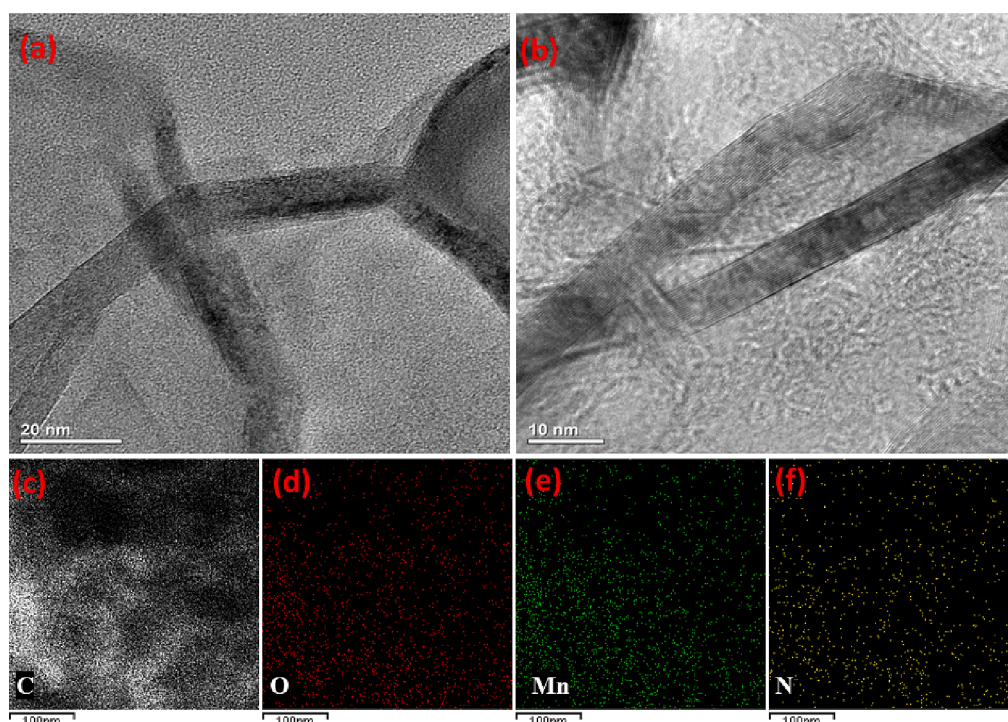


Fig. 5. (a, b) HRTEM images at various magnifications, and (c–f) EDX elemental images of PAC/MnO₂ composite.

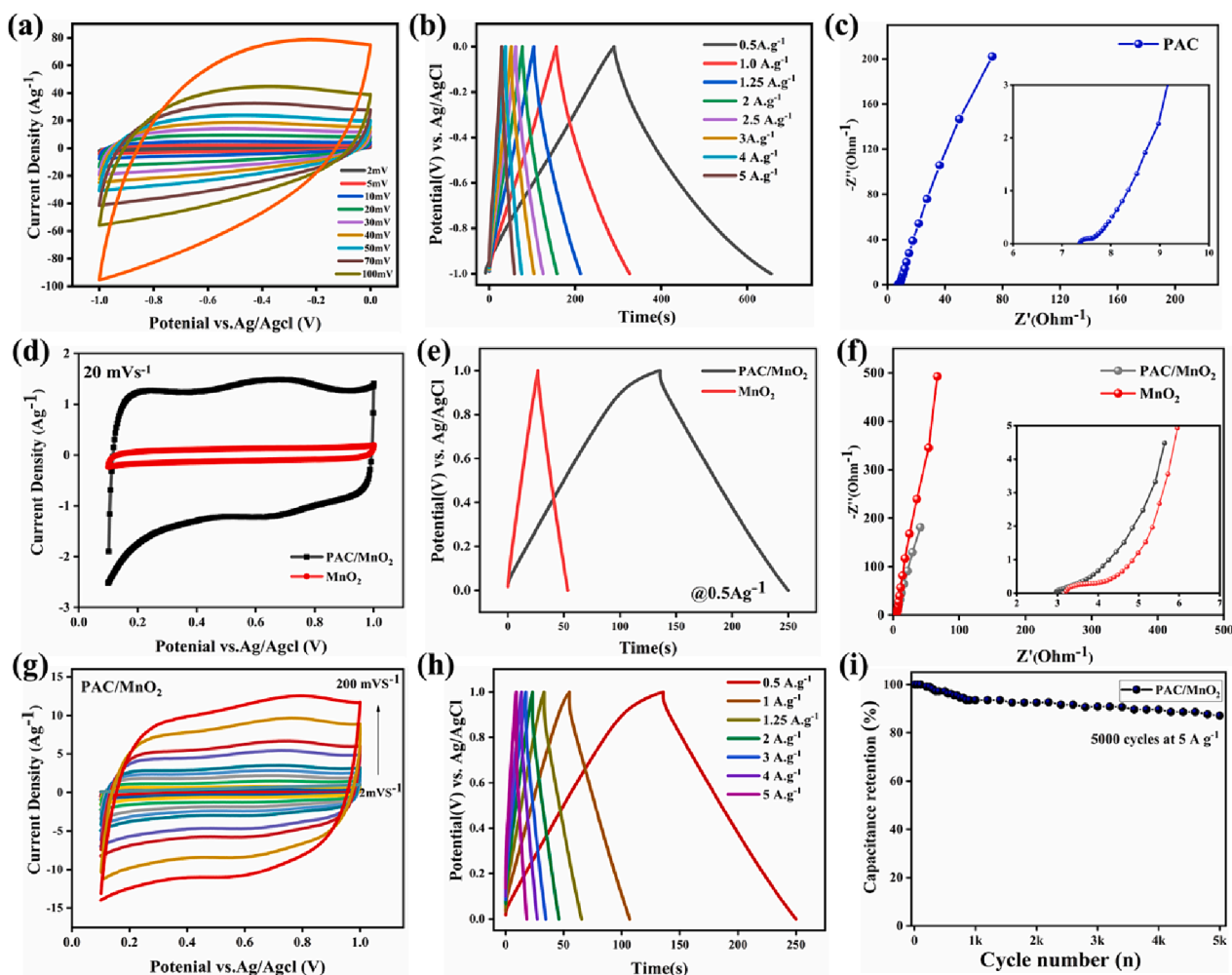


Fig. 6. Electrochemical behavior of negative PAC electrode: (a) CV curves at different scan rates, (b) GCD at different current densities, (c) Nyquist plot (Inset: high-frequency region). Electrochemical comparison of MnO₂ and PAC/MnO₂: (d) CV curves (20 mV s⁻¹), (e) GCD curves (0.5 A/g), (f) EIS spectra, (g) CV curves at different sweep rates (h) GCD curves at current densities, and (i) Cyclic stability of PAC/MnO₂ at 5 A/g for 5000 cycles in a three-electrode system.

–200 mV s⁻¹ clearly shows ideal rectangular shape, without any redox reactions clearly showing capacitive behavior [46,47]. The GCD curves (Fig. 6h) of PAC/MnO₂ show symmetrical triangular GCD responses displaying a specific capacitance of 208.75F g⁻¹ at 0.5 A/g. Also GCD curves with little fluctuation in higher current densities, indicating a suitable supercapacitor electrode material [21,48]. Fig. 6i displays the cyclic stability of PAC/MnO₂ composites showed capacitance retention of 87.43 % even after 5000 cycles due to their comparable mesoporous pore structures in carbon skeleton [49]. Based on the characterizations, it can be deduced that the PAC/MnO₂ composite has promising attributes as an electrode material. This is primarily attributed to the composite's possession of PAC mesoporous structure, which offers a substantial surface area, hence facilitating efficient ion diffusion. Additionally, the inclusion of MnO₂ imparts pseudocapacitor properties to the composite, further enhancing its electrochemical performance [50,51].

To comprehensively evaluate the composite electrodes for practical applications, an ASC device was constructed by integrating the PAC/MnO₂ composite electrode as the positive electrode and PAC as the negative electrode, with a 1 M Na₂SO₄ aqueous electrolyte, as illustrated in Fig. 7i. The CV curves of the ASC (PAC//PAC/MnO₂) are presented in Fig. 7a, demonstrating rectangular CV shapes and good reversibility throughout the entire voltage range, up to 1.4 V [36,38]. Fig. 7c showcases the CV curves of the ASC at different scan rates, exhibiting favorable capacitive and pseudocapacitive characteristics with quasi-

rectangular CV shapes across scan rates ranging from 2 to 200 mV s⁻¹ [21,52]. Even at higher scan rates (as seen in Fig. 7b), the quasi-rectangular shape remains intact, highlighting the high-rate capability of the asymmetric device. Furthermore, the GCD curves (Fig. 7d & e) exhibit a triangular shape with slight deviations, further confirming the synergistic effect of both EDLC behavior and pseudocapacitive contributions [33]. This observation is consistent with the CV results [21,53]. Fig. 7f displays the Nyquist plots of the ASC, featuring a semi-circle arc in the high-frequency region ($R_s = 6.5 \Omega$ and $R_{ct} = 0.8$), indicative of pseudocapacitive behavior. In the low-frequency region, a straight Warburg tail is evident, indicating the capacitive process of the electrode materials [54,55]. The ASC device demonstrates an impressive capacitance retention of 90.3 % over 6000 cycles, as shown in the cycle life plot (Fig. 6g). This remarkable cycle life can be attributed to the excellent layered structure of PAC, which enhances the accessibility of electrolyte cations through interlayer spaces, and the intrinsic stability of MnO₂ nanorods [18,56]. Analyzing the GCD curves presented in Fig. 7e, the specific capacitance, energy and power densities of the ASC device were determined to be 279.8F g⁻¹, 23.3 Wh kg⁻¹ and 350.4 W kg⁻¹, respectively (see Fig. 7h). The higher potential window, energy, and power density of the PAC//PAC/MnO₂ ASC are primarily attributed to the synergistic effect between the EDLC of porous AC and the pseudocapacitive effect of MnO₂ nanorods [57].

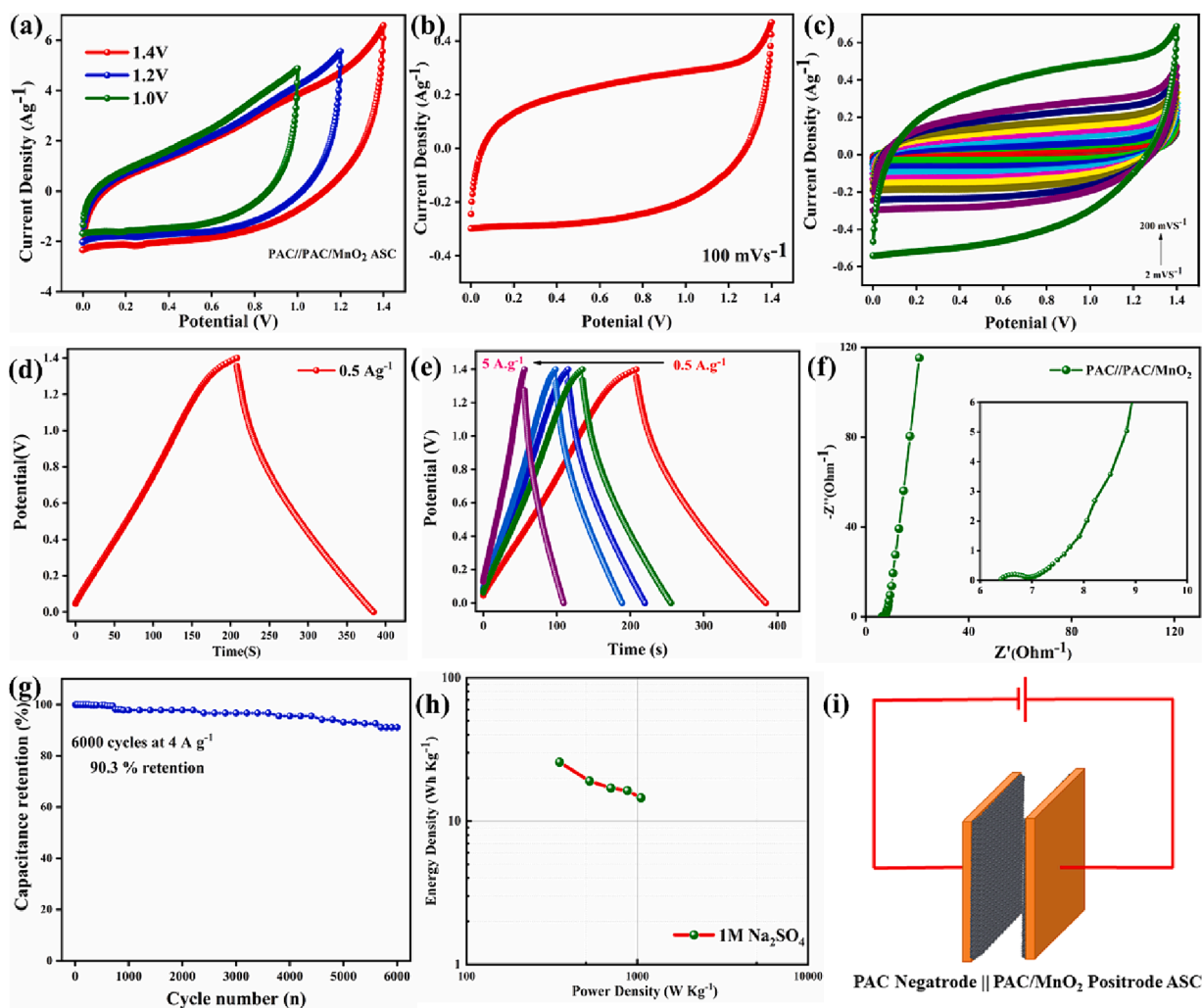


Fig. 7. Electrochemical behavior of PAC//PAC/MnO₂ ASC (a) CV curves at different potential windows (b) CV curves of the electrode at 100 mV s⁻¹, (c) CV curves at different scan rates ranging from 2 to 200 mV s⁻¹, (d) GCD curves at 0.5 A/g, (e) GCD curves at different current densities, (f) Nyquist plots, (g) cyclic stability at 4 A g⁻¹ for 6000 cycles, (h) Ragone plot, and (i) schematic fabrication of ASC.

4. Conclusion

In conclusion, this study successfully developed a cost-effective and high-performance ASC device using a PAC/MnO₂ as the positive electrode and PAC as the negative electrode. The enhancement of energy densities in ASCs was achieved through several strategies: improving the capacitance of the porous carbon electrode via chemical activation, incorporating MnO₂ nanorods, and integrating them into a hierarchical porous structure. The PAC/MnO₂ composite electrodes exhibited exceptional electrochemical performance in three-electrode experiments, maintaining 87.43 % of their capacitance after 6000 cycles and displaying a specific capacitance of 208.75F g⁻¹ at 0.5 A/g. The superior performance can be attributed to the synergistic effects resulting from the combination of micro/meso/macroporosity, which led to an increased surface area of up to 643.5 m²/g and a high pore volume of 0.6 cm³ g⁻¹. Additionally, the pseudocapacitive effect of the MnO₂ structure and the excellent stability of MnO₂ nanorods contributed to the enhanced performance. The assembled PAC//PAC/MnO₂ ASC device exhibited a higher potential window (0–1.4 V) and demonstrated specific energy and power density values of 23.3 Wh kg⁻¹ and 350.4 W kg⁻¹, respectively. For the advancement of next-generation high-energy-density supercapacitors, we explore the direct carbonization and hydrothermal preparation of other metal oxide/carbon composites, which hold significant promise in achieving even more powerful energy

storage capabilities. Also, our findings will contribute to the creation of high surface area carbon electrodes through environmentally friendly synthesis techniques. These electrodes will further increase use in other energy storage and conversion applications.

CRediT authorship contribution statement

Young-Seok Lee: Formal analysis, Data curation, Conceptualization. **Aravindh Raja Selvaraj:** Methodology, Formal analysis, Data curation, Conceptualization. **Nikolaos Kostoglou:** Formal analysis, Writing – review & editing. **Claus Rebholz:** Formal analysis, Writing – review & editing. **Rajmohan Rajendiran:** Software, Methodology, Investigation. **Vivekanandan Raman:** Validation, Software. **Heeje Kim:** Formal analysis, Investigation, Software. **John Anthuvan Rajesh:** Investigation. **Vijay Mohan Nagulapati:** Validation, Resources, Methodology. **Tae Hwan Oh:** Resources, Project administration, Funding acquisition. **Peter Jerome:** Writing – review & editing, Writing – original draft. **Sung-Shin Kim:** Writing – review & editing, Writing – original draft, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

The data that has been used is confidential.

Acknowledgments

P.J. and T.H.O. acknowledge the Core Research Support Center for Natural Products and Medical Materials (CRCNM) at Yeungnam University, along with the National Research Foundation of Korea grant sponsored by the Korean government (MSIT) (No. 2022R1A2C1004283).

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mseb.2024.117368>.

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